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Influence of low nitrogen gas pressures (<1.0 MPa) and additives on the nitridation, formation and densification of β and O-SiAlON ceramics produced by reaction bonding and silicothermal reduction

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical and Materials Engineering, The University of Auckland, 2013
ABSTRACT

β and O-SiAlON materials have been synthesised by both reaction bonding and silicothermal reduction techniques under different nitrogen pressures. These two methods which use Si and/or halloysite clay in place of Si₃N₄ in the starting mixture represent a cost efficient alternative to the traditional liquid phase sintering typically employed to produce SiAlONs. The influence of the initial compositions and of different additives on the nitridation behaviour and SiAlON phase formation have been studied. All of the additives did not have the same effects on the nitridation of SiAlONs as on the nitridation of pure Si. Indeed, typically, CaO had a negative effect on the nitridation of SiAlONs while Y₂O₃, Dy₂O₃ and ZrO₂ enhanced the nitridation. The two cost efficient processing routes led to similar final products after sintering under several combinations of the following parameters: nitriding and sintering additives, temperature, N₂ pressures. The work was therefore focused on the silicothermal reduction route since it facilitates forming by pressing, slip casting and extrusion, and gives a greater flexibility in the size and shape of SiAlONs that can be produced. Nitrogen overpressures typically enhanced the nitridation of Si in SiAlONs. For SiAlONs that started to densify at low temperature and that reached open porosity as low as 10%, nitrogen overpressures were essential to lead to full nitridation. SiAlONs with lower open porosity could not be nitrided under overpressure up to 1.0 MPa.

The possibility of quickly nitriding Si and forming β and O-SiAlON materials has been studied through their reaction sequence of formation. β and O-SiAlONs were fully nitrided and formed after a 1-h hold at 1400°C under 0.7 MPa of N₂ while this was not achievable under static atmospheric pressure. The amount of SiO₂ in the starting material played an important role during the formation of SiAlONs. It could react with Si and lead to significant mass losses by evaporation, but it could also lower the eutectic temperature in the ternary systems leading to early densification and pore elimination, explaining why O-SiAlONs start to densify at lower temperature than β-SiAlONs and why N₂ pressures have a greater influence on their formation. Sintering of β and O-SiAlONs under nitrogen pressure led to materials which exhibited hardness as high as typically reported for similar techniques.
(15 and 13 GPa respectively). Longer sintering times can be used to further densify β-SiAlONs since their decomposition at high temperature leads to the formation of a α-SiAlON surface layer with low porosity, which then stops such decomposition. In contrast O-SiAlONs have to be densified with shorter dwelling times as their decomposition into β-SiAlON leads to the formation of a highly porous surface layer which allows further decomposition. In conclusion, the use of low nitrogen pressures during nitriding and sintering of SiAlON materials produced by silicothermal reduction is of interest with regard to the production of low cost SiAlON refractory materials.
PUBLICATIONS

Part of the work presented in this thesis has already been published. Here is a list of the publications arising from the thesis:


• Rouquie Y, Jones MI. Influence of additives and compositions on the nitridation and formation of SiAlONs produced by reaction bonding and silicothermal reduction. Journal of Asian Ceramic Societies, in press.
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(3.23) \[ 6\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} \rightarrow \text{Si}_{5.7}\text{Al}_{0.3}\text{O}_{0.3}\text{N}_{7.7} + 6\text{SiO}(g) + 2\text{N}_2(g) \] ................................................. 84

(4.1) \[ \text{Si}(s) + \text{SiO}_2(s) \rightarrow 2\text{SiO}(g) \] ............................................................................. 119

(5.1) \[ 2\text{Si} + \text{SiO}_2 + \text{N}_2(g) \rightarrow \text{Si}_2\text{O}_2 + \text{SiO}(g) \] ............................................................................. 132

(5.2) \[ 3\text{Si}_3\text{N}_4 + \text{SiO}_2 + 2\text{AIN} \rightarrow 2\text{Si}_5\text{AlON}_7 \] ............................................................................. 135

(5.3) \[ 2\text{Si}_3\text{N}_4 + 2\text{SiO}_2.3\text{Al}_2\text{O}_3 + 7\text{AIN} \rightarrow 13\text{Si}_5\text{AlON}_7 \] ............................................................................. 135

(5.4) \[ \text{Si}_2\text{O}_2 + \text{AIN} + \text{Si}_3\text{N}_4 \rightarrow \text{Si}_5\text{AlON}_7 \] ............................................................................. 136

(5.5) \[ 5/3(2\text{SiO}_2.3\text{Al}_2\text{O}_3) + (26/3)\text{SiO}_2 + 183\text{Si} + 122\text{N}_2(g) + 29\text{AIN} + \text{Dy}_2\text{O}_3 \rightarrow 3\text{Dy}_{2/3}\text{SiO}_9\text{Al}_3\text{ON}_{15} + 30\text{AIN} + 39\text{SiO}(g) + 129\text{Si} + 99\text{N}_2(g) \] ............................................................................. 138

(5.6) \[ 5/3(2\text{SiO}_2.3\text{Al}_2\text{O}_3) + (26/3)\text{SiO}_2 + 183\text{Si} + 122\text{N}_2(g) + 29\text{AIN} \rightarrow 39\beta - \] \text{Si}_5\text{AlON}_7 ............................................................................. 138

(5.7) \[ \text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{O}_2 \] ............................................................................. 141

(5.8) \[ 3(\text{Al}_2\text{O}_3.2\text{SiO}_2.2.2\text{H}_2\text{O}) \rightarrow 2\text{SiO}_2.3\text{Al}_2\text{O}_3 + 4\text{SiO}_2 + 6.6\text{H}_2\text{O}(g) \] ............................................................................. 141

(5.9) \[ 5/3(2\text{SiO}_2.3\text{Al}_2\text{O}_3) + 26/3\text{SiO}_2 + 85.5\text{SiO}_2 + 97.5\text{Si}_3\text{N}_4 \rightarrow 200\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} \] ............................................................................. 142

(6.1) \[ H_V = 2\sin \left( \frac{\theta}{2} \right) \times \frac{F}{(d)^2} [114] \] ............................................................................. 149

(6.2) \[ H_V = 1854.4\times \frac{F}{(2a)^2} \] ............................................................................. 149

(6.3) \[ H_V = 18.19\times \frac{F}{(2a)^2} \] ............................................................................. 150

(6.4) \[ K_{IC} = 0.016(E/H_V)^{1/2} \left( \frac{P}{c_{V/2}} \right) [115] \] ............................................................................. 150

(6.5) \[ 567\beta - \text{Si}_5\text{AlON}_7 + 81\text{Dy}_2\text{O}_3 + 135\text{Al}_2\text{O}_3 \rightarrow 234\text{Dy}_{9/13}\text{Si}_{219/26}\text{Al}_{93/26}\text{O}_{32/3} \text{N}_{29/2} + 864\text{SiO}(g) + 288\text{N}_2(g) \] ............................................................................. 168

(A.1) \[ m_{\text{pure SiALON}} = m_{\text{sample initial}} - m_{\text{additive}} \] ............................................................................. 193

(A.2) \[ \text{mass\%H}_2\text{O} = \frac{2.2a \times M_{\text{H}_2\text{O}}}{a \times M_{\text{halloysite}} + b \times M_{\text{Si}, \text{SiC} \text{omill}} + c \times M_{\text{AIN}}, \text{Tokuyama or SI} \text{O}_2} \] ............................................................................. 193

(A.3) \[ m_{\text{sample initial without H}_2\text{O}} = m_{\text{sample initial}} - \text{mass\%H}_2\text{O} \times m_{\text{pure SiALON}} \] ............................................................................. 193

(A.4) \[ m_{\text{N}_2} \text{that entered the sample} = m_{\text{sample final}} - m_{\text{sample initial without H}_2\text{O}} \] ............................................................................. 194

(A.5) \[ \text{mass\%Si in SI, SiC} \text{omill} = \frac{1}{2} \times \frac{m_{\text{O}} \times M_{\text{SiO}_2}}{a \times M_{\text{halloysite}} + b \times M_{\text{Si}, \text{SiC} \text{omill} + c \times M_{\text{AIN}}, \text{Tokuyama or SI} \text{O}_2} \times m_{\text{pure SiALON}} \] ............................................................................. 194

(A.6) \[ m_{\text{Si}} = \frac{b \times M_{\text{Si}, \text{SiC} \text{omill}} \times \text{mass\%Si in SI, SiC} \text{omill}}{a \times M_{\text{halloysite}} + b \times M_{\text{Si}, \text{SiC} \text{omill} + c \times M_{\text{AIN}}, \text{Tokuyama or SI} \text{O}_2} \times m_{\text{pure SiALON}} \] ............................................................................. 194

(A.7) \[ m_{\text{N}_2} \text{that can theoretically enter the sample} = \frac{2}{3} \times \frac{M_{\text{N}_2}}{M_{\text{Si}}} \times m_{\text{Si}} \] ............................................................................. 194

(A.8) \[ \text{Degree of nitridation} = \frac{m_{\text{N}_2} \text{that entered the sample}}{m_{\text{N}_2} \text{that can theoretically enter the sample}} \] ............................................................................. 194
GLOSSARY

CIP: cold isostatic pressing
CFS: cationic field strength
CRN: carbothermal reduction and nitridation
DyAG: dysprosium aluminium garnet, Dy$_3$Al$_5$O$_{12}$
EDS: energy dispersive x-ray
ESEM: environmental scanning electron microscopy
GPS: gas pressure sintering
HIP: hot isostatic pressing
HP: hot pressing
HPSN: hot pressed silicon nitride
JCPDS: joint committee on powder diffraction standards
LPS: liquid phase sintering
MAS NMR: magic angle spinning nuclear magnetic resonance
Re: stands for rare-earth, in some cases is used to describe all metals used as additives
RSBN: reaction bonded silicon nitride
SENB: single edge notched beam
SHS: self-propagating high-temperature synthesis
Si$_2$ON$_2$: silicon oxynitride
Si$_3$N$_4$: silicon nitride
SiAlON: silicon aluminium oxynitride
SPS: spark plasma sintering
TGA: thermogravimetric analysis
VLS: vapour liquid solid
XRD: X-ray diffraction
YAG: yttrium aluminium garnet, Y$_3$Al$_5$O$_{12}$
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Influence of additives and compositions on the nitridation and formation of SIAIONs produced by reaction bonding and silicothermal reduction. *Journal of Asian Ceramic Societies*, in press.

**Corresponds to Chapter 3 Section 3.4.1 p56-75**

**Nature of contribution by PhD candidate**

Lead author, wrote the paper and carried out the experiments

**Extent of contribution by PhD candidate (%)**

85%

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<td>Mark Jones</td>
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Corresponds to Chapter 3 Section 3.4.2 p76-85

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Corresponds roughly to Chapter 5 Section 5.3 p125-143

| Nature of contribution by PhD candidate | Lead author, wrote the text and carried out the experiments |
| Extent of contribution by PhD candidate (%) | 85% |

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CHAPTER 1
INTRODUCTION

1.1 Introduction
Advanced ceramics have been developed because they show better properties than the best metallic alloy above 1000°C, with the exception of their inherent brittleness. Ceramics indeed have higher strengths at high temperatures, better corrosion and oxidation resistance, as well as lower density. Advanced ceramics can be divided into two groups: the oxide and non-oxide ceramics. In the former group, only alumina and zirconia are strong enough to be considered for structural applications. However alumina has a poor thermal shock resistance while unstabilised zirconia has a destructive phase change on cooling from above 1200°C. Among the non-oxide ceramics, the carbides, e.g. B₄C or SiC, have the best hardness but exhibit low strength and toughness. Thus nitrides, which show better hardness and thermal shock resistance than oxide ceramics, and better strength and toughness than carbides, are the most suitable materials for use in high performance applications. Amongst these materials, silicon nitride is the predominant material because of its combination of mechanical properties, but the normal practice of production is expensive because of the cost of raw powders and requirement for high temperature sintering. Moreover sintering is impossible via a solid state process because of the low self-diffusion coefficients of Si and N atoms, and therefore metal oxides are added to the starting mixture to promote liquid phase sintering. However, these oxides remain in the solid as an intergranular boundary phase after the sintering, which is usually amorphous, and this phase will affect the high temperature properties of the silicon nitride. One way of overcoming this is to incorporate these sintering aids into the silicon nitride structure. The materials that are able to do this are known as “SiAlON”.
The term “SiAlON”, or silicon aluminium oxynitride, encompasses a family of compounds or phases comprised of the following elements: silicon, aluminium, oxygen and nitrogen. Each phase is described by a composition range over which that particular structure is stable. Five different types of SiAlONs have been discovered so far: \(\alpha\)-SiAlON, \(\beta\)-SiAlON, O-SiAlON, X-SiAlON and AlN-polytypes. The solid solubility of \(\text{Al}_2\text{O}_3\) in the \(\beta\)-\(\text{Si}_3\text{N}_4\) lattice was discovered independently at about the same time (1971-1972) in the United Kingdom by Jack and Wilson [1] and in Japan by Oyama [2]. One of the reasons for the exploration of this system was to determine if a material could be produced that would combine the good thermal shock resistance of \(\text{Si}_3\text{N}_4\) with the sinterability of \(\text{Al}_2\text{O}_3\).

Whilst SiAlONs can be used as high performance materials such as impact resistant materials, there is also a market for SiAlONs that does not require the mechanical properties necessary for high performance applications, but takes advantage of, for example, their high temperature stability properties: refractory applications. As ceramics, SiAlONs require high heat treatment temperatures and this can be prohibitive for the transfer of a technology from laboratory to industrial environment. In this context, research aiming to improve the performance of these materials also includes the perspective of reducing the cost of production in order to facilitate the transition between research laboratories and industry. Cost benefits can be realised through both cheaper alternative starting materials and lower sintering temperatures. This work aims at using gas pressure sintering in combination with cheap processing routes in order to produce SiAlON materials suitable for refractory applications both in terms of cost and properties.

1.2 Objectives

The main objective of this work is to investigate the effects of low nitrogen gas pressures on the formation of different SiAlON phases produced by various methods, with a view to a reduction in costs associated with material and processing for a use in refractory applications. Specific objectives include:

- Investigating the effects of low nitrogen gas pressure on the formation and densification of \(\beta\) and O-SiAlONs produced by reaction bonding and silicothermal reduction routes with a view to producing low temperature and low cost materials suitable for liquid metal handling and refractory applications.

- Observing the effects of gas pressure during the nitridation of \(\beta\) and O-SiAlONs to investigate whether overpressures can be used to improve nitridation of Si in various SiAlON compositions and to determine whether there is a limit to the enhancement of the nitridation stage.
• Establishing the reaction sequence of formation of SiAlONs prepared by silicothermal reduction with and without nitrogen overpressure to demonstrate that overpressures are of importance not only at high temperatures to limit decomposition but also at lower temperatures during the formation of SiAlON, since nitrogen gas is a reactant.

• Studying the effects of gas pressure on the microstructure of SiAlON since the access to nitrogen and the speed of the nitridation reaction can be influenced by the variation of gas pressure.

• Investigating the influence of gas pressure on the decomposition of β and O-SiAlONs produced by silicothermal reduction. This would be relevant in view of transferring the silicothermal reduction production process of SiAlONs to industry where larger components would require longer dwelling times.

1.3 Thesis outline

The literature review first introduces the SiAlON materials, their compositions, properties and applications. It then focuses on the different production routes for these materials as well as the effects of processing variables on their structure and properties. Chapter 3 describes experimental work based on a Taguchi methodology designed to identify and quantify the effects of various experimental parameters on the properties of gas pressure sintered SiAlONs prepared by both reaction bonding and silicothermal reduction routes. According to the results obtained in this chapter, subsequent work was mainly focused on the production of SiAlONs by the silicothermal reduction route. Therefore, Chapter 4 investigates the effects of nitrogen pressure on the nitridation and formation of SiAlONs designed to have various open porosities during the nitridation. Chapter 5 establishes the feasibility for an improved heating schedule to fully nitride and form SiAlONs prepared by silicothermal reduction. It also determines the reaction sequence of formation of β and O-SiAlONs with and without nitrogen overpressure. Chapter 6 deals with the effects of nitrogen pressure on the microstructure and mechanical properties of SiAlONs, on the decomposition of SiAlONs at their sintering temperature and investigates the possibility of obtaining dense materials without decomposition using the silicothermal reduction route. All of the experimental chapters (Chapters 3-6) investigate distinct areas of research and include a discussion, summary and conclusions drawn from that particular area of study. Chapter 7 provides a brief overall summary of the findings and importance of the research. The conclusions of the study as well as recommendations for future work are presented in Chapter 8.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

SiAlONs are advanced ceramic materials which exhibit useful properties such as high strength and hardness, low density, good wear and corrosion resistance, and are able to retain these properties at high temperatures. The mechanical performances of ceramic materials are closely dependent on their densities and microstructures. Indeed tendency of hardness is in good agreement with densities whilst strength and fracture toughness are more sensitive to their microstructures. In general α-SiAlON, when fully dense, is a very hard but brittle material; β-SiAlON is less hard but tougher [3, 4]. A composite comprised of the two phases can yield very good mechanical strength and wear resistance. β-SiAlON has similar properties to silicon nitride which includes excellent resistance to attack by molten metal, X-SiAlON is also resistant to molten iron and steel and O-SiAlON has a very good resistance to oxidation and thermal shock. All of these characteristics make SiAlON materials excellent candidates for refractory applications.

SiAlONs are thus used in refractories and for a variety of engineering applications such as cutting tools, spray nozzles, pump seals and more recently for creating ballistic ceramic armours and for optical applications [3, 5-7]. The exact properties of a given SiAlON depend on the chemical composition and fabrication variables, such as purity, grain size and shape, and the method of fabrication.

The development of this material has included the aim of reducing its cost of production, thus cheaper raw materials, additives and cost efficient processes have been studied. There are now several distinct processes for producing SiAlONs. Pressureless, gas pressure and hot pressed reaction sintering were
the first techniques employed, but SiAlONs are now also produced by a number of processes including reaction bonding, carbothermal reduction and nitridation reaction, combustion synthesis, silicothermal reduction or more recently by spark plasma sintering.

2.2 SiAlONs

Although the thesis treats mainly the β and O-SiAlON phases, the five known phases in the Si-Al-O-N system are described in this section as they appear as intermediate phases or remain in the final product and modify its properties. Each phase has different mechanical and chemical properties that make them suitable for different applications. The α-SiAlON phase is the hardest phase and can be produced with additives that can be incorporated to its structure to limit the amount of remaining intergranular phase [3, 4]. For these reasons, α-SiAlONs have been subject to more research than any other SiAlON phase. There is therefore information that can be of interest when studying the other SiAlON phases, with for instance the influence of the microstructure on the mechanical properties and the possibility to tailor them. The characteristics displayed by the different SiAlON phases make SiAlONs suitable for a range of applications from high performance materials such as impact resistant materials to refractory applications.

2.2.1 SiAlON phases

This section details the five SiAlON phases in terms of composition and mechanical and chemical properties. A focus is also made on the intermediate phases that may appear during the formation of SiAlON and remain as intergranular phases.

2.2.1.1 β-SiAlON

Phase composition

The unit cell of β-SiAlON is composed of two unit cells of silicon nitride (Si₃N₄) and is formed by the substitution of z Si-N bonds by Al-O bonds. Therefore it is described by the formula Si₆₋₂zAl₂O₂N₈₋₂ where z can vary from 0 to 4.2 [4]. β-SiAlON is a solid solution that possesses a hexagonal crystal structure based on that of β-Si₃N₄. Its region of homogeneity extends along the Si₁₋₄₋₂Al₆N₄₋₂Al₂O₃ line of the phase diagram as shown in Figure 2.1 [8, 9]. A MAS NMR analysis on a β-SiAlON with z=1.3 on ²⁹Si and ²⁷Al has revealed that both Si and Al were coordinated with four nitrogen atoms [10] and that [SiN₄] and [AlN₄] were the most dominant species in β-SiAlON. Furthermore XRD analysis has shown that the peaks associated with β-SiAlON were shifted to lower diffraction angles when z value
was increased [11]. This was due to an increase of the lattice parameters associated with the increasing degree of substitution of Al and O into the Si$_3$N$_4$ structure.

![SiAlON behaviour diagram at 1700°C](image.png)

**Figure 2.1:** SiAlON behaviour diagram at 1700°C [8, 9].

**Mechanical and chemical properties**

The microstructure of β-SiAlON is made up of elongated grains with an aspect ratio of typically between 4 and 10 [4] of which the size increases with increasing z value [11]. This shape which is due to the anisotropic growth of the β-SiAlON grains has been attributed to both the intrinsic chemical potential difference between the crystal facets [12] and to the intrinsic segregation and bonding of rare-earth atoms to the prism surfaces at the interfaces when additives such as rare-earth oxides are used to help densification [13, 14].

The fracture toughness of ceramics can be correlated with grain shape [9], and the high aspect ratio of the β-SiAlON microstructure promotes toughening mechanisms such as grain pull-out, debonding and crack deflection. The latter is the most predominant mechanism for toughening but in order to be effective, the cracks need to propagate through the intergranular phase and not through the grains. Therefore, the intergranular phase needs to be weak enough to offer an easier path to the crack propagation than the grains [15]. The crystallisation of the intergranular phase can improve the fracture toughness by weakening the interface grain/intergranular phase through which the cracks can propagate [3]. The hardness and fracture toughness of β-SiAlONs are typically within the 14-17 GPa range and the 3-6 MPa.m$^{1/2}$ range respectively, depending on both the processing route and the type of additive used [3].

The structure and physical and mechanical properties of β-SiAlON (z=3) are similar to those of β-Si$_3$N$_4$, but its chemical properties are closer to Al$_2$O$_3$. Its thermal expansion coefficient (2.7x10$^{-6}$°C$^{-1}$) is less than that of β-Si$_3$N$_4$ (3.5x10$^{-6}$°C$^{-1}$) and so it has superior thermal shock properties [16]. The
oxidation resistance of β-SiAlON is greater than that of Si₃N₄ because a protective and coherent layer of mullite can be formed on the surface. Its compatibility with molten metal is also better than that of Si₃N₄ as shown in Figure 2.2.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Mass loss (%)</th>
<th>RBSN</th>
<th>HPSN</th>
<th>SiAlON</th>
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<tr>
<td>Mild steel</td>
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<tr>
<td>Stainless steel</td>
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<td>15</td>
<td>100</td>
<td>17</td>
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</table>

Figure 2.2: Resistance of SiAlON and Si₃N₄ to attack by molten metal [16].

Suzuki et al. [17] have prepared β-SiAlONs by a slip casting method and have found that the β-SiAlONs reach their optimal properties for z between 0.5 and 1. Above z=1, the strength and the fracture toughness decrease and the thermal expansion coefficient increases.

2.2.1.2 α-SiAlON

Phase composition

α-SiAlONs are formed by the substitution of Al-O and Al-N for Si-N bonds in a unit cell that is composed of four Si₃N₄ units. The replacement of Si-N by Al-N bonds destroys the electron balance, hence α-SiAlONs need to be stabilised by the addition of metal ions such as Li, Na, Mg, Ca, Y and lanthanides ions such as Nd, Sm, Gd, Dy, Er, Yb, Lu. Thus the composition of α-SiAlON can be described by the formula Reₙ/ρSi₁₂₋ₘ₋ₙ₋ₘ⁻ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ₋ₙ_-n |

The number of Si-N bonds substituted by the Al-O bonds is represented by n, and m is the number of Si-N bonds substituted by the Al-N bonds. The electron balance is maintained by the addition of m/ρ metal ions [4]. Single phase α-SiAlONs can be stabilised in a limited two-dimensional phase region in the plane Si₃N₄-4/(Al₂O₃·AlN)-ReN·3AlN of the Re-Si-Al-O-N phase diagram. Figure 2.3 shows the position of the α-plane and the α-phase region [18] in the Jänecke prism. As a four-component system, the phase diagram of Si-Al-O-N could be represented as a tetrahedron. Due to the predominant covalent bonding in SiAlONs there is a great advantage assuming normal charges for these elements and using their charge equivalent. Instead of a tetrahedron, the phase diagram of Si-Al-O-N can be represented as a square whose four corners are
Si$_3$N$_4$, Al$_2$O$_3$, SiO$_2$ and AlN. The Jänecke prism extends this diagram to the third dimension with the addition of the rare-earth element, as its charge equivalent, in the diagram thus forming the remaining two corners of the prism: ReN and Re$_2$O$_3$ [19].

![Jänecke prism for Re-Si-Al-O-N system and α-SiAlON region](image)

Figure 2.3: (a) Jänecke prism for Re-Si-Al-O-N system and (b) α-SiAlON region [18].

The formation of α-SiAlON can be described as a two-step replacement process. The first step consists of the replacement of Si-N bonds, which have a length of 1.75 Å, by Re$_{m/p}$Al-N bonds; this step stretches the network structure because of the larger Al-N bond distance of 1.87 Å. The second stage produces a slight lattice distortion as the Al-O bond length is very close to the Si-N bond length [16, 20]. This explains why the lattice parameters are dependent mainly on m and are almost insensitive to changes in n. Moreover, the type of the modifying cation does not have much of an influence on the lattice parameters, but it does affect the stability region for single-phase α-SiAlON formation as described in more detail below [20, 21].

Mechanical and chemical properties

α-SiAlONs show excellent hardness (typically about 19-20 GPa), oxidation, thermal shock and erosion resistance but poor fracture toughness (typically about 2-4 MPa.m$^{1/2}$) [3, 22]. Recent works have shown the possibility for improving the fracture toughness of these materials by modifying their microstructure and especially the shape of their grains [23-25]. The α-SiAlONs present a high hardness but a low fracture toughness due to the fact that their microstructure is made of equiaxed grains. The fracture toughness has been shown to be improved (up to 5-5.5 MPa.m$^{1/2}$) by the presence of elongated grains [26, 27] since crack deflection and grain pull-out mechanisms are possible.

The good thermal shock resistance of these materials is explained by their low thermal expansion and the relatively high thermal conductivity. The improved high temperature properties of α-SiAlON are mainly due to the absence or reduced amount of intergranular phase. Indeed the particularity of these SiAlONs is that there are two large isolated interstitial sites in their structure where some metal ions can be accommodated [28] as shown in Figure 2.4 [26]. However, during the formation of the α-SiAlON phase, if all of the sintering aids are not able to be incorporated into the SiAlON structure, a
residual glassy phase remains and degrades the mechanical and chemical properties above the glass-softening temperature (900-1100°C).

Figure 2.4: Structure of \( \alpha \) and \( \beta \)-Si\(_3\)N\(_4\) on which \( \alpha \) and \( \beta \)-SiAlON structures are based. (a) shows the AB layers and (b) shows the CD layers. The \( \beta \)-SiAlON structure is type ABAB whilst the \( \alpha \)-SiAlON structure is ABCD. The ABAB stacking gives long continuous channels along the c axis for \( \beta \)-SiAlON and the ABCD stacking gives two large isolated interstices for \( \alpha \)-SiAlON [26].

\( \alpha \)-SiAlONs formed at high temperatures (above 1750°C) are unstable when held at lower temperatures (below 1550°C) and decompose into a mixture of a \( \beta \)-SiAlON phase plus either a crystalline or glassy intergranular phase. However, below 1200°C, the kinetic of decomposition is so slow that the material can be used up to this temperature [29]. The single-phase \( \alpha \)-SiAlON stability region is strongly temperature dependent: it decreases as the temperature decreases. This dependence is especially pronounced when larger rare-earth cations are involved as the phase region becomes smaller with increasing size of the rare-earth ions [4, 21].

2.2.1.3 O-SiAlON

*Phase composition*

Silicon oxynitride (Si\(_2\)ON\(_2\)) was first reported in 1954. Its composition and structure were confirmed in 1964 and it has been shown that Si\(_2\)ON\(_2\) structure can accommodate small amounts of aluminium. The resulting material was termed O-SiAlON. It has the same structure as Si\(_2\)ON\(_2\), both having an orthorhombic crystal structure. The Si\(_2\)ON\(_2\) structure is made of SiON\(_3\) tetrahedra, linked to give a series of parallel puckered sheets of hexagonal Si\(_3\)N\(_3\) rings separated by Si-O-Si bridges as shown in Figure 2.5 [16].
Figure 2.5: Structure of Si$_2$ON$_2$ on which is based the O-SiAlON structure. Black, white and dashed disks represent Si, N and O atoms respectively [16].

O-SiAlON is formed by the substitution of an equal amount $x$ of Al and O for Si and N respectively in the Si$_2$ON$_2$ structure. Therefore its formula is Si$_{2-x}$Al$_x$O$_{1+x}$N$_{2-x}$ where $x$ can vary from 0 to 0.2 at 1600°C. The level of substitution can be increased up to $x=0.4$ at 1900°C [30] showing that the amount of Al and O which can be substituted increases with temperature. The substitution of Al and O for Si and N causes an expansion of the unit cell which is noticeable along the lattice parameter, $a$, as the Si-O bonds are replaced by longer Al-O bonds whereas only little dimensional change is observed in the b-c plane, as the Al-O and Si-N bonds are of similar length.

Mechanical and chemical properties

O-SiAlON can contain more oxygen than $\beta$-SiAlON and, therefore, is much more resistant to oxidation with no significant oxidation detected until 1200°C. From 1200°C to 1450°C, parabolic oxidation occurs and the rate of oxidation is controlled by the diffusion of the nitrogen to the surface [8]. Barris et al. [30] have carried out experiments with O-SiAlON-SiC dipped in molten aluminium and aluminium/magnesium alloy at 900°C for 400 h. They have compared the results with a Si$_3$N$_4$-SiC composite and have found that the former composite was more resistant to attack by both the molten metal and the oxide freeze. Brown [8] has produced a pressureless sintered 99.5% O-SiAlON ($x=0.14$) - 0.5% X-SiAlON with no additives at 1720°C. Table 2.1 shows the mechanical properties of this product and other additional literature data.

Table 2.1: Properties of O-SiAlON and Si$_2$ON$_2$ [8].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fabrication method</th>
<th>Temperature (°C)</th>
<th>Additives</th>
<th>Density (g.cm$^{-3}$)</th>
<th>Hardness (HV10)</th>
<th>Bend strength (MPa)</th>
<th>Modulus of elasticity (GPa)</th>
<th>Thermal expansion (x10$^{-4}$ °C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.5% O-SiAlON ($x=0.14$) and 0.5% X-SiAlON</td>
<td>Pressureless sintering</td>
<td>1720</td>
<td>none</td>
<td>2.81</td>
<td>1700</td>
<td>445</td>
<td>221</td>
<td>3.3 (25-1000°C)</td>
</tr>
<tr>
<td>Si$_2$ON$_2$ ($x=0$)</td>
<td>Hot pressing at 29 MPa</td>
<td>1750</td>
<td>2.5% CeO$_2$</td>
<td>2.90</td>
<td>2200</td>
<td>550-740</td>
<td>235-239</td>
<td>3.3-3.4 (25-800°C)</td>
</tr>
<tr>
<td>Si$_2$ON$_2$ ($x=0$)</td>
<td>Hot pressing at 33 MPa</td>
<td>1750</td>
<td>5% MgO</td>
<td>2.83</td>
<td>-</td>
<td>280</td>
<td>216-222</td>
<td>3.55 (25-1000°C)</td>
</tr>
<tr>
<td>O-SiAlON ($x=0.04-0.16$)</td>
<td>Pressureless sintering</td>
<td>1800</td>
<td>8% Y$_2$O$_3$</td>
<td>2.86</td>
<td>-</td>
<td>350-430</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O-SiAlON ($x=0.1$)</td>
<td>HIP at 200 MPa</td>
<td>1750</td>
<td>none</td>
<td>2.82</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2.1.4 X-SiAlON

**Phase composition**

X-SiAlON has a structure similar to mullite (2SiO₂·3Al₂O₃), and it exists as a narrow solid solubility region at 1650°C, on the line between Si₃N₄ and mullite in the Si₃N₄-Al₂O₃-AlN-SiO₂ phase diagram (see Figure 2.1). A number of formulae that describe X-SiAlON can be found in literature ranging from SiAlON₂N to Si₁₆.₉Al₂₂.₇O₄₈.₈N₁₁.₆ with the composition described as Si₁₂Al₁₈O₃₉N₈ being the most commonly used [31].

**Mechanical and chemical properties**

A hot-pressed X-SiAlON has been reported to be chemically stable with ferrous alloys at 1200°C [31]. However this X-SiAlON shows only a modest hardness of about 12.5 GPa, a toughness of 1.2 MPa.m¹/² and an elastic modulus of 213 GPa. The linear thermal expansion coefficient of X-SiAlON is in the range of 3.7-4.5x10⁻⁶°C⁻¹ and its density is 3.0 g.cm⁻³ [32]. Table 2.2 shows a summary of the properties found for X-SiAlON prepared by different methods.

Table 2.2: Properties of several X-SiAlONs [32].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fabrication method</th>
<th>Density (g.cm⁻³)</th>
<th>Modulus of elasticity (GPa)</th>
<th>Hardness (GPa)</th>
<th>Strength (MPa)</th>
<th>Fracture toughness (MPa.m¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-SiAlON</td>
<td>Reaction bonding</td>
<td>3.00</td>
<td>206</td>
<td>15</td>
<td>233</td>
<td>1.4</td>
</tr>
<tr>
<td>X-SiAlON</td>
<td>Synthesis + sintering</td>
<td>3.05</td>
<td>217</td>
<td>12</td>
<td>253</td>
<td>1.05</td>
</tr>
<tr>
<td>X-SiAlON</td>
<td>Hot pressing</td>
<td>3.04</td>
<td>213</td>
<td>12.5-12.8</td>
<td>-</td>
<td>1.17-1.76</td>
</tr>
<tr>
<td>X-SiAlON</td>
<td>CRN by pressureless sintering</td>
<td>3.01</td>
<td>-</td>
<td>10.4-11.1</td>
<td>-</td>
<td>3.1-3.3</td>
</tr>
</tbody>
</table>

2.2.1.5 AlN-polytypes

The AlN-polytype phases are all located in the Al and N rich corner of the Si₃N₄-Al₂O₃-AlN-SiO₂ phase diagram (see Figure 2.1). The polytypes of AlN have a wurtzite-type structure based on the AlN structure. These different polytype phases are identified with the Ramsdell notation that uses the structural characteristics of the AlN-polytypes to differentiate them. Indeed AlN-polytypes form a series of components with either hexagonal or rhombohedral cells. Their structure is composed of m=n/3 layers along the c axis for rhombohedral cells and of m=n/2 layers for hexagonal cells [16]. Hence rhombohedral polytypes contain a three, and hexagonal polytypes contain a two, symmetry related block, each of m layers per unit cell as shown in Figure 2.6.
Figure 2.6: The 2H AlN structure and projections of 15R and 12H structures on the (110) plane [16].

These structural characteristics have led to their Ramsdell notations, nR or nH. Polytypes with n even are hexagonal whereas those with n odd are rhombohedral. Each type of polytype has a different metal/non-metal atoms (M/X) ratio and the pure phases show an extensive range of homogeneity along lines of constant M/X ratio but are extremely limited in other directions [16]. The different polytypes of AlN are listed in Table 2.3 with their M/X ratio.

<table>
<thead>
<tr>
<th>AlN-polytype</th>
<th>8H</th>
<th>15R</th>
<th>12H</th>
<th>21R</th>
<th>27R</th>
<th>2H⁴</th>
<th>2H</th>
</tr>
</thead>
<tbody>
<tr>
<td>M/X ratio</td>
<td>4/5</td>
<td>5/6</td>
<td>6/7</td>
<td>7/8</td>
<td>9/10</td>
<td>&gt;9/10</td>
<td>1/1</td>
</tr>
</tbody>
</table>

Johnson and Hendry [33] have observed a microstructure of thin elongated grains for AlN-polytypes prepared by hot-pressing. Thus the AlN-polytypes can be used to improve the fracture toughness in a composite SiAlON due to their fibrous microstructure [16].

2.2.1.6 Intermediate phases
The intermediate phases in SiAlONs are usually composed of the five elements that enter the composition of SiAlON, i.e. Re, Si, Al, O and N, with Re representing the metal ion(s) used for the sintering of SiAlON. Most of the SiAlON products are located in the nitrogen rich side of the Jänecke prism, whereas most of the oxynitride glasses are situated in the oxygen rich side of the prism. In addition there are many different oxynitride glass compositions for a single Re-Si-Al-O-N system, for instance, Figure 2.7 represents the Jänecke prism for the Y-Si-Al-O-N system, showing all known phases for this system [34].
The properties of SiAlON materials are to a large extent determined by the properties of these intergranular phases which typically exist in liquid phase sintered materials. The reduction of the amount of grain boundary phase is thus important for tailoring the properties. Indeed a large amount of grain boundary phase strongly deteriorates the mechanical properties of the materials. In order to improve the performances at high temperature, the glassy grain boundary phase needs to be eliminated or at least minimised and/or crystallised. The material is therefore often subjected to a post-sintering heat treatment whereby the material is heated above the glass transition temperature but without melting it so the glass can devitrify and be converted into a refractory crystalline phase [4].

The sintering additives used to facilitate the densification have to be also effective in improving the properties of the grain boundary phase. In addition, it has been observed that for rare-earth oxynitride glasses with constant nitrogen content, properties such as hardness, viscosity, Young’s modulus, glass softening and glass transition temperatures increase for smaller rare-earth cations as shown in Figure 2.8 [35, 36]. This was attributed to the fact that the cationic field strength (CFS = v/r², where v is the valency and r is ionic radius) increases with decreasing cationic radius which leads to a stronger glass network [37].
2.2.2 Tailoring of SiAlON microstructures

The mechanical performances of ceramic materials are typically closely dependent on their density and microstructure. The $\alpha$-SiAlON phase possesses equiaxed grains that display the greatest hardness amongst the SiAlON phases, thus research has been focused on improving their fracture toughness. Whilst $\beta$ and O-SiAlON phases are not of primary interest for their mechanical properties (but for their chemical properties and lower production cost since they are mainly use in refractory applications), improved mechanical properties still contribute to enhance durability of these products. As $\beta$ and O-SiAlONs are not the most suitable SiAlON phases for high performance applications, little attention has been given to the development of these materials in terms of mechanical properties. On the other hand the $\alpha$ phase has been the object of a lot more research. Nevertheless ideas developed for improving the $\alpha$ phase could be used to fill the gap in literature regarding the improvement of mechanical properties of $\beta$ and O-SiAlON through the tailoring of their microstructure. This section describes the techniques used to tailor the microstructure of the $\alpha$ phase in view to highlight...
information relevant to β and O-SiAlONs. Tailoring of mechanical properties is possible through controlling the ratio of two phases, here α and β, which possess different microstructures, or by controlling seeding and grain growth of a phase in order to obtain grains with a desired morphology.

2.2.2.1 By controlling the ratio of two phases: the α/β-SiAlON transformation

When two phases possess different microstructures, and therefore have different properties and suitability for different applications, mechanical properties can be tailored by varying the phase ratio in the material. In the well-studied case of α-SiAlON, the hardness of the α phase is combined with the toughness of the elongated β phase. Besides starting with a mixed composition [38], another important feature that allows tailoring the α/β ratio is the α/β transformation.

Generalities

In contrast to the Si₃N₄ where the α phase is unstable and transforms to β phase at high temperatures (>1400°C), the α/β-SiAlON transformation is observed when an α-SiAlON that has been prepared at higher temperatures is held at lower temperatures. This highlights the instability of α-SiAlON that decomposes at low temperatures, typically below 1600°C, into a rare-earth rich intergranular phase and β-SiAlON with an elongated crystal morphology. Mandal et al. [39] have reported that the transformation from α to β-SiAlON occurs in Re-(α+β)-SiAlONs when heat treated between 1000°C and 1600°C and that it was more pronounced with increasing temperatures. Furthermore α-SiAlONs that have been stabilised with light rare-earth cations are more inclined to this transformation, i.e. the reaction rate is faster than the ones stabilised with heavier cations [21]. The α-SiAlON compositions located near the borders of the α-phase region, and the composite SiAlONs that already contain some β-SiAlON in addition to α-SiAlON, tend to be less stable than pure α-SiAlON located in the middle of its phase region [20].

As α and β-SiAlON phases do not have the same atomic arrangement, the transformation involves the breaking of chemical bonds and substantial atomic diffusion. Therefore the reconstructive nature of this transformation requires significant amount of thermal energy. The atomic diffusivity of the species is low due to the strong covalent nature of the bonding of α and β-SiAlON. Thus, in order to occur, the α/β-SiAlON transformation needs the presence of a liquid phase. As a matter of fact, Mandal et al. [40] have suggested that the grain boundary liquid phase was one of the most important factors influencing the transformation and that the rate of transformation was dependent on the amount and viscosity of this intergranular liquid phase.
Mechanism

The α/β-SiAlON transformation is expected to occur in two stages. The first stage involves relatively high amounts of intergranular phase which provides the liquid phase necessary for the transformation at temperatures above the melting point of the glass. The volume of the liquid phase will then be reduced as the newly formed phase is stable at these temperatures. The second stage shows a lower transformation rate than the first [4]. Since it was previously suggested that the process could not occur without a liquid phase, the fact that the transformation continues to proceed suggests the presence of another liquid which is expected to be the product of the decomposition of the α-SiAlON phase itself. Finally, these observations show that the α/β-SiAlON transformation does not need much grain boundary phase to proceed and that a steady rate for this transformation can still be expected even with little amount of grain boundary phase [4].

The decomposition of α-SiAlON was at first a consequence of the post-heat treatment aiming to devitrify the intergranular glassy boundary phase, but this transformation has become an advantage since it allows the modification of the α/β-SiAlON ratio and therefore of the microstructure and properties of these materials with the use of the same starting composition. Thus α/β-SiAlONs with different properties can be created by controlling the heat treatment variables such as temperature and holding time. The more recent discovery of elongated α-SiAlON [41] has drawn more interest since it is possible to improve the toughness of α-SiAlONs without decreasing their intrinsic high hardness and generating an extra intergranular phase.

 Whilst the decomposition of α-SiAlON into β-SiAlON is well known, the decomposition of O-SiAlON into β-SiAlON has not been studied as much. It seems to be a surface phenomenon and the transformation of O-SiAlON into β-SiAlON is accompanied by a loss of material from the surface [42]. Few attempts have been made to reduce this decomposition. A method consisting of sintering O-SiAlONs under a powder bed [42] in order to modify the local environment around the samples is described in detail later in Section 2.4.2.2. As a consequence, this thesis describes in Chapter 6 the decomposition of O-SiAlON and another method to control it: the use of nitrogen gas pressure.

2.2.2.2 By controlling seeding and grain growth: elongated α-SiAlON

The reason the properties of these materials are so different is not necessarily because of the different phases, but because of their growth behaviour. For instance in Si₃N₄, the α phase only exists with an equiaxed microstructure whereas the anisotropic growth in the β-Si₃N₄ crystals results in elongated grains that provide toughening. One interesting recent development has been the discovery that, unlike Si₃N₄, such elongated grains can be obtained in the α-SiAlON phase [43].
The different techniques
Chen and Rosenflanz [41] have found that the driving force is an important parameter in the development of \(\alpha\)-SiAlON grains. The formation of elongated \(\alpha\)-SiAlON grains is more likely to occur when the driving force is low and the nucleation rate is slow. Thus different methods have been investigated to obtain such elongated \(\alpha\)-SiAlON materials, where the aim is to control the nucleation and growth of the \(\alpha\)-SiAlON grains. One method employs a two-step firing process as the nuclei need to develop at low temperatures and the final product needs to be fired at higher temperatures for the growth of elongated grains and in order to get a fully dense material [28]. Another method consists of adding seed crystals to the powder compact in order to provide nuclei [44] (which are called, in this case, external nuclei since they are not the product of any reaction between the starting powders). This method does not require a two-step firing process as the nuclei are already present in the starting composition.

Kushan et al. [28] have observed that \(\alpha\)-SiAlON grains initially nucleate on \(\alpha\)-Si\(_3\)N\(_4\) particles during the precipitation process and then grow to a larger size. Elongated \(\alpha\)-SiAlON can therefore be obtained either by nucleation on \(\beta\)-Si\(_3\)N\(_4\) powder or by using a two-stage sintering process. Finally, it has been shown that the use of high heating rates, either by spark plasma sintering (600°C.min\(^{-1}\)) [43] or by traditional sintering with unusual heating rates (25°C.min\(^{-1}\)) [23], limits or avoids nucleation at low temperatures which allows the growth of elongated grains at higher temperatures.

Factors influencing the nucleation and the growth of \(\alpha\)-SiAlON grains
The possibility of obtaining elongated grains is directly related to sintering parameters such as temperature, isothermal holding time, heating rate, characteristics of the starting powder, composition and amount of additives.

Elongated grains have been obtained with the addition of an extra liquid phase (based on Y\(_2\)O\(_3\)) at 1800°C whereas such grains were not obtained without it at 1900°C therefore the presence of a liquid phase seems essential for the formation of elongated \(\alpha\)-SiAlON grains [45]. The abnormal grain growth of \(\alpha\)-SiAlON is strongly temperature dependent, it has been shown that high sintering temperatures are important for obtaining elongated \(\alpha\)-SiAlON grains [46], and takes place rapidly even after the completion of \(\alpha\)-SiAlON formation allowing the use of high heating rates [47].

Chen et al. [41] have argued that using \(\beta\)-Si\(_3\)N\(_4\) powder instead of \(\alpha\)-Si\(_3\)N\(_4\) retards the nucleation rate of the \(\alpha\)-SiAlON phase, so that less \(\alpha\)-SiAlON nuclei are formed and therefore the formation of elongated
α-SiAlON grain is promoted. However Kim et al. [44] have shown, using the two-step process, that α-Si$_3$N$_4$ can also be used as starting powder and that it is possible to control its transformation into α-SiAlON at low temperatures in order to then tailor the population of nuclei in situ for future growth. Moreover, the size of the starting powder also has an influence as the formation of elongated α-SiAlON grains was promoted by the use of a fine grained α-Si$_3$N$_4$ precursor instead of a coarser powder [45]. Elongated grains have been obtained by the two-step process method in α-SiAlON compositions near the α-phase boundary since these compositions are expected to have a low driving force for the nucleation of α-SiAlON [44]. In this way, few α-SiAlON seeds are obtained after the first step of firing and they are therefore able to grow during the second stage. In contrast, for the compositions near the centre of the α-phase region, the high driving force is expected to lead to a high nucleation rate and therefore to a higher number of nuclei. This higher number of nuclei will prevent the growth of elongated grains as they will impinge on each other. In summary, as the α-SiAlON phase region increases with increasing size of the stabilising cation, α-SiAlONs stabilised with smaller cations are expected to be more prone to develop elongated grains because they will have a lower driving force [44].

It should be possible to tailor the microstructure of the generally elongated β-SiAlON grains to obtain less elongated and therefore maybe harder β-SiAlON grains. One way to do it would be to favour the nucleation rate in β-SiAlON to obtain a higher number of nuclei that will impinge on each other and limit the growth of elongated grains. The thesis investigates this possibility in Chapter 6 through the use of nitrogen pressures during the nitridation (reaction of Si and N$_2$ to form Si$_3$N$_4$, see Section 2.3.3.1) of SiAlONs prepared by silicothermal reduction.

Regarding the seeding method, Kim et al. [44] have shown that a maximum in fracture toughness can be obtained for an optimum amount of seeds as seen in Figure 2.9. Indeed a small amount of seeds does not develop sufficient elongated grains and a too large amount prevents the growth of elongated grains. Finally, the development of these elongated α-SiAlON grains improves their fracture toughness as this morphology increases frictional bridging, crack deflection [9] (Figure 2.9), and the pull-out toughening contribution.
In conclusion, the intrinsic high hardness of $\alpha$-SiAlON combined with an elongated morphology of their grains would appear to make them excellent candidates for high performance applications. In the same way, it would be interesting to investigate the possibility of tailoring the microstructure of other SiAlON phases to improve their mechanical properties for their use in other applications, such as refractory applications, where mechanical properties are not the main concern but are still of importance.

### 2.2.3 Applications

The SiAlON phases on which the thesis focuses are designed to be used as refractories; however they are not the only applications where SiAlIONs can be found. This section describes the main fields in which SiAlIONs can be found and explains the main properties that make them of interest for a given application.

#### 2.2.3.1 Refractory materials

SiAlON materials exhibit excellent chemical and mechanical properties at high temperatures. Some SiAlONs such as O-SiAlONs are known for their resistance to oxidation whereas others, such as X-SiAlONs, have shown a good resistance to molten metals like iron or steel, and $\beta$-SiAlIONs have good fracture toughness [48]. Moreover these materials generally have a low thermal expansion coefficient compared to the other ceramic materials; for instance, O-SiAlONs have a thermal expansion coefficient of about $3.3\times10^{-6} \text{C}^{-1}$ [8]. Thus, as they are strong, durable and resistant to physical and chemical attack by molten metals, SiAlIONs are of special interest for applications in molten metal handling [48]. Finally they also present the advantage of being able to be sintered at temperatures lower than Si$_3$N$_4$ and can be produced from inexpensive raw materials such as clay which greatly facilitates green forming.

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Figure 2.9: (a) Variation in indentation fracture toughness ($K_{IC}$) relative to the amount of seed crystals [44] and (b) schematisation of the effect of elongated grains on the crack deflection [9].
2.2.3.2 Impact resistant materials

Protective armour for heavy military equipment is usually composed of a thick layer of alloy steel which provides protection against heavy and explosive projectiles [49]. As this type of protection is used for tanks and ships, its weight and size is not an inconvenience. However, when it comes to the protection of light vehicles such as automobiles, jeeps, light boats or aircraft and personnel, these two aspects of compactness and weight become of major importance. A thick armour panel will increase the target profile of the vehicle as well as its wind resistance. In addition, it is obvious that if such armour can be fabricated, a low cost will present another non negligible advantage.

Armours, aiming to fulfil the specifications for the protection of light and fast vehicles or for body armour, should be able to prevent penetration of bullets of any weight at high speeds (e.g. speeds in the range of 700 to 3000 m.s\(^{-1}\)) and must satisfy certain weight limitations (for light vehicles it generally is in the range of 40 to 70 kg.m\(^{-2}\)) [49]. Thus SiAlONs with high hardness, over 18 GPa, and high fracture toughness, over 6 MPa.m\(^{1/2}\), are interesting materials for this application [49] as they also present the advantages of possessing a low density, usually around 3200 kg.m\(^{-3}\), in comparison with the alloy steel, and are made from cheaper raw material as compared to the armours made of synthetic fibres.

Among the SiAlONs, \(\alpha\)-SiAlONs are more likely to be used for this kind of application because they present mechanical properties that suit the cited requirements, such as a high hardness. However the poor fracture toughness of the \(\alpha\)-SiAlONs has led researchers to tailor new \(\alpha\)-SiAlONs with elongated grains that improve this property [25, 44]. Others have preferred to develop composite materials made of \(\alpha\)-SiAlON and \(\beta\)-SiAlON to combine the high hardness of the former with the good fracture toughness of the latter [38].

2.2.3.3 Other applications

The wide range of properties, achievable by the possibility of creating various types of SiAlONs and tailoring their microstructure, makes SiAlONs a material that can suit a lot of different applications. For instance, their excellent wear resistance at low temperatures allows their use as a milling medium. Their good chemical resistance at high temperatures is of interest in metal-forming tools such as wire or tube drawing tools for non-ferrous alloys, especially aluminium and copper alloys [3]. Furthermore, the combination of mechanical and chemical resistances at high temperatures makes them an excellent candidate for metal-cutting tools applications. They can also be used for some engine applications such as pump seals or ceramic gas turbines where Si\(_3\)N\(_4\) is already being used [3].
More recently, SiAlONs have been studied not only for their properties as a structural material but also for their functional properties. Chen et al. [50] have observed the translucency of α-SiAlON ceramics in visible and near-middle infrared band and Jones et al. [51] have produced a highly transparent Lu-α-SiAlON, with an optical transmission as high as 70% in the visible region. SiAlONs can also serve as a new host lattice for phosphor and the luminescence spectrum of Re-doped Ca-α-SiAlON has been reported [52]. For instance, high purity α-SiAlON phosphor was prepared by Yamada et al. for optical applications [7]. These new materials can find applications in medicine, optical communications or space flying vehicles as they combine good mechanical properties, thermal and chemical stabilities, and optical properties.

2.3 Processing routes

There are several processes that can be used to produce SiAlONs. The main processes dealt with in this section use different raw materials but some other techniques also imply the use of different type of heating process. A general experimental procedure common to the various routes is first described then the traditional and most frequently used process is detailed. Following this traditional liquid phase sintering, two processing routes using cheaper raw material, the reaction bonding and the silicothermal reduction routes, are discussed. The SiAlON materials investigated in this work were prepared by one of these two routes. Finally, in order to be exhaustive, another three alternative processes are briefly described.

2.3.1 Typical experimental procedure for the production of SiAlON

SiAlONs are obtained from a mix of usually three or more of the following powders: Si₃N₄, AlN, Al₂O₃, SiO₂, Si, Al or clay as kaolin or halloysite and metal ion oxides. The latter help the sintering of all SiAlON phases and can enter the composition of α-SiAlON. The starting powders are mixed in a dispersant such as isopropanol or alcohol using Si₃N₄ balls or another non-contaminant milling media on a roller bench for at least 12 h or in a planetary mill for a shorter time (around 2 h). The dispersant is then removed by rotary evaporation. The powder is usually cold pressed in pellet form before the heat treatment but sometimes the powder mix can be heat treated first to form a SiAlON powder prior to being pressed.

The heat treatment can comprise several steps depending on the different intermediate reactions that are expected, or it can be composed of several independent firing schedules. The first one is usually to obtain an intermediate product, such as decomposing CaCO₃ (i.e. in case of CaO additive added in
indirect form) or reacting Si with N\textsubscript{2} to obtain a Si\textsubscript{3}N\textsubscript{4} and consequently form the SiAlON phases. A second firing is used to sinter the product and obtain the final composition. It can be followed by a post-sintering heat treatment in order to minimise or devitrify the glassy grain boundary phases. Only the sintering stage allows advanced densification of SiAlONs, the pre and post-sintering are only used to prepare the powder for sintering and to improve the properties of the sintered product.

X-ray diffractometry (XRD) is used to determine the phase composition of a sample and although it can only identify crystalline phases, it can be used to determine their lattice parameters which in turn allow to investigate how the structure changes with different amounts of substitution. A good complement to XRD analysis is the use of magic-angle spinning nuclear magnetic resonance (MAS NMR) on the \textsuperscript{29}Si and \textsuperscript{27}Al because it can distinguish the local coordination of these atoms \cite{53}. X-ray energy dispersive spectroscopy (EDS) analyses the individual elemental concentrations of a sample, and can be used for both crystalline and glassy phases.

For mechanical properties characterisation, strength measurements can be carried out with either three-point or four-point flexural methods where the samples typically need to be polished on the tensile face. Hardness is measured on polished surfaces using a Vickers diamond indenter under a load of typically 98 N (10 kg) and fracture toughness is determined by the indentation fracture method usually under the same load. Indentation fracture method is not the most accurate method to evaluate the fracture toughness \cite{54} of a sample but is the fastest and easiest to realise for ceramic materials \cite{55}. The wear resistance can be measured using a ball-on-ring or block-on-ring test \cite{38}. Finally, the microstructure of polished and etched surfaces of samples are analysed with a scanning electron microscope (SEM). The room temperature Young’s modulus is measured by the ultrasonic pulse echo method \cite{42}. The apparent density is determined in water using the Archimedes’ technique. Thermogravimetric analysis (TGA) can be used to follow the nitridation and decomposition behaviour at increasing temperatures and to carry out oxidation experiments \cite{30}.

2.3.2 Traditional liquid phase reaction sintering

Si\textsubscript{3}N\textsubscript{4} is a highly covalent material, so the bulk diffusion rate of Si and N is too low to give effective densification, hence solid state sintering is inconceivable. In consequence sintering additives, that can form a liquid phase with the other species in the material, are used so that densification occurs via a liquid phase sintering process, producing a fully densified product. The first process \cite{1} that was used to form SiAlON ceramics was the sintering of a Si\textsubscript{3}N\textsubscript{4} powder in the presence of sources of Al and O such as Al\textsubscript{2}O\textsubscript{3}, AlN or SiO\textsubscript{2} as well as rare-earth or metal oxides in the case of \textalpha-SiAlONs \cite{16}. It has the advantage of being able to produce the most dense and purest SiAlONs, but this process takes a lot
of energy and a long time. Furthermore it requires the use of Si$_3$N$_4$ powder which is an expensive powder.

**Mechanism of liquid phase reaction sintering in SiAlONs**

Independently of the processing route used, the densification of SiAlION ceramics always occurs via a liquid phase sintering process. This process is described in three partly overlapping stages.

First of all, once the temperature reaches the temperature of the formation of the eutectic liquid ($T_1$), the rare-earth oxides react with SiO$_2$ and Al$_2$O$_3$ to form a low melting point liquid phase. This liquid, which is a ternary eutectic oxide melt, allows the remaining solid particles to slide over each other under the action of the capillary forces, resulting in primary particle rearrangement.

At higher temperatures, this liquid phase wets the powder and further shrinkage occurs. It has been shown that generally the most basic oxides, from Li to Gd, wet Si$_3$N$_4$ first, whereas the most acidic wet AlN [56]. A second shrinkage is thus observed when the liquid phase wets the majority of the nitride powder at a temperature $T_2$, if Si$_3$N$_4$ is wetted first, or at a higher temperature $T_3$, if AlN is wetted first as shown in Figure 2.10 [57]. In consequence the temperatures $T_2$ and $T_3$ are dictated by the basicity of the melt. The rate and extent of shrinkage does not just depend upon the viscosity, but more so upon the quantity of the liquid and its wetting properties. If the particles have some solubility in the liquid phase, the liquid dissolves them until it reaches its saturation. Once the liquid phase is supersaturated, particles, which will then be of a SiAlON composition, precipitate and lead to a secondary rearrangement.

![Figure 2.10: Schematic shrinkage curves when the eutectic melts wets (a) Si$_3$N$_4$, and (b) AlN first [57].](source)

Generally, in liquid phase sintering (LPS), the liquid phase is still present in the final material, but, in the case of $\alpha$-SiAlON, it can be incorporated into the structure and appears just as a transient liquid. Finally, the densification proceeds in the same way as it does in a solid state sintering mechanism which implies the coalescence of the newly formed grains and the elimination of the closed pores [57].
**Characteristics in SiAlONs**

In general the eutectic temperature is dependent on the composition, but in the case of $\alpha$-SiAlONs and for a given $\text{Re}_x\text{O}_y$-$\text{SiO}_2$-$\text{Al}_2\text{O}_3$ system with a single eutectic point, the eutectic temperature is independent of the composition at low nitrogen contents [56]. However, the eutectic temperature changes when the $\text{Re}_x\text{O}_y$ is changed. The temperature at which the $\alpha$-SiAlON starts to precipitate depends on the rare-earth system and its basicity, with higher basicity expected to lower this temperature. Table 2.4 presents the eutectic temperatures and the temperatures when the $\alpha$-SiAlON starts to precipitate for some of the most commonly used metal oxides. To achieve full densification at relatively low temperatures, low wetting temperature for the second nitride ($T_3$) and low dissolution temperature of the intermediate phase ($T_4$) are required.

**Table 2.4: Temperatures of formation of the eutectic melt and of the precipitation of $\alpha$-SiAlON for various oxides [56, 57].**

<table>
<thead>
<tr>
<th>Oxides</th>
<th>pH</th>
<th>Eutectic temperatures (°C)</th>
<th>Temperatures of precipitation of $\alpha$-SiAlON (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiO</td>
<td>11.76</td>
<td>1010</td>
<td>1420</td>
</tr>
<tr>
<td>CaO</td>
<td>10.67</td>
<td>1360</td>
<td>1550</td>
</tr>
<tr>
<td>MgO</td>
<td>10.27</td>
<td>1350</td>
<td>1575</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>8.93</td>
<td>1400</td>
<td>1420</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>8.88</td>
<td>1370</td>
<td>1575</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>8.86</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>8.77</td>
<td>1380</td>
<td>1420</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>8.75</td>
<td>1360</td>
<td>1575/1675</td>
</tr>
<tr>
<td>Er$_2$O$_3$</td>
<td>8.72</td>
<td>1400</td>
<td>1580</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>8.49</td>
<td>1380</td>
<td>1680</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>7.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>3.36</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Without rare-earth additives, i.e. for the $\beta$, O and X-SiAlONs, the process of formation remains the same. The formation of SiAlON occurs with the same liquid phase sintering process, but the liquid phase is based only on $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$. In these materials, rare-earth oxides can be employed but their role is different to the $\alpha$-SiAlONs where they are a necessary requirement to stabilise the structure. In this case, their role is solely to facilitate the sintering by lowering the reaction temperature and providing more liquid phase to promote densification; they do not enter the structure of these SiAlONs and remain as an intergranular phase. This traditional liquid phase reaction sintering has been used to produce all kinds of SiAlONs from $\alpha$-SiAlON and $\beta$-SiAlON to O-SiAlON and even X-SiAlON. Table 2.5 presents the starting powders used to produce SiAlONs from the traditional reaction sintering process.
Table 2.5: Starting powders generally used to produce SiAlON from the traditional reaction sintering process [3, 31].

<table>
<thead>
<tr>
<th>Starting powders</th>
<th>Si₃N₄</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>AlN</th>
<th>RE₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-SiAlON</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>β-SiAlON</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>*</td>
</tr>
<tr>
<td>O-SiAlON</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>X-SiAlON</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>*</td>
</tr>
</tbody>
</table>

* Represents the addition of metal oxides used to facilitate the sintering but that does not enter the final composition of the SiAlON.

2.3.3 Reaction bonding

The reaction bonding route uses the same starting powders as the traditional liquid phase reaction sintering route with the exception of Si which is used instead of Si₃N₄ powder. The goal of this process is to reduce the cost of production by lowering the cost of the raw powder, Si being cheaper than Si₃N₄. The main difference between these two processes in terms of mechanism of formation is the reaction of Si with nitrogen atmosphere to form in situ Si₃N₄. After formation of Si₃N₄, the mechanism remains identical to the liquid phase reaction sintering described in the previous section.

2.3.3.1 Nitridation of Si, the reaction bonded Si₃N₄ (RBSN)

This step concerns the SiAlONs formed from both reaction bonding and silicothermal reduction routes (see Section 2.3.4). Nitridation of Si in a SiAlON mixture differs from the nitridation of a pure Si powder due to the presence of other species in the mixture, for instance Mitomo has shown that the addition of Al₂O₃ has an influence on the nitridation of Si [58]. Nevertheless the mechanism remains similar and the study of the RBSN can contribute to some useful information on the ways to improve the first step of the reaction bonding process for the formation of SiAlON. It may also be of importance to be able to manage the α/β ratio in the newly formed Si₃N₄ as it can have an influence on the type and morphology of SiAlON formed. The following sections deal with the nitridation of a Si powder.

Generalities

Silicon nitride, Si₃N₄, exists in two hexagonal crystalline phases, or polymorphs, termed α and β with α-Si₃N₄ having the slightly higher free energy at the formation temperature. α-Si₃N₄ is unstable with respect to β-Si₃N₄ [59], but the transformation from α-Si₃N₄ to β-Si₃N₄ does not occur without the presence of a liquid phase in which α-Si₃N₄ grains can dissolve above 1400°C [60]. The bonding in the Si₃N₄ is estimated to be 70% covalent and Si₃N₄ can be formed by reaction of Si, under any of the solid, liquid or gas states, with nitrogen gas. In nitrogen atmosphere, the starting temperature of
nitridation between Si and N₂ is about 700°C but rapid nitridation begins at higher temperature, about 1050°C [61]. Si powder can be considered almost fully reacted after 5 h at 1300°C where the nitridation ratio reaches up to 97.6% [61].

Formation

To form a RBSN component, the compact, composed of Si powder, is first subjected to a cold isostatic pressing in order to obtain its shape. This compact is then heated, usually in N₂ at 0.1 MPa, at temperatures between 1250°C and 1450°C when the reaction bonding reaction takes place. The solid volume increases by about 22% on conversion to Si₃N₄ but the volume expansion is accommodated entirely within the pore structure of the compact. As a result, only a slight change in size is observed. The RBSN has generally a porosity of around 20% in volume, with 80% (in volume) of the pores of size less than 0.1 µm, and typically a commercial RBSN is composed of 60 to 90% in mass of α-Si₃N₄, with the remaining part being comprised of β-Si₃N₄ [5, 62].

Mechanism

The direct nitridation of Si is one of the most commonly used processes for the mass production of α phase dominant Si₃N₄ [63]. The nitridation of a compact involves two partly overlapping steps. The first one is the diffusion of the nitrogen into the pores of the compact, and the second is the chemical reaction between Si and N₂ according to:

\[ 3\text{Si} + 2\text{N}_2(\text{g}) \rightarrow \text{Si}_3\text{N}_4 \]

The stages of the reaction between a high purity Si powder and N₂ are therefore proposed as follows. The volatilisation of Si and the vapour phase reaction with N₂ leads to the formation of α-Si₃N₄. The formation of Si₃N₄ nuclei starts on the surface of the Si grains by solid-gas reaction or by precipitation from the liquid phase, leading to the growth of β-Si₃N₄ [62]. It was observed that the areal density of nuclei increases as nitrogen pressure increases and temperature decreases. The nuclei grow laterally and vertically and Si is supplied to the growth site by both surface diffusion and evaporation/condensation. For a nitrogen pressure below 0.1 MPa, the reaction rate is determined by the rate of arrival of nitrogen on the growth site. The direct nitridation slows as the free Si surface area decreases and because the surface diffusion distance increases. On the other hand, the reaction of Si in a vapour state continues, and ceases when the reactants are separated. Indeed the nitridation of solid Si by gaseous N₂ leads to a coherent layer of β-Si₃N₄. The formation of such a layer is rapid when the nitrogen pressure is 0.1 MPa, but it can be delayed, permitting continued nitridation of the Si, if nitrogen pressure is reduced. This model explains the dependence of the kinetics on changes in temperature and pressure. Under low nitrogen pressure, the supply of N₂ to the reaction sites becomes rate-determining. The α and β-Si₃N₄ forming reactions are, therefore, competing for N₂ [62, 64]. Finally, β-Si₃N₄ results from reactions between N₂ and unoxidised Si surfaces, Si vapour or liquid Si
whereas $\alpha\text{-Si}_3\text{N}_4$ forms from reactions involving SiO and N$_2$, with SiO acting as the transport medium for Si in the porosity network to the reaction site according to:

$$3\text{SiO}(g) + 2\text{N}_2(g) \rightarrow \alpha\text{-Si}_3\text{N}_4(s) + 1.5\text{O}_2(g)$$

Therefore there probably is a minimum effective SiO pressure which aids network formation but eliminates the formation of surface layers and loss of SiO from the compact [64].

### 2.3.3.2 Reaction bonding of SiAlON

This process uses the same starting mixture as the reaction sintering process (see Table 2.5) with the exception of the expensive Si$_3$N$_4$ being replaced by the cheaper Si powder. The reaction bonding of SiAlONs occurs in two steps. The first one is the nitriding stage, where the nitridation takes place, and the second one is the sintering stage, which is similar to the stage described for the liquid phase reaction sintering process. The mechanical properties of reaction bonded SiAlONs generally cannot meet the high reliability and performance specifications required for advanced engineering applications due to the existence of pores and residual Si [61, 65]. However it is of interest for applications such as refractories that focuses on low production costs and good chemical properties rather than high performances.

The mixture is fired under nitrogen pressure and the Si powder is expected to react with N$_2$ to form Si$_3$N$_4$ as described by reaction (2.1). Due to the formation of a eutectic liquid phase during the nitridation, a relatively large amount of $\beta\text{-Si}_3\text{N}_4$, ranging from 40 to 50% in mass, is formed in the reaction bonded SiAlONs. Chen et al. [61] described a possible reaction path to form $\beta\text{-SiAlON (z=2)}$ from the reaction bonding of a starting mix composed of Al, Si and Al$_2$O$_3$. They have observed that the nitridation of Al and Si occurred first, with rapid nitridation of Al and Si starting respectively at about 900°C and 1050°C. Temperature was found to be the most important factor affecting the rate of the nitridation reaction, but it was possible to lower the starting temperature of rapid nitridation by decreasing the grain size of Si. The reaction sequence that leads to the formation of $\beta\text{-SiAlON (z=2)}$ prepared by the reaction bonding route is suggested as follows [61].

First Al reacts with N$_2$ according to:

$$2\text{Al} + \text{N}_2(g) \rightarrow 2\text{AlN}$$

In the case where AlN is used, this first step obviously does not occur. Then Si reacts with the nitrogen atmosphere following equation (2.1). Finally Si$_3$N$_4$ and AlN react with Al$_2$O$_3$ to form $\beta\text{-SiAlON (z=1)}$:

$$\text{AlN} + \text{Al}_2\text{O}_3 + 5\text{Si}_3\text{N}_4 \rightarrow 3\beta\text{-Si}_5\text{AlON}_7$$
AlN and Al_2O_3 can further react with the newly formed SiAlON to form a SiAlON with a higher level of substitution (z=2):

$$2\text{AlN} + \text{Al}_2\text{O}_3 + 4\beta-\text{Si}_4\text{AlON}_7 \rightarrow 3\beta-\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$$

Here the authors have suggested two steps to form a $\beta$-SiAlON with $z=2$, as in a progressive substitution of Al and O in the Si_3N_4 structure but it could have also been written directly as:

$$2\text{AlN} + 2\text{Al}_2\text{O}_3 + 4\beta-\text{Si}_3\text{N}_4 \rightarrow 3\beta-\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$$

In a variation of the reaction bonding process, Peelamedu and Kalya [10] have suggested a three-stage process for the formation of $\beta$-SiAlON from Si and AlN powders (Al_2O_3 was not used) under a nitrogen/oxygen controlled atmosphere.

The first stage requires a very low oxygen partial pressure because it is necessary to ensure that the primary reaction is the nitridation of Si and that the product formed is Si_3N_4.

The second stage is the reaction of Si_3N_4 and AlN where Si_3N_4 units begin to incorporate AlN which is structurally similar (they both have tetrahedral bonding with nitrogen as their structural units are [SiN_4] and [AlN_4] respectively).

The charge imbalance created by this substitution of tetravalent Si with trivalent Al acts as a driving force for the incorporation of oxygen from the ambient gas into the structure. Incorporation of oxygen is therefore the third stage of the reaction. As the AlN/Si ratio increases, the proportion of $\beta$-SiAlON in the mixture increases. When the AlN/Si ratio is above 0.66, only $\beta$-SiAlON is formed.

To conclude, the reaction bonding route allows the formation of all SiAlON phases, the only difference with the reaction sintering in terms of processing being the use of Si. Although the process of formation is similar to when Si_3N_4 is used, the final product does not achieve the same mechanical properties. For instance the products are generally more difficult to sinter to full density: Park et al. [65] did not manage to densify $\beta$-SiAlON ($z=0.45, 0.92$ and $1.87$) to more than 90% of the theoretical density by pressureless sintering without an excess liquid phase.

### 2.3.4 Silicothermal reduction

The silicothermal route is the most recent one seen so far and, as with reaction bonding, it has been developed to reduce the cost of fabrication of the SiAlON. In this process, SiAlONs are prepared from Si and any clay with a kaolinite type structure such as kaolin [66] or halloysite. The use of clay in the starting powder presents the advantages to both lower the reaction temperature and facilitate forming by pressing, slip casting and extrusion. This gives a much greater flexibility in the shape and size of the ceramic products which can be produced [30].
2.3.4.1 Behaviour of a clay material: halloysite

Halloysite has the same theoretical chemical composition as kaolinite with the exception of its higher water content. The formula for halloysite is then $Al_2Si_2O_5(OH)_4\cdot nH_2O$ however this composition may be subject to some variation due to the presence of impurities [67]. The material, which has a tubular morphology, is composed of layers of crystalline halloysite separated by interlayer water and is composed of a two-layer monoclinic structure as shown in Figure 2.11.

![Figure 2.11: Crystal structure of halloysite [67]. Dark and white disks represent oxygen and hydrogen atoms respectively. Silicon and aluminium are located at the centre of the tetraedras.](image)

Halloysite is fired along with other powders to produce SiAlON. It is therefore important to know how halloysite behaves with respect to temperature. Differential thermal analysis of halloysite shows a three-step process when fired at temperatures up to 1100°C. A first endothermic peak is observed between 50°C and 150°C and corresponds to the loss of adsorbed water, which is the humidity located inside the tubes and zeolitic water located between the layers (Figure 2.11). This step does not damage the structure of halloysite. At temperatures of between 450°C and 600°C, the constitution water leaves; this is the structural dehydroxylation, it destroys the structure of the mineral and is represented by a second endothermic peak. Finally, an exothermic peak is observed between 885°C and 1000°C which corresponds to the formation of new phases, SiO$_2$ and mullite [67], according to:

$$3(Al_2O_3\cdot 2SiO_2\cdot 2H_2O) \rightarrow 2SiO_2\cdot 3Al_2O_3 + 4SiO_2 + 6H_2O(g)$$

(2.7)

2.3.4.2 Silicothermal reduction of SiAlON

The process uses the same starting mixture as the reaction bonding route with the exception of the main source of Al$_2$O$_3$, which is halloysite instead of alumina. Therefore the reaction that leads to the formation of SiAlON proceeds in several steps. The first step is the thermal decomposition of the clay to form mullite and amorphous SiO$_2$. This occurs between 885°C and 1000°C for the halloysite [67] according to reaction (2.7), and it is expected to be fully completed by 1100°C [68]. Partly overlapping with the previous step, Si begins to be nitrided at about 957°C [69] according to reaction (2.1). In the
absence of nitriding enhancers, this reaction proceeds in two stages because of the formation of a gas-impermeable nitride layer around the Si grains [68]. The last steps depend on the targeted SiAlON and the starting powder used. In the case of an X-SiAlON, for instance, the alumina from the starting mixture reacts with the amorphous SiO$_2$ from the decomposition of the clay to form an aluminosilicate. Most of this reaction occurs between 1250°C and 1300°C [68]:

$3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow (2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3)$

This latter product reacts with the Si$_3$N$_4$ formed earlier to give X-SiAlON:

$3(2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3) + 2\text{Si}_3\text{N}_4 \rightarrow \text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$

Some intermediate SiAlONs can be detected as a result of an early-stage nitridation of oxygenated phases. Another alternative mechanism has been proposed suggesting the formation of an intermediate silicon oxynitride (Si$_2$ON$_2$) phase. Thus after the clay is decomposed, SiO$_2$ will react with Si and N$_2$ to produce Si$_2$ON$_2$ according to:

$3\text{Si} + \text{SiO}_2 + 2\text{N}_2(g) \rightarrow 2\text{Si}_2\text{ON}_2$

Si$_2$ON$_2$ will then react with Al$_2$O$_3$ and mullite to form X-SiAlON [70]. X-SiAlON has been produced at temperatures of around 1500°C with holding times varying from 2 to 8 h with an overall equation such as:

$2.87(\text{Al}_2\text{O}_3 \cdot 2.09\text{SiO}_2) + 6\text{Si} + 6.13\text{Al}_2\text{O}_3 + 4\text{N}_2(g) \rightarrow \text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$

All types of SiAlONs have been achieved by silicothermal reduction route at lower temperatures than encountered with the previous methods. Following are some examples of SiAlON formed by this method.

Na-$\alpha$-SiAlON (m=1, n=0.5) was successfully prepared by White [66] at 1300°C for 2 h according to:

$0.064(\text{Al}_2\text{O}_3 \cdot 2.4\text{SiO}_2 \cdot 2.2\text{H}_2\text{O}) + 10.45\text{Si} + 1.37\text{AlN} + 7.06\text{N}_2(g) + \text{NaF}$

$\rightarrow \text{NaSi}_{1.0.5}\text{Al}_{1.5}\text{O}_{0.5}\text{N}_{15.5} + 0.14\text{H}_2\text{O}(g) + 0.25\text{SiF}_4(g)$

The porosity of the samples fired was still high at 1500°C (30-40%) but reduced to 1% at 1775°C. However $\alpha$-SiAlON was mainly transformed into the $\beta$-SiAlON phase.

$\beta$-SiAlON (z=0.5) could also be synthesised and the reaction took place at 1350°C as follows:

$0.064(\text{Al}_2\text{O}_3 \cdot 2.4\text{SiO}_2 \cdot 2.2\text{H}_2\text{O}) + 5.35\text{Si} + 0.37\text{AlN} + 2.57\text{N}_2(g)$

$\rightarrow \text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{0.5}\text{N}_{7.5} + 0.14\text{H}_2\text{O}(g)$

With the addition of Y$_2$O$_3$, the $\beta$-SiAlON yield was close to 100% [71].

Finally O-SiAlON (x=0.2) has been sintered to full density at 1700°C without additives and without application of pressure at high temperatures [71] according to:

$(\text{Al}_2\text{O}_3 \cdot 2.4\text{SiO}_2 \cdot 2.2\text{H}_2\text{O}) + 13.5\text{Si} + 2.1\text{SiO}_2 + 9\text{N}_2(g) \rightarrow 10\text{Si}_{1.8}\text{Al}_{0.2}\text{O}_{1.2}\text{N}_{11.8} + 2.2\text{H}_2\text{O}(g)$
In conclusion, the synthesis of SiAlON via the silicothermal reduction route provides the opportunity to lower the sintering temperatures, to use cheaper raw materials and to benefit from the advantages of clay in terms of forming. These factors combine to make silicothermal reduction one of the most economical routes for the production of SiAlONs. However it is still a long process due to the time required to complete the nitridation reaction and to date all the SiAlONs prepared by this method contain high levels of porosity that lower the mechanical properties of the ceramics.

2.3.5 Other processing routes

2.3.5.1 Carbothermal reduction and nitridation

The carbothermal reduction and nitridation process was invented in 1976 by Cutler et al. [72]. Like the silicothermal reduction process, it uses cheap raw materials but releases CO as waste. This method consists of firing clay materials with C in a nitrogen atmosphere. The composition can be adjusted to produce \( \alpha, \beta, O \) and \( X \)-SiAlON by adding \( \text{SiO}_2, \text{Al}_2\text{O}_3 \) or Si and, in the case of \( \alpha \)-SiAlONs, rare-earth oxides.

The carbothermal reduction and nitridation occurs in three steps. The first step of the reaction is similar to the silicothermal reduction as it consists of the thermal decomposition of the clay into mullite and \( \text{SiO}_2 \). The second step is the reduction of \( \text{SiO}_2 \) by C to form SiC and CO or CO\(_2\) according to:

\[
(2.15) \quad \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}(g)
\]

or \( (2.16) \quad \text{SiO}_2 + 2\text{C} \rightarrow \text{SiC} + \text{CO}_2(g) \)

This intermediate SiC phase has not always been detected [73] as it seems to depend on the content of carbon [74]. Thus another reduction of \( \text{SiO}_2 \) can occur and lead to \( \text{SiO} \) [74] as follows:

\[
(2.17) \quad \text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}(g)
\]

Furthermore, when \( \text{SiO} \) is formed as an intermediate phase, it can react with C and \( \text{N}_2 \) as:

\[
(2.18) \quad 2\text{SiO} + \text{C} + \text{N}_2(g) \rightarrow \text{Si}_2\text{ON}_2 + \text{CO}(g)
\]

The incorporation of \( \text{Al}_2\text{O}_3 \) into the \( \text{Si}_2\text{ON}_2 \) structure can form O-SiAlON or X-SiAlON as an intermediate phase. Finally C, \( \text{N}_2 \), SiC and mullite react to produce SiAlONs. The first two steps are independent of nitrogen atmosphere, but the presence of excess \( \text{N}_2 \) during the third stage is critical to ensure complete nitridation [75].
2.3.5.2 Combustion synthesis

Combustion synthesis, or self-propagating high-temperature synthesis (SHS), is a process which utilizes heat generated by the exothermic reactions of the nitridation of Si and Al to sustain itself after external ignition. Because of the very high temperatures quickly achieved in such a combustion process, the products are of high activity and purity, and are produced with high energy efficiency and a short processing time. This process involves the same mixture of powders as previously seen, i.e. a combination of three or more of the following powders: Si, Al, Al$_2$O$_3$, AlN or SiO$_2$ and, in the case of α-SiAlONs one or more rare-earth oxides.

The products of this method are not as dense and hard as the SiAlONs obtained by other methods. However this apparent disadvantage can be of interest in preparing seed crystals as the product obtained can be pulverised more easily. The combustion synthesis route has already been used by Liu et al. [24] to prepare Y-α-SiAlON seed crystals and by Aoyagi et al. [76] and Wu et al. [77] to produce β-SiAlONs.

2.3.5.3 Spark plasma sintering (SPS)

Spark plasma sintering is a sintering method that enables rapid heating (up to 600°C.min$^{-1}$) and promotes low temperature sintering. It consists of applying a pulsed direct current through the sample, which will cause localised spark discharge heating at the particle surface, thus enhancing the sintering. This technique allows the preparation of fully dense compacts within a few minutes. In addition, it provides the possibility of reducing weight losses by evaporation as it has a rapid heating and short dwell time [78]. Shen et al. [43] have also shown this method to be efficient to develop elongated α-SiAlION grains. SPS has been used to produce all types of SiAlONs. In two studies, Barris et al. have observed that X-SiAlON [79] and O-SiAlON [80] produced by this method exhibit unusually high strengths compared to the common values obtained for these materials.

2.4 Influence of different variables on SiAlON formation

Previous sections have described the existing SiAlON phases and the different processes used to produce them. It has been seen that temperature plays a major role in the formation of SiAlON, but it is not the only factor that has a significant influence. This section bears upon all the other factors encountered in the literature that modify the formation of SiAlON. These factors have been sorted in two categories. On one hand there are factors related to the composition of the SiAlON, namely all the modifications that can be made to the starting material before any heat treatment, such as additions of nitriding or sintering enhancers or selection of a specific Si$_3$N$_4$ phase. On the other hand there are
factors related to the environment of the sample such as alterations of the gas atmosphere and changes in the local environment by means of powder beds.

2.4.1 Composition related factors
Additives are generally targeted to promote a reaction or to improve a specific property. In SiAlONs, two types of additives can be distinguished. The ones used to catalyse the nitridation by either removing the oxide layer at the surface of Si particles or by facilitating the transport of N₂ to the reaction site and the additives used to promote the densification of the samples by forming a eutectic liquid at low temperature. Even though they are used in small quantities, usually a few mass per cent of the starting mixture, all these additives are susceptible to remain in the product as an intergranular phase. Therefore, even if they are firstly selected for their effects on nitridation or densification, the properties of the intergranular phase that will be generated needs also to be taken into account when additives are chosen.

2.4.1.1 Influence of nitriding enhancers
In the production processes that rely on the nitridation of Si, a number of different factors may influence the course of the nitridation reaction. Such factors include gas permeability of the compact, temperature gradient within the compact as it is known that the nitridation reaction is exothermic, impurities in the nitriding gas and in the Si compact. The following paragraph focuses on the effects of the type and quantity of additives that are used to enhance the nitridation of Si.

While Alumina (Al₂O₃) is the most common sintering additive for Si₃N₄ as it results in a decrease in the eutectic temperature of around 200-300°C during the sintering process, it can also affect the formation of nitride in reaction bonded processes, since its addition has been reported to enhance the growth of β-Si₃N₄ and retards the formation of α-Si₃N₄. The reaction of aluminium nitride (AlN) with the surface layer of SiO₂ to form Al₂O₃ and Si₃N₄, is responsible for the lowering of the O₂ partial pressure which retards the formation of α-Si₃N₄ [58].

Iron (Fe) is considered a promoter of the nitridation [10]. It induces the volatilisation of the native oxide layer on each Si particle and leads to the growth of extra Si₃N₄ in proportion to the amount of Fe. Fe catalyses the removal of the oxide film following the reaction:

\[ 2\text{SiO}_2(s) + Fe \rightarrow 2\text{SiO}(g) + O_2(g) \]  

FeSiₓ is present at temperatures above 1207°C, and nitridation is enhanced by the diffusion of N₂ into the FeSiₓ liquid leading to the formation of β-Si₃N₄ as well as by the increase of Si vaporisation.
leading to the $\alpha$-Si$_3$N$_4$ formation [62]. The fast growth of Si$_3$N$_4$ in the melt occurs by a vapour-liquid-solid (VLS) mechanism. Furthermore the spreading of the melt from the Fe sourcing out into the compact microstructure is expected. The resulting increase in reactive surface, remaining free of reactions inhibiting Si$_3$N$_4$ growth, could explain the accelerated reaction. Such a melt provides a route for Si to move from the solid to the vapour state, where it can react with N$_2$. Finally Fe enhances the $\beta$-Si$_3$N$_4$ formation and, below the melting point of Si (1410°C), the amount of $\beta$-Si$_3$N$_4$ grown correlates well with the Fe content of the powder. Iron oxides Fe$_3$O$_4$ and Fe$_2$O$_3$ are also used to promote nitridation of Si [25]. However Fe deteriorates the mechanical properties of the material. Indeed Fe reacts with Si to form a liquid, which migrates into the microstructure leaving a pore at the site of each Fe particle. The microstructure is therefore composed of microstructural inhomogeneities, namely voids, surrounded by a dense region of mainly $\beta$-Si$_3$N$_4$. Fe then acts as a defect for reducing properties such as fracture strength and Weibull modulus [11]. As Fe induced defects increase with temperature, the lower the nitriding temperature, the smaller the inhomogeneity and the higher the strength [62].

**Calcium** (Ca) promotes the conversion of Si to $\alpha$-Si$_3$N$_4$; however the overall conversion decreases when the content of Ca increases to 1% in mass or higher [81]. This phenomenon has not yet been explained in powders; but in compacts, a preliminary experiment carried out by the author shows that the presence of excess CaO promotes the densification of the samples which may hinder the beneficial effect on nitridation as shown in Figure 2.12. With Ca additions, raising the temperature is effective in promoting the overall conversion and in enhancing the suppression of $\beta$-Si$_3$N$_4$. A drawback to the addition of Ca is that it has been found to degrade the subcritical crack growth resistance and the creep resistance of Si$_3$N$_4$ [82].

![Figure 2.12: Effects of CaO additions on the overall conversion and densification of Si compacts after 3 h at 1400°C under 0.4 MPa of nitrogen.](image-url)
The addition of copper (Cu) [81] significantly increases the overall conversion at low temperatures but the enhancement of nitridation decreases as the temperature increases. At 1200°C, the overall conversion with Cu is twice as high as with pure Si whereas at 1300°C the overall conversion is lower than the latter. Cu also tends to enhance the growth of β-Si3N4 at 1300°C while it suppresses its formation at lower temperatures. Although Cu additions have conflicting effects on the nitridation of Si, there is no study that explains this phenomenon.

Zirconia (ZrO2) has been shown to be an effective enhancer for the nitridation of Si. ZrO2 additions decrease the starting temperature of the main reaction step [11], and increase the amount of Si converted to Si3N4 at a given temperature. For instance, for pure Si powder and for ZrO2 added Si powder, the mass gain starts at 957°C and 952°C respectively but the starting temperature of the main reaction step decreases with increasing ZrO2 content. Moreover, the degree of conversion of Si increases with increasing ZrO2 content. Hyuga et al. [69] have reported that 71.23% of the Si was nitrided with 29.45% in mass of ZrO2 in the Si powder at 1400°C (with a 20°C.min⁻¹ ramp) whereas there was only 14.58% of the Si nitrided when no additive were used at the same temperature. The nitridation rate at higher temperatures (1380°C-1400°C) indicates similar values for both pure Si and Si with ZrO2 additions. It has also been observed that the presence of Al2O3 does not affect the nitridation enhancing effect of ZrO2 and the latter does not form any solid solution with Si3N4 [11].

In the case of rare-earth additions (and yttria), the effects on nitridation are mixed. Yttria (Y₂O₃) performs a nitridation enhancing role in the early stages of nitridation due to the reaction with SiO₂ on the surface of Si powder to form yttrium silicates [83] and suppresses the β-Si3N4 formation. Cerium (Ce) delays the nitridation of Si regardless of the processing temperature [84]. On the other hand cerium increases the β-Si3N4 content at high temperatures. Ytterbium (Yb) is the only metal found by Pavarajarn et al. [84] that has no effect on the overall conversion of Si into Si3N4 but improves the α-Si3N4 content. A more recent paper [85] shows that all rare-earth oxides (and Y₂O₃) have an enhancing effect on the nitridation of Si, with Eu and Ce showing a larger enhancing effect than the other oxides. These results are different from the observations of Pavarajarn [84] especially with the addition of Ce. These differences may come from the experimental conditions which are different between the two studies. In his paper, Pavarajarn fired his powders with metal additions – not oxides – under a flowing gas composed of 90% N₂ and 10% H₂, while Hyuga et al. [85] used oxide additives and fired their powders in flowing N₂. Even though intermediate phases such as N-apatite, rare-earth silicides or silicates have been observed, none of the authors have yet proposed a mechanism for the catalytic effect of these additives.
Ammonium fluoride \((\text{NH}_4\text{F})\) has also been used to enhance the nitridation of Si powder. The paper of Liu et al. [24] shows that an increase of NH\(_4\)F addition decreases the final amount of residual Si in products. Indeed the decomposition of NH\(_4\)F generates HF and NH\(_3\) which enhance the concentration of nitrogen in the product. The formation of silicon fluorides is considered to be associated with the catalytic effect of NH\(_4\)F on the nitridation of Si. This catalytic effect is possible because fluoride species (SiF\(_x\)) can react with N\(_2\) or NH\(_3\) in the gas phase and thus provide an easier route for the nitridation of Si [86].

![X-ray patterns of a Y-\(\alpha\)-SiAlON (m=1.44 and n=0.96) combusted in the presence of different amounts of NH\(_4\)F under a constant nitrogen pressure of 4 MPa [86].](image)

All the modifications of the nitridation reaction seen so far can have an effect on the later stage of formation of SiAlON. These effects are mainly related to the preferential formation of \(\alpha\) or \(\beta\)-Si\(_3\)N\(_4\) phases and are discussed further in more detail. In the case of NH\(_4\)F, it is more the rapidity of the conversion that influences the later formation of SiAlON rather than the seeding effect of one phase. Indeed with an excess of NH\(_4\)F [24], \(\alpha\)-Si\(_3\)N\(_4\) is produced very quickly and this \(\alpha\)-Si\(_3\)N\(_4\), which cannot be consumed by the formation of \(\alpha\)-SiAlON, will transform into \(\beta\)-Si\(_3\)N\(_4\) or \(\beta\)-SiAlON. Therefore, an increase of NH\(_4\)F content firstly increases the \(\alpha/\beta\)-SiAlON ratio [86], but above certain amounts of NH\(_4\)F, it increases the formation of \(\beta\)-SiAlON as shown in Figure 2.13. If the addition of NH\(_4\)F is carefully controlled, it is possible to tailor the \(\alpha/\beta\) ratio to obtain the desired material. However NH\(_4\)F has only been used as a nitriding enhancer with the combustion synthesis processing route. It is perhaps due to the fact that the gases issued from the decomposition of NH\(_4\)F are so volatile that they need to be contained within the product.
2.4.1.2 Influence of sintering additives

Sintering additives are not essential for the formation of β, O and X-SiAlONs, but when they are used, they are expected to achieve the same goals as those in the formation of α-SiAlONs. The introduction of sintering aids, usually rare-earth oxides, generally promotes both the formation of SiAlONs at lower temperatures, and the densification of the material as it forms a liquid phase at low temperatures. Mandal et al. [29] have established a list of criteria that the sintering aids used to produce α-SiAlONs and (α+β)-SiAlONs should satisfy. The first is that the rare-earth cation used has to be able to stabilise the α-SiAlON structure as detailed in Section 2.2.1.2. The eutectic temperature of the oxide-containing liquid should be lower than the temperature formation of the α-SiAlON phase (see Table 2.4) but high enough to give a good creep resistance. The intermediate phase produced by the oxide should not remain in the final product or the amount should be as low as possible. A high solubility of N₂ in this liquid phase is also an interesting characteristic as it can facilitate the diffusion of N₂ through the sample and enhance the nitridation of Si. Finally, the crystalline phases issued from the devitrification of the glassy grain boundary phase after any post-sintering heat treatment should exhibit a good resistance to oxidation and corrosion. The same criteria apply to the intermediate phases present in the β, O or X-SiAlON systems except that these phases will not be incorporated into the structure of these SiAlONs. When the atomic size (Z) of the rare-earth additives increases, it has been observed that the α-SiAlON content increases and the amount of intergranular phase decreases [29]. This is probably due to the fact that with an increasing Z, the ionic radius of the rare-earth tends to decrease, which facilitates the incorporation of the rare-earth into the α-SiAlON structure.

2.4.1.3 Influence of starting Si₃N₄ phases

The Si₃N₄ powders used in the starting powder mix have been shown to have an influence on the phase development and on the final microstructure of SiAlONs. As it is possible to favour the development of either α or β-Si₃N₄ phases, notably with the use of additives, for the processing routes which do not use Si₃N₄ as a starting powder, it is necessary to be aware of the role that these phases play when they appear as intermediate products during the sintering of SiAlONs.

It was found that the use of different Si₃N₄ starting powders does not significantly affect the final phase assemblage of a Ca-α-SiAlON (m=3.6, n=1.8, pressureless sintered at 1800°C) with the exception of traces of unreacted β-Si₃N₄ remaining in the sintered compact containing 100% β-Si₃N₄ starting powders [87]. The remaining β-Si₃N₄ has been completely dissolved at temperatures above 1825°C whereas the α-Si₃N₄ has already disappeared as early as 1550°C. Even if the final phase assemblage is not affected significantly by the Si₃N₄ starting powders, there are detectable differences
in the phase development such as the amount of intermediate phases created, and their temperatures of formation and dissolution. When $\beta$-$\text{Si}_3\text{N}_4$ is used, its dissolution and the formation of $\alpha$-$\text{SiAlON}$ are the fastest for the heavier cations, like Yb, and the slowest for the lighter cations [21]. Thus $\beta$-$\text{Si}_3\text{N}_4$ to $\alpha$-$\text{SiAlON}$ transformation increases with decreasing ionic radius of the stabilising cation. The same general trend was observed for the formation of $\alpha$-$\text{SiAlON}$ from $\alpha$-$\text{Si}_3\text{N}_4$ starting powder. However the formation of $\alpha$-$\text{SiAlON}$ from $\alpha$-$\text{Si}_3\text{N}_4$ starting powder generally proceeds at a lower temperature than when $\beta$-$\text{Si}_3\text{N}_4$ is used as a starting powder. For instance, Rosenflanz and Chen [21] have shown that when the starting powder is $\alpha$-$\text{Si}_3\text{N}_4$, the formation of $\alpha$-$\text{SiAlON}$ is essentially complete after holding at 1600°C for 1 h for all rare-earth oxide compositions (Dy, Er, Yb) and Y except Gd, Sm and Nd. This is to be compared with the highest amount of $\alpha$-$\text{SiAlON}$ obtained for Yb (72%) when a $\beta$-$\text{Si}_3\text{N}_4$ powder is used at the same temperature. $\beta$-$\text{Si}_3\text{N}_4$ to $\alpha$-$\text{SiAlON}$ transformation proceeds slower than that of $\alpha$-$\text{Si}_3\text{N}_4$, because $\beta$-$\text{Si}_3\text{N}_4$ possesses a higher stability than $\alpha$-$\text{Si}_3\text{N}_4$ [10], which retards its dissolution into the transient liquid, thus delaying the densification [21]. Consequently, the very slow reactivity of $\beta$-$\text{Si}_3\text{N}_4$ results in lower density as well as later shrinkage. Because of the similarity in both structure and composition between $\alpha$-$\text{SiAlON}$ and $\alpha$-$\text{Si}_3\text{N}_4$, nucleation of $\alpha$-$\text{SiAlON}$ on $\alpha$-$\text{Si}_3\text{N}_4$ is energetically more favourable than nucleation of $\alpha$-$\text{SiAlON}$ on $\beta$-$\text{Si}_3\text{N}_4$ or other phases. Thus the higher the $\alpha$-$\text{Si}_3\text{N}_4$ phase content in the starting composition, the more favourable it is for the nucleation of $\alpha$-$\text{SiAlON}$, and a higher $\beta$-$\text{Si}_3\text{N}_4$ phase content in the starting powder results in lower grain density with a higher aspect ratio. For instance, Kushan and Mandal [28] have noticed that $\beta$-$\text{Si}_3\text{N}_4$ powders have a seeding effect for the formation of elongated $\alpha$-$\text{SiAlON}$s, these elongated grains are thought to be formed because of the slow nucleation of $\alpha$-$\text{SiAlON}$s on $\beta$-$\text{Si}_3\text{N}_4$.

To the author’s knowledge, little or no research has been done on the influence of the $\text{Si}_3\text{N}_4$ phases on the formation of $\beta$-$\text{SiAlON}$, $\text{O-SiAlON}$ and $\text{X-SiAlON}$.

2.4.2 Environmental factors

This section details the parameters, with the exception of temperature, that can be modified in the general or local environment of the samples and that can have a significant influence on the formation of SiAlONs.

2.4.2.1 Effects of gas composition and pressure

*Generalities*

There are different common methods to produce SiAlON ceramics. Hot pressing (HP) and hot isostatic pressure (HIP) are relatively expensive methods so pressureless sintering and gas pressure sintering
(GPS) are the most attractive techniques. The main difference between HP or HIP and GPS is the type and value of pressure. It is possible to obtain fully dense materials by HIP and HP even without additives whereas higher amounts of additives are generally required to achieve the same density in GPS.

GPS is applied to nitrogen ceramics which are thermodynamically unstable at high temperatures and is therefore used for the fabrication of Si$_3$N$_4$ and SiAlON. N$_2$ has the advantage to prevent the thermal decomposition of Si$_3$N$_4$ at temperatures above 1800°C and to provide an extra driving force for sintering which helps to lower the amount of additives. By suppressing the decomposition of Si$_3$N$_4$, it allows higher sintering temperatures to be used [88]. However the use of high pressures is not necessarily effective for the sintering of Si$_3$N$_4$ and SiAlON. Indeed, high pressures in the early stages of sintering can be detrimental to densification if a gas under high pressure is entrapped inside the pores [89]. Nevertheless, it is important to have a sufficient nitrogen pressure to prevent decomposition and to diffuse N$_2$ into the pores to avoid pressurising with a non-interacting gas [90]. Thus GPS can be employed as a two-stage process: the first step using lower pressures to allow densification, followed by a second stage where higher pressures are applied to suppress decomposition at higher temperatures once most of the shrinkage has been achieved.

**Influence of gas composition and pressure on sintering of Si$_3$N$_4$ via nitridation of Si**

For the reaction bonding process, gas pressure sintering of Si$_3$N$_4$ has been studied using a wide range of gas pressures, from 0.1 MPa to 10 MPa, and of temperatures, from 1700°C to 2140°C [90]. A summary of this research is given in Table 2.6. It can be seen that fully dense materials have been obtained for a range of different systems, pressures and temperatures, but it is difficult to ascertain the effects solely related to gas pressure since the sintering behaviour of these materials will be greatly influenced by the nature and amount of sintering additives as was described previously.
Table 2.6: Summary of earlier results on gas pressure sintering of Si$_3$N$_4$ [90].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Additives</th>
<th>Density (g.cm$^{-3}$)</th>
<th>Theoretical density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800-1900</td>
<td>2</td>
<td>20% CeO$_2$</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1900</td>
<td>1</td>
<td>5% MgO</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>1900</td>
<td>2</td>
<td>5% CeO$_2$</td>
<td>2.98</td>
<td>-</td>
</tr>
<tr>
<td>1950</td>
<td>2</td>
<td>15% Y$_2$O$_3$</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>1800</td>
<td>2</td>
<td>15% Y$_2$O$_3$ and 3% Al$_2$O$_3$</td>
<td>&gt;3.00</td>
<td>-</td>
</tr>
<tr>
<td>1770</td>
<td>2</td>
<td>10% Y$_3$Al$_2$O$_12$</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>2000</td>
<td>2-7</td>
<td>7% SiO$_2$ and 7% BeSiN$_2$</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1900-2090</td>
<td>2.5</td>
<td>5.3-8.7% SiO$_2$</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>2140</td>
<td>2.5</td>
<td>4-6.3% rare-earth oxides and 3.6-4% SiO$_2$</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>2000</td>
<td>4</td>
<td>10% CeO$_2$</td>
<td>3.23</td>
<td>-</td>
</tr>
<tr>
<td>1780</td>
<td>10</td>
<td>8% Al$_2$O$_3$-La$_2$O$_3$-MgO</td>
<td>3.24</td>
<td>-</td>
</tr>
<tr>
<td>1700</td>
<td>0.1</td>
<td>10% Y$_2$O$_3$ and 5% Al$_2$O$_3$</td>
<td>3.22</td>
<td>-</td>
</tr>
<tr>
<td>1700</td>
<td>2-70</td>
<td>10% Y$_2$O$_3$ and 5% Al$_2$O$_3$</td>
<td>3.30</td>
<td>-</td>
</tr>
<tr>
<td>1800</td>
<td>2-4</td>
<td>0-5% Al$_2$O$_3$ and 5% rare-earth oxide</td>
<td>3.27</td>
<td>-</td>
</tr>
<tr>
<td>1950-2050</td>
<td>10</td>
<td>1.13-3.4% Al$_2$O$_3$ and 5-15% Y$_2$O$_3$</td>
<td>-</td>
<td>98.5</td>
</tr>
<tr>
<td>1800-1900</td>
<td>0.5-5</td>
<td>5% Y$_2$O$_3$ and 2.82% Al$_2$O$_3$</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>1850-1900</td>
<td>0.3-3.5</td>
<td>6% Y$_2$O$_3$ and 2% Al$_2$O$_3$</td>
<td>-</td>
<td>99.8</td>
</tr>
<tr>
<td>1900-1950</td>
<td>0.6-3.5</td>
<td>Y$_3$SiO$_2$</td>
<td>-</td>
<td>97.6</td>
</tr>
<tr>
<td>1900-1950</td>
<td>0.6-1.0</td>
<td>Sr$_2$La,Yb$_2$(SiO$_3$)$_3$O$_2$</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

In GPS, it is not only the temperature and pressure that can affect the sintering behaviour, but also the composition of the gas. Following is a description of the effects of the type and purity of gas.

Nitrogen (N\textsubscript{2}) is obviously essential for the nitridation process but at sufficient partial pressure, it can also prevent the decomposition of Si$_3$N$_4$ at high temperatures. The mechanical strength can be sensitive to the precise nitriding conditions. In particular, it depends upon whether N\textsubscript{2} is in a static condition around the samples or whether it flows past them. For instance, gas flow during nitridation has been shown to degrade strength, and even undetected leaks in a nominally static nitriding system could produce sufficient gas flow to affect the strength. This is claimed to be due to the slower reaction rate between Si and N\textsubscript{2} under flowing N\textsubscript{2} as compared to static N\textsubscript{2} [91]. However Lindley et al. [64] showed that the use of flowing N\textsubscript{2}/H\textsubscript{2} gas mixtures eliminates the adverse effect of gas flow on strength when N\textsubscript{2} alone is used such that the strengths of compacts reacted in static N\textsubscript{2}, static N\textsubscript{2}/H\textsubscript{2} gas mixtures, or flowing N\textsubscript{2}/H\textsubscript{2} gas mixtures are not significantly different.

The relative concentration of silicon monoxide (SiO) within the compact determines the amount of α-Si$_3$N$_4$ formed whereas the β-Si$_3$N$_4$ content is controlled by the relative contribution of N\textsubscript{2} reacting with pure Si [64]. In flowing N\textsubscript{2}, the partial pressure of SiO within the compact is probably reduced because SiO is taken away from the compact, thus leading to increased β-Si$_3$N$_4$ contents [64]. Hence the amount of β-Si$_3$N$_4$ increases as the rate of nitrogen flow increases. In summary, static N\textsubscript{2} leads to the
formation of higher amounts of $\alpha$-Si$_3$N$_4$ which, since $\alpha$-Si$_3$N$_4$ is less stable than $\beta$-Si$_3$N$_4$ [92], would enhance the formation of SiAlONs.

**Hydrogen** ($H_2$) can be expected to modify the course of the reaction as it can react with SiO$_2$ according to:

$$SiO_2(s) + H_2(g) \rightarrow SiO(g) + H_2O(g)$$

The addition of $H_2$ increases the rate of the isothermal reactions and promotes the development of a finer microstructure of the Si$_3$N$_4$ network [64]. $H_2$ increases the SiO partial pressure and the reaction rate, particularly in the early stages of the nitridation, thereby minimising the loss of vapour-transported species and favouring the rapid formation of the skeletal Si$_3$N$_4$ network [64]. Furthermore, reactions which encourage network formation should favour high strength. The addition of $H_2$ is one mechanism that increases network formation and eliminates the adverse effect on strength observed with samples reacted in flowing N$_2$ [64].

With added $H_2$, the SiO(g)/N$_2$ reaction proceeds at a faster rate compared to the Si(g)/N$_2$ reaction and to the $\beta$-Si$_3$N$_4$ forming reactions. Indeed $H_2$ increases the partial pressure of SiO and the model suggests that this increases the amount of $\alpha$-Si$_3$N$_4$ formed since the nitridation of SiO becomes the dominant reaction. This results in an exceptionally fast reaction rate and a high $\alpha/\beta$-Si$_3$N$_4$ ratio [62, 93]. $\beta$-Si$_3$N$_4$ contents are thus reduced as the $H_2$ concentration increases.

A different type of bond and microstructure is developed when $H_2$ is added to the nitriding gas. A small addition of $H_2$ to N$_2$ has a marked effect on mechanical properties as it leads to a relatively void free microstructure and to a material having much improved creep characteristics. This improvement might be a consequence of the evaporation or redistribution of the impurities, or of better oxidation resistance associated with a finer textured microstructure [62].

Under high **oxygen** (O$_2$) partial pressures, oxidation of the compact proceeds to such an extent that SiO$_2$ forms on the Si particles, thus preventing their nitridation. Moulson [62] has claimed that this oxidation occurred when the O$_2$ partial pressure was higher than $5.10^{-4}$ MPa.

The addition of **water vapour** will affect the course of the reaction since H$_2$O can react with Si to form SiO and H$_2$ [64] according to:

$$Si(s, g) + H_2O(g) \rightarrow SiO(g) + H_2(g)$$

This will increase partial pressures of SiO and enhance the rate of formation of $\alpha$-Si$_3$N$_4$. As for the O$_2$ addition, above a critical H$_2$O pressure, SiO$_2$ will form according to reaction (2.22) and prevent nitridation [62].
$$ \text{Si(s, g)} + \text{H}_2\text{O(g)} \rightarrow \text{SiO}_2\text{(s)} + 2\text{H}_2\text{(g)} $$

Despite the relatively few studies that have been made on the effects of GPS on SiAlONs, the previous observations can be of interest as SiAlONs are expected to have similar behaviours to Si$_3$N$_4$ with respect to the GPS variables, particularly in those cases where the SiAlON formation occurs via the production of Si$_3$N$_4$ such as in reaction bonding and silicothermal reduction.

*Influence of GPS on sintering of SiAlON*

As in the case of Si$_3$N$_4$, GPS of SiAlON is expected to prevent thermal decomposition and higher pressures can help minimise the loss of vapour phases. For instance, Li et al. [94] have observed that the mass losses occurring under high nitrogen pressures are smaller than the losses obtained with pressureless sintering. The densities they have obtained at 1700°C under 1 MPa were all higher than those obtained at 1800°C under 0.1 MPa. However, these authors showed that when the nitrogen pressure is raised to a certain level, it has an adverse effect on densification and mechanical properties. Thus the materials that had optimum mechanical properties were obtained under a gas pressure of 1-3 MPa [94].

Densification does not always occur uniformly throughout the specimen [89]. It can start at the surface and progress to the interior of the compact. This non-uniform densification has been found to be influenced by nitrogen pressure and can be attributed to the effect of the atmosphere on the ability of N$_2$ entrapped in pores to diffuse out. Indeed gas entrapped in pores can significantly affect the shrinkage behaviour of a material, particularly in the final stage of sintering once the pores become isolated from the surface. For example, the diffusion of the entrapped gas, if slow, can control the kinetics of the pore elimination. Kang et al. have noticed the presence of gas bubbles in some liquid pockets of the β-SiAlON they have prepared [95]. This observation suggests that the entrapped gas, which was a mixture of the gas used for the GPS and the gas from the decomposition of Si$_3$N$_4$ or SiAlON, was diffusing slowly. If it could dissolve easily in the matrix and diffuse out, these bubbles should rarely be present in the material. Because N$_2$ can be dissolved into oxynitride liquids, which are usually present during the sintering of Si$_3$N$_4$ based ceramics, the entrapped N$_2$ gas is expected to be able to diffuse out. However, the N$_2$ diffusion through these highly viscous liquids may not be quick enough not to have an effect on the densification rate. Cho and Yoon [89] have noticed reduced densification kinetics when the nitrogen pressure was increased from 3 MPa to 6 MPa whereas it has been proposed that the maximum size of pores filled with liquid increases with increasing gas pressure and sintering time [95]. Moreover Hirosaki et al. [96] observed that a nitrogen gas pressure higher than 10 MPa resulted in lower density. They also suggested that the high gas pressure inside the closed
pores could inhibit densification in the final stage of sintering. All these observations lead to the same conclusion that a higher nitrogen pressure is not always beneficial for densification.

Another technique of GPS with a two stage process has been used [94] to avoid filling pores with high gas pressure in the first stage of the sintering and, once the pores are closed at around 90% of the theoretical density, higher pressures can be applied to benefit from the advantages of GPS previously cited.

2.4.2.2 Influence of powder bed

The use of powder beds was first developed to minimise the depletion of Si and O\textsubscript{2} from the surface of SiAlON products. Indeed, the powder bed allows to create a local gas equilibrium immediately adjacent to the compact, thus minimising volatilisation. For instance, in the case of O-SiAlON, without protection of a powder bed, a very thick and porous layer of mainly β-SiAlON is observed on the surface of the O-SiAlON products. Barris et al. [42] have tried several powder beds and found that powder beds composed of Si\textsubscript{3}N\textsubscript{4}:O-SiAlON (ratio 1:1) and BN:O-SiAlON (ratio 1:2) resulted in a thinner layer of β-SiAlON. The requirement for the powder bed is to have enough SiO\textsubscript{2} in the immediate environment of the product to minimise the depletion of Si and O\textsubscript{2} from the sample as shown in Figure 2.14.

![Figure 2.14: Effect of the powder bed on the surface composition and the apparent porosity of sintered O-SiAlON [42].](image)

More recently, powder beds have been used to promote the formation of a layer of a composition different from the product [97]. This has been carried out in order to create a SiAlON product that can exhibit the hardness of α-SiAlON at the surface and the toughness of β-SiAlON in the core. In this study, a powder bed comprised of AlN: BN is found to be more effective than an α-SiAlON powder bed for the formation of α-SiAlONs at the surface. It is assumed that the material transfer occurs via
vaporisation of reactants from the powder bed and condensation on the surface of the compact for reaction. The AlN present in the powder could evaporate from the powder bed and subsequently react with the compact surface causing $\alpha$-SiAlON formation as the surface became richer in AlN [97]. Two other factors are known to influence the efficiency of this powder bed. On one hand, the green compacts, which offer a higher porosity, have a better interaction with the powder bed than a pre-sintered compact. On the other hand, an increase of gas pressure seems to enhance the thickness of the gradient zone. However, this method has shown its limits as the maximum thickness that has been obtained so far is only about a few hundred microns.

### 2.5 Summary of literature

#### 2.5.1 Current state of knowledge

Nitrogen ceramics include a wide range of materials. Among them, SiAlON materials are divided into five groups where each group exhibits specific properties that make them suitable for many different applications: $\alpha$-SiAlONs tend to be used for high performance materials whereas the others possess interesting chemical properties and are therefore appropriate for refractory applications. It is also possible to create composite materials in order to combine their properties. As their mechanical properties depend mainly on the microstructure and density of the material, they can be modified by tailoring these characteristics. For instance, $\alpha$-SiAlON with elongated grains combines the intrinsic hardness of the $\alpha$-SiAlON and an improved toughness due to the new shape of grains.

Different methods can be used to produce SiAlONs, but each method possesses advantages and disadvantages that make them suitable for different applications. Generally the most expensive processes that lead to the purest and the most dense SiAlONs are used for high performance applications whereas cheaper routes are developed to produce materials where chemical properties are of greater relevance than mechanical properties.

Since, in the Si-Al-O-N system, each phase usually exists over a wide range of homogeneity, the formation and properties of SiAlON ceramics can be influenced by a large number of variables. The starting compositions obviously play a major role in tailoring the chemical and mechanical properties. Although starting powders can have the same chemical composition, the use of different polymorph phases, such as $\alpha$ and $\beta$-$\text{Si}_3\text{N}_4$, has an impact on the formation and evolution of the SiAlON phases. Furthermore the additives employed to either enhance the nitridation, or to improve the sintering/densification behaviour, can be chosen in order to obtain a more stable, a more refractory or a
tougher material. The external factors, such as the heating schedule and the immediate environment of the product, have also been found to influence the development of SiAlONs.

To conclude most of the investigations carried out on the SiAlON ceramics have been aimed at the improvement of their properties and at the development of cheaper routes that can be applicable to mass production in the industry. The most common route for the production of these materials (i.e. liquid phase sintering of Si₃N₄ based powders) requires high sintering temperatures typically in excess of 1800°C. This kind of temperature requires specialised furnaces that are often highly capital intensive. Lowering the sintering temperature whilst still maintaining properties suitable for a given application should allow for wider industrial adoption of these materials.

2.5.2 Outstanding research questions

Literature has shown that gas pressure sintering has often been used for the production of Si₃N₄. However high sintering temperatures are required and the role of GPS has been mainly focused at the prevention of the decomposition of the product at these temperatures. Research questions that arise from a review of the literature, and which inform the objectives of this project (see Section 1.2) are described below:

- Whilst GPS has been used for the production of SiAlON materials, studies on the effects of the gas pressure are limited. The little research that is available on this subject has been carried out only for traditional liquid phase sintering, i.e. it has been directed exclusively at SiAlON materials formed from a starting mixture already containing a Si₃N₄ phase. Furthermore the pressures used were generally above 1 MPa and the sintering temperatures still high (above 1700°C).

- GPS has been employed for a very specific purpose, i.e. preventing decomposition. However it has not been systematically studied as a tool for reducing the cost of production, for example by enhancing the nitridation of SiAlONs produced by alternative routes, and still allowing the formation of SiAlONs of the required composition and properties.

- The literature review has not found any research carried out on the effects of GPS on SiAlON materials produced by other processing routes such as reaction bonding or silicothermal reduction. In these two cases, nitrogen is a reactant, but the literature does not show studies bearing upon the influence of nitrogen pressure on the nitridation and formation of SiAlONs produced by these two processing routes.
• Little information is available on the effects of lower gas overpressures (<1 MPa) on the microstructure and the decomposition of β and O-SiAlONs produced by these two alternative routes.

The study of the effects of GPS on the formation of SiAlONs designed to be produced using cheaper processing routes and lower sintering temperatures is of interest, not only scientifically, but also with regards to technology transfer to industry.
CHAPTER 3
OPTIMISATION OF THE NITRIDATION,
FORMATION AND DENSIFICATION OF $\beta$
AND O-SiAlONs

3.1 Introduction
The scope of the study of the effects of GPS on SiAlON materials is wide considering the number of SiAlON phases, of processing routes, and the range of parameters susceptible to have an influence on their nitridation, formation, densification, and mechanical and chemical properties. Therefore this work was focused on the materials used for refractory applications and this chapter bears upon the $\beta$ and O-SiAlON phases produced by reaction bonding and silicothermal reduction routes.

Most studies mainly deal with the effects of one factor on different properties of a given material. Thus it is not easy to compare the magnitude of the effects that each factor has on a property. In answer to this, and in order to create an optimised material that will be used thereafter, an experimental methodology based on Taguchi method was implemented. This experimental design determined the effect of a factor on a property and compared the magnitude of this effect with that of any other factors. Finally it could be used to find a set of parameters that should lead to a material presenting optimal properties such as low porosity, low mass losses and high degrees of nitridation.
3.2 Experimental design

The objective of this study was to establish a hierarchy of the influence of selected factors on a group of properties. It is typically more difficult to obtain dense SiAlONs with reaction bonding or silicothermal reduction routes than with the traditional liquid phase reaction sintering. High sintering temperatures and long dwell times can still promote their densification, but SiAlONs will be more susceptible to decomposition. Therefore this chapter investigates the effects of key factors on the densification and decomposition of SiAlONs prepared by the two alternative routes.

3.2.1 Selection of optimisation factors and levels

3.2.1.1 Selection of factors

There are a lot of factors that have an influence on densification and decomposition of SiAlONs. This work focussed on the factors that were expected to have the greatest effects on SiAlONs. Hence the selection of factors was one of the most important steps when designing the experimental plan. In order to keep the experimental design of a manageable size, four factors were selected. Temperature was expected to have an effect on both densification and decomposition of SiAlONs. Nitrogen pressures are typically used to reduce decomposition and provide extra driving force for sintering. Additives are used to lower sintering temperatures, and assist in the formation and densification of SiAlONs, but are also used to facilitate the nitridation reaction during the formation of Si₃N₄ from Si powder. Therefore additives were divided in two categories: those whose main effect was expected to take place during the sintering were called “sintering aids” and those whose purpose was to promote nitrogen pick-up during the nitridation were called “nitriding enhancers”.

The experimental plan was designed to compare the effects of the four factors – temperature, nitrogen pressure, sintering aids and nitriding enhancers – and determine the optimal combination that leads to SiAlONs with high density and low decomposition. All the other factors such as gas and powder bed composition, type of crucible, amount of additives and particles sizes were not investigated in this study and were thus kept constant throughout the experiment. The experimental plan was built according to one of Taguchi’s designs [98, 99], also known as Graeco-Latin square design. This plan is an orthogonal experimental design and since 4 factors were selected, they each needed to have 3 levels. A level is a state in which a factor is set during the experiment. Table 3.1 presents the 4 factors and the 3 levels they were set to.
3.2.1.2 Selection of levels

Temperatures were chosen to be able to densify β-SiAlON as well as O-SiAlON. The lowest temperature was set to 1600°C since below this temperature long dwelling time would be required to densify β-SiAlONs. The highest temperature was set to 1800°C which is typical for sintering of SiAlONs. Moreover at 1800°C, decomposition was expected to be already great and higher temperatures were not of interest since the SiAlONs produced are intended to be used for refractory applications. One of the properties to observe was the possibility to obtain dense SiAlONs at 1600°C since lower sintering temperatures contribute to lowering the production costs. 1700°C was selected as an intermediate temperature.

Nitrogen pressures were used to modify the environment of the product during sintering; they were not high enough to provide any physical pressure on the samples, this was not HIP. The pressures selected ranged from atmospheric pressure of nitrogen (0.1 MPa) to 0.7 MPa. The purpose was to observe the impact of different amounts of N₂ on the sintering and to compare the magnitude of this effect with the other factors. The first step of reaction bonding and silicothermal reduction processes is nitridation of Si. During this step, nitrogen pressure was kept constant at 0.4 MPa to ensure that nitrogen pressure changes only affect the sintering stage. Chapters 4, 5 and 6 discuss the effects of nitrogen pressure during the first step.

Y₂O₃ and Al₂O₃ are the most common sintering additives for SiAlONs and were used in this work as a typical additive system. In the presence of Al₂O₃, Y₂O₃ reacts to form yttrium aluminium garnet (YAG) above 1100°C [100]; therefore the addition of Y₂O₃ and Al₂O₃ was calculated considering the formation of the garnet phase. Moreover no difference in phase assemblage and density was found in α-SiAlONs with the addition of either the garnet phase or the stoichiometric mixture of Al₂O₃ and Y₂O₃ [101]. Dysprosia (Dy₂O₃) was chosen as an alternative to Y₂O₃ whilst still maintaining the garnet, DyAG, composition and was used to represent the rare-earth oxide garnet phases. Most of the rare-earth oxide effects and properties in SiAlON systems depend on their cationic radius, and Dy has a median cationic radius – La having the biggest and Lu the smallest – and was therefore expected to

---

**Table 3.1: Factors and levels for the experimental design.**

<table>
<thead>
<tr>
<th>Factors</th>
<th>Temperature (°C)</th>
<th>Nitrogen pressure (MPa)</th>
<th>Nitriding enhancers</th>
<th>Sintering aids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Levels 1600</td>
<td>1600</td>
<td>0.1</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Levels 1700</td>
<td>1700</td>
<td>0.4</td>
<td>CaO</td>
<td>YAG</td>
</tr>
<tr>
<td>Levels 1800</td>
<td>1800</td>
<td>0.7</td>
<td>ZrO₂</td>
<td>DyAG</td>
</tr>
</tbody>
</table>

---
have average effects. The third level was the absence of sintering aids. The amount of additives was set to a constant molar amount to simplify the comparison of observed properties by potentially generating the same volume of intergranular liquid. The amount selected (2 mol%) was based on Ekström and Nygren observations on the minimum amount of additive necessary to give dense β-SiAlON with Y₂O₃ and rare-earth oxides [3]. In order to be consistent the same amount was also used for the nitriding enhancers.

Nitriding enhancers were chosen according to their effects and type of action. Two additives with two possibly different behaviours regarding the nitridation of Si were selected. CaO and ZrO₂ promote the overall conversion of Si to Si₃N₄ and favour the formation of α-Si₃N₄ [82, 102]. However ZrO₂ enhances the nitridation by reacting with N₂ to form ZrN which acts as an internal source of nitrogen [102] while CaO, whose mechanism to promote nitridation is not reported in literature, could possibly be able to catalyse the removal of the SiO₂ layer at the surface of the Si grains by forming calcium silicates [103]. Finally they have very different eutectic temperatures [104-107] as shown in Table 3.2. In the same manner as for the sintering aids, the third level was the absence of additives.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Eutectic temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1170</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>1371</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>1389</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>1700-1710</td>
</tr>
</tbody>
</table>

Table 3.2: Eutectic temperatures of the additives used in the SiO₂-Al₂O₃-oxide system [104-107].

3.2.2 Experimental plan
All possible combinations of the 4 factors and their 3 levels define the experimental domain. The domain includes a total of 3⁴=81 combinations and this number was obviously too large to consider doing them all. In a traditional approach to this problem, a reference setting would be selected and only one factor would be changed at a time. Figure 3.1 shows the domain and the experiments that would be realised in this traditional approach. The distribution of the experiments would not allow to cover the whole domain and the study of particular levels for each factor would therefore be favoured, biasing the statistical results.
Optimisation of the nitridation, formation and densification of β and O-SiAlONs

Figure 3.1: Illustration of the experimental domain and the experiments required (black discs) according to a traditional approach consisting in varying only one factor at a time. No NE: no nitriding enhancer.

Graeco-Latin designs are built such that each experiment that is realised has a unique combination of factors and levels within which the same arrangement of two parameters can never be found. Table 3.3 shows a Graeco-Latin square and how the experiments to be realised are drawn from it.

Table 3.3: Graeco-Latin square, cells coordinates and orthogonal design from which the experiments to realise are drawn.

<table>
<thead>
<tr>
<th>Run</th>
<th>Line number</th>
<th>Column number</th>
<th>Latin letter</th>
<th>Greek letter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>I</td>
<td>a</td>
<td>α</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>II</td>
<td>b</td>
<td>β</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>III</td>
<td>c</td>
<td>γ</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>I</td>
<td>b</td>
<td>γ</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>II</td>
<td>c</td>
<td>α</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>III</td>
<td>a</td>
<td>β</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>I</td>
<td>c</td>
<td>β</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>II</td>
<td>a</td>
<td>γ</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>III</td>
<td>b</td>
<td>α</td>
</tr>
</tbody>
</table>

The design of Graeco-Latin squares allows for each factor and all its respective levels to be represented the same number of times. Moreover, for the same factor/level combination, all of the other factors are used the same number of times at all levels. The study of particular levels for each
factor is not favoured. The mean effects of each factor is therefore estimated with the same uncertainty. Figure 3.2 locates the experiments realised according to the orthogonal design. The whole domain is now covered by the experiment. With the same number of experiments as with a traditional design of experiment, it is possible to compare the effects of each factor and to determine the optimised parameters that should lead to the desired properties.

Figure 3.2: Illustration of the experimental domain and the experiments required (black discs) according to a Taguchi design. No NE: no nitriding enhancer.

3.2.3 Extension of the plan to different SiAlON compositions

The experimental design described was planned such a way that different SiAlONs could be investigated at the same time. Indeed the sintering conditions were of interest regarding the densification and decomposition of both β and O-SiAlONs. Literature describes the formation of SiAlONs through both reaction bonding and silicothermal reduction routes, but there is no study comparing the effects of the same parameters on both processing routes. Indeed one parameter could have a different impact on the material depending on its production route since different starting powders are involved. Similarly one factor could have different effects when changing the level of substitution of a SiAlON. In this work, the Taguchi design was used simultaneously on eight powders: β and O-SiAlONs with low and high level of substitution and produced by both reaction bonding and silicothermal reduction routes. Table 3.4 recapitulates the SiAlON powders that were investigated.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Route employed</th>
<th>Level of substitution</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-SiAlON</td>
<td>Reaction Bonding (2)</td>
<td>z=1</td>
<td>B21</td>
</tr>
<tr>
<td>β-SiAlON</td>
<td>Reaction Bonding (2)</td>
<td>z=4</td>
<td>B24</td>
</tr>
<tr>
<td>β-SiAlON</td>
<td>Silicothermal Reaction (3)</td>
<td>z=1</td>
<td>B31</td>
</tr>
<tr>
<td>β-SiAlON</td>
<td>Silicothermal Reaction (3)</td>
<td>z=4</td>
<td>B34</td>
</tr>
<tr>
<td>O-SiAlON</td>
<td>Reaction Bonding (2)</td>
<td>x=0.05</td>
<td>O2.05</td>
</tr>
<tr>
<td>O-SiAlON</td>
<td>Reaction Bonding (2)</td>
<td>x=0.2</td>
<td>O2.2</td>
</tr>
<tr>
<td>O-SiAlON</td>
<td>Silicothermal Reaction (3)</td>
<td>x=0.05</td>
<td>O3.05</td>
</tr>
<tr>
<td>O-SiAlON</td>
<td>Silicothermal Reaction (3)</td>
<td>x=0.2</td>
<td>O3.2</td>
</tr>
</tbody>
</table>
3.3 Experimental procedure

This section describes the experimental procedure. The procedure for producing SiAlONs from either reaction bonding or silicothermal reduction routes was essentially the same, with the exception of different starting powder compositions.

3.3.1 Powder preparation

The starting materials were Si (Sicomill, grade 4D, D$_{50} \approx$ 7 µm), halloysite clay (NZCC, ultrafine-H, D$_{50} \approx$ 0.3 µm), Al$_2$O$_3$ (Sumitomo, AKP-30, D$_{50} \approx$ 0.3 µm), AlN (Tokuyama, grade E, D$_{50} \approx$ 1 µm) or SiO$_2$ (Commercial Minerals, Silica Superfine, D$_{50} \approx$ 1.5 µm), and additives if required. The powders described in Table 3.4 were prepared according to the following reactions for the formation of:

- $\beta$-SiAlON ($z=1$ and 4 respectively) by reaction bonding route:
  
  \[
  3(\text{Al}_2\text{O}_3\cdot2.4\text{SiO}_2\cdot2.2\text{H}_2\text{O}) + 29\text{AlN} + 183\text{Si} + 122\text{N}_2(g) \rightarrow 39\beta$-Si$_5$AlON$_7 \\
  \]

- $\beta$-SiAlON ($z=1$ and 4 respectively) by silicothermal reduction:
  
  \[
  5(\text{Al}_2\text{O}_3\cdot2.4\text{SiO}_2\cdot2.2\text{H}_2\text{O}) + 29\text{AlN} + 183\text{Si} + 122\text{N}_2(g) \rightarrow 39\beta$-Si$_5$AlON$_7 + 11\text{H}_2\text{O}(g) \\
  \]

- O-SiAlON ($x=0.05$ and 0.2 respectively) by reaction bonding route:
  
  \[
  292.5\text{Si} + 97.5\text{SiO}_2 + 5\text{Al}_2\text{O}_3 + 195\text{N}_2(g) \rightarrow 200\text{O-Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} \\
  \]

- O-SiAlON ($x=0.05$ and 0.2 respectively) by silicothermal reduction:
  
  \[
  5(\text{Al}_2\text{O}_3\cdot2.4\text{SiO}_2\cdot2.2\text{H}_2\text{O}) + 85.5\text{SiO}_2 + 292.5\text{Si} + 195\text{N}_2(g) \\
  \rightarrow 200\text{O-Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} + 11\text{H}_2\text{O}(g) \\
  \]

For those mixtures that employed AlN and Si, the oxygen content of the powder was taken into consideration when determining powder amounts, but was left out of the equations above for clarity.

The precursor powders were planetary milled in isopropanol for 2 h at 300 rpm with Si$_3$N$_4$ balls in a Si$_3$N$_4$ container, then dried in a rotary evaporator, passed through a 250 µm sieve and pressed into pellets (approximately ø12 mm x 5 mm) by uniaxial pressing at 50 MPa followed by cold isostatic pressing at 200 MPa. In this work, all the powders were prepared as described above. The only differences in the experimental procedure resided in the firing schedules. In this experiment the firing schedule was realised in two steps to allow investigation of the samples after the so-called nitridation stage.
3.3.2 Firing schedules

The samples were fired in a graphite gas pressure furnace with graphite heating elements and were placed in boron nitride (BN) crucibles. The temperature was controlled by a pyrometer focussed on the exterior wall of the crucible. There was no control of the heating ramp under 800°C, which is the threshold above which the pyrometer starts to read. However the time required to reach this threshold was constant, therefore in all experiments the average heating rate from room temperature to 800°C was always the same: about 4.3°C.min⁻¹. The experiments were realised under nitrogen gas pressure and since contamination with other gases can modify the phase formation, the samples were heated up under vacuum until 1000°C so the water released by the samples, including the constitution water of the halloysite clay, could be eliminated before the beginning of the nitridation. A powder bed was used to protect the samples and its composition was designed to be similar to that of the samples, e.g. a β-SiAlON powder bed was used for the β-SiAlON samples, to limit decomposition by modifying the local environment [42].

3.3.2.1 Nitridation stage

The nitriding schedule was chosen according to a common heating schedule used for reaction bonded SiAlONs. Figure 3.3 details this schedule which included a final 6-h hold at 1350°C under 0.4 MPa of nitrogen. At the end of the firing, the furnace was cooled down at 10°C.min⁻¹ down to 1000°C. The rest of the cooling down was done at the natural rate of the furnace.

![Figure 3.3: Heating schedule and nitrogen pressure profile of the nitridation stage.](image)

3.3.2.2 Sintering stage

Whilst the nitriding schedule remained the same for all the experiments, the sintering schedule was different from one run to the other. Typically, it included a final 2-h hold at the maximum temperature and nitrogen pressure described by the experimental plan (see Table 3.3). Figure 3.4 describes the sintering schedule for run 1.
Optimisation of the nitridation, formation and densification of $\beta$ and O-SiAlONs

3.3.3 Characterisation

3.3.3.1 Degree of nitridation

Degree of nitridation represents the amount of $N_2$ that actually entered the structure in comparison with that required theoretically to convert the starting mixture to SiAlON. This can also be considered as the amount of $N_2$ required to fully convert the elemental Si in the starting powder to $Si_3N_4$. I.e. all of the reactions described in Section 3.3.1 could be equally written in terms of reaction between $Si_3N_4$ and the other starting components. For instance, the reaction of formation of $\beta$-SiAlION ($z=4$) produced by reaction bonding (3.2) could be written:

$$2Si_3N_4 + 4Al_2O_3 + 4AlN \rightarrow 3\beta-Si_2Al_4O_4N_4$$

Degree of nitridation in pure Si is typically evaluated by comparing the actual mass gain of the samples with their theoretical mass gain according to:

$$Degree \ of \ nitridation = \frac{Actual \ mass \ gain}{Theoretical \ mass \ gain} = \frac{m_{nitrided}-m_{800^\circ C}}{m_{100\% \ nitrided}-m_{800^\circ C}}$$

where $m_{800^\circ C}$ represents the mass of Si at $800^\circ C$; at this temperature all humidity water potentially contained in the Si powder is considered eliminated. The calculation is made without taking into account any other eventual mass losses by evaporation. Therefore the results show in general lower degree of nitridation than it actually is. The results can be coupled with other techniques such as X-ray diffraction to verify if any remaining crystalline Si can be detected.

The calculation of the degree of nitridation in SiAlONs was based on the same principle, however Si is only part of the powder mixture and the mass of these powders was not measured at $800^\circ C$ but calculated considering all the powders were water free with the exception of halloysite whose water...
content is given by the supplier. A detailed calculation is given in Appendix A. Some powders were heated up to 800°C under vacuum to verify whether the water content of the powders used in the calculations was appropriate, and the difference was below 1% in comparison with the expected mass loss.

3.3.3.2 Phase identification
Crystalline phase identification was carried out using XRD analysis with a Bruker 2D Phaser with Cu Kα radiation. Data were collected over the range 2θ = 10° to 70° with a Lynxeye detector (about 4° wide) at 0.1 s.step⁻¹ and a step size of 0.02°. Peak analysis was carried out using DIFFRAC EVA v1.4 software. The relative amounts of different phases were determined from the peak heights. It is recognised that these are only semi-quantitative, and can be affected by preferred orientation and inhomogeneities in the solid samples. Therefore the goal was not to have a fully quantitative assessment of the relative amounts, but rather to provide a reasonable description of the phase assemblage and to identify the major and minor phases. This method was used in order to be able to present in a synthesized manner the large number of samples analysed by XRD. Errors bars are not shown on these figures since most of them were results gathered from single samples. However when repeats of these measurements were carried out, the results of these repeats were similar with the results of the original measurements.

Typically XRD analysis are carried out on powder samples but since crushing the samples would be destructive and time consuming, most of the samples were analysed as solids. However the relative peak intensities obtained showed a good match with powder standards from the JCPDS library and so it was assumed that preferred orientation did not have a large effect.

Internal calibration with Si was only used when peak shifts were of importance, for example in accurate determination of cell parameters. Therefore, in general no calibration was carried out so that the level of substitution of SiAlONs, which can be determined by unit cell size, could only be estimated. For example without calibration and accurate lattice parameter determination, it could not be determined with total certainty whether a sample contained β-Si₃N₄ or β-SiAlON with a very low level of substitution. The internal calibration was carried out by surrounding the pellets with Si powder, both pellet and Si powder on the same plane. The XRD gives the pattern of the Si powder on top of the one from the sample. The know position of the very sharp Si peaks can be compared with that of the database and the whole XRD pattern can be shifted back to its theoretical position if the Si peak from the samples did not match the one from the database.

Micrographs and energy dispersive x-ray spectrometry (EDS) elemental mapping were carried out on polished samples coated with Pt with a FEI Quanta 200 F environmental scanning electron microscope.
Optimisation of the nitridation, formation and densification of $\beta$ and O-SiAlONs

(ESEM) set at 20 kV and a SiLi (lithium drifted) EDS detector to determine the distribution of the phases in the pellets.

3.3.3.3 Bulk density and open porosity

Bulk density ($d_{bulk}$) and open porosity ($P_{open}$) were measured by Archimedes' method respectively according to:

$\begin{align*}
\text{(3.11)} \\
d_{bulk} &= \frac{m_{dry}}{m_{out}-m_{in}} \times d_{water} \\
\text{and (3.12)} \\
P_{open} &= \frac{m_{out}-m_{dry}}{m_{out}-m_{in}}
\end{align*}$

where $m_{dry}$ is the mass of the dry sample, $m_{in}$ is the mass of the sample infiltrated with water measured while immersed in water, and $m_{out}$ is the mass of the sample infiltrated with water but measured out of water.

The relative density (ratio of the bulk density to the theoretical density) cannot be evaluated with accuracy in SiAlONs because of the presence of intergranular phases. Moreover the formation and densification of SiAlON occurs during reaction sintering, and therefore several phases appear and disappear at different stages during sintering. The quantification of each phase and their density cannot be accessed with precision so as to be able to calculate an accurate theoretical density. Therefore the observations and comments were made only based on bulk density and open porosity. It would be possible to measure the theoretical density by crushing the samples into a fine powder but it would be time consuming and destructive of the sample therefore this option was discarded.

3.3.3.4 Decomposition or mass loss

Decomposition is an important phenomenon in SiAlONs that can prevent getting fully dense materials. It represents the mass loss of a SiAlON sample during the sintering step which is typically carried out at temperatures above 1400°C. Therefore decomposition was assessed by mass loss between nitridation and sintering stages according to the equation:

$\begin{align*}
\text{(3.13)} \\
\text{mass loss} &= \frac{m_{after \ nitridation}-m_{after \ sintering}}{m_{after \ nitridation}}
\end{align*}$

If the samples were fully nitrided at the end of the nitriding step, the value would be positive; but if some Si remained not nitried after the nitridation step, the samples would be susceptible to pick up more $N_2$ and the mass loss may be negative (i.e. mass gain).
3.4 Results and discussions

The firing schedule was carried out in two stages. As a result it was possible to investigate the nitridation of Si and the formation of SiAlON at low temperature (1350°C) with different combinations of additives before studying the effects of the four parameters (temperature, nitrogen pressure, sintering aids and nitriding enhancers) on the sintering stage.

3.4.1 Effects of additives and initial compositions on the nitridation stage under nitrogen overpressure

To the author’s knowledge, studies on the effects of additives on nitridation of Si have typically been carried out under either gas flow or atmospheric pressure of nitrogen. Moreover only a few papers [11] discuss the effects of additives on the nitridation of Si in SiAlONs produced by one of the alternate routes investigated in this work. This section focuses on the nitridation of Si and formation of β and O-SiAlONs by reaction bonding and silicothermal reduction routes under low nitrogen overpressure (0.4 MPa) with some of the most commonly used additives and combination of these additives.

3.4.1.1 Effects of additives and initial composition on the nitridation of Si in a SiAlON mixture

*Effects of the “nitriding enhancers”: CaO and ZrO₂*

The degrees of nitridation of four different β and O-SiAlON compositions, with CaO and ZrO₂ as additives, are shown in Figure 3.5. The effect of these additives on the nitridation of pure Si has been established [69, 81], and it has been shown that their main role was to enhance the nitrogen pick-up during heating. In the present work their effect on the nitridation of Si in SiAlON forming compositions was different to that of pure Si and was dependent on the type of SiAlON being formed. Indeed the CaO and ZrO₂ were shown to have almost no effect on the nitridation in β-SiAlONs. In O-SiAlON compositions the nitridation was enhanced with the ZrO₂ additions, but the CaO actually hindered nitridation.
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Figure 3.5: Effects of CaO and ZrO₂ on the nitridation of β-SiAlON (\(z=1\) and 4) and O-SiAlON (\(x=0.05\) and 0.2) prepared by reaction bonding (2) and silicothermal reduction (3) routes.

In these O-SiAlONs, ZrN and/or ZrO₂ and different calcium silicide or silicate phases were observed in XRD patterns. The ZrO₂ may have the same beneficial effect as described by Hyuga et al. [69] when added to Si for the formation of Si₃N₄ where it was reported to convert in to ZrN during heating and provide an internal nitrogen source that enhanced the nitridation. The presence of calcium silicate and silicide phases in the O-SiAlONs (and not in the β-SiAlONs) suggests that CaO reacted with the free SiO₂ of the O-SiAlON powders. Moreover XRD semi-quantitative analysis showed that the O-SiAlONs with CaO contained more Si which was not nitrided than the O-SiAlONs without additives, confirming that the lower degrees of nitridation were achieved in O-SiAlONs with CaO additions. CaO probably reacted with the large amount of SiO₂ and Al₂O₃ in the O-SiAlON mixtures to form a eutectic liquid at low temperature which, upon wetting the Si grains, would have isolated them from the nitrogen atmosphere. This effect was particularly noticeable in the samples produced by silicothermal reduction (O3.05 and O3.2) where the higher amount of SiO₂ and Al₂O₃ in the high substitution sample led to the formation of more liquid which further reduced the nitridation (Figure 3.5).

CaO was expected to enhance nitridation by reacting with the SiO₂ layer at the surface of Si grains, which would have exposed the underlying Si to the nitrogen atmosphere. However in the O-SiAlON mixtures that contain large amounts of additional SiO₂, the CaO may have reacted preferentially with these species rather than with the native oxide layer.

The addition of CaO did not have the same negative effect on the nitridation of β-SiAlON mixtures as it did for the O-SiAlONs. In the starting powders for these materials there were no additions of SiO₂,
and its only source was from either the halloysite clay or the native oxide layer on the Si powder. The amount of SiO$_2$ in these samples was therefore much less than it was in the O-SiAlONs.

Note that two samples were nitrided for each condition. Therefore the error bars on the figures do not represent the standard deviation. The lower and upper limits represent the actual measurements and the value plotted on the graphs is an average of these two data, which were typically very similar.

**Effects of the “sintering aids”: YAG, DyAG, Y$_2$O$_3$ and Dy$_2$O$_3$**

The degree of nitridation of β and O-SiAlON compositions, with YAG, DyAG, Y$_2$O$_3$ and Dy$_2$O$_3$ additives are shown in Figure 3.6. Rare-earth oxide and garnet phases such as YAG and DyAG are typically added in order to enhance the densification of SiAlONs during the sintering stage [108], however in this work they were also observed to enhance the nitridation of Si in all of the SiAlON compositions with the exception of the O-SiAlON produced by silicothermal reduction route (O3.2) where the degree of nitridation was slightly decreased.

![Figure 3.6: Effects of YAG, Y$_2$O$_3$, DyAG and Dy$_2$O$_3$ on the nitridation of β-SiAlONs (z=1 and 4) and O-SiAlONs (x=0.05 and 0.2) prepared by reaction bonding (2) and silicothermal reduction (3) routes.](image)

The rare-earths in general had the same effect of increasing nitridation regardless of whether they were added individually as Y$_2$O$_3$ and Dy$_2$O$_3$ or as the respective garnet phases, although the magnitude of enhancement was slightly different. The compositions with individual Y$_2$O$_3$ and Dy$_2$O$_3$ actually contained less rare-earth oxide than the garnet phases since all the additives were added at 2 mol%, and 1 mol of rare-earth garnet contains 1.5 mol of rare-earth oxide (e.g. YAG = 3/2 Y$_2$O$_3$·5/2 Al$_2$O$_3$).

The replacement of Y$_2$O$_3$ with YAG therefore led to slightly higher degrees of nitridation in β and O-SiAlION compositions, in the same way as an increase in Y$_2$O$_3$ content (from 3 to 6% in mass) increased the conversion of Si to Si$_3$N$_4$ in the work of Brown et al. [83]. The replacement of Dy$_2$O$_3$ with DyAG also led to slightly higher degrees of nitridation in β-SiAlION compositions, but to slightly lower degrees in O-SiAlON. As Pavarajarn et al. [84] have shown for metal additions in pure Si,
higher mass amounts of additives do not necessarily lead to higher conversions. Low additions can promote the nitridation while, above a certain threshold depending on the additive used, the beneficial effect can decrease and even lead to lower conversions than without additive. It is likely that the same phenomenon occurred in the O-SiAlONs, since in these materials the mass of Dy\textsubscript{2}O\textsubscript{3} in the starting mixture was much larger than in the β (where nitridation was enhanced). It was also higher than the Y\textsubscript{2}O\textsubscript{3} in the O (where nitridation was also enhanced) as shown in Table 3.5. The fact that the degree of nitridation with DyAG additions was lower than with Dy\textsubscript{2}O\textsubscript{3} (but still higher than without additive) suggests that the optimal amount of Dy\textsubscript{2}O\textsubscript{3} necessary to enhance nitridation in these O-SiAlONs is lower than 10% in mass.

Table 3.5: Mass percentage of rare-earth oxide if SiAlON compositions were fully nitrided.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Y\textsubscript{2}O\textsubscript{3}</th>
<th>YAG</th>
<th>Dy\textsubscript{2}O\textsubscript{3}</th>
<th>DyAG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mass% of Y\textsubscript{2}O\textsubscript{3}</td>
<td>mass% of Y\textsubscript{2}O\textsubscript{3}</td>
<td>mass% of Dy\textsubscript{2}O\textsubscript{3}</td>
<td>mass% of Dy\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>B21</td>
<td>1.6</td>
<td>2.4</td>
<td>2.7</td>
<td>3.9</td>
</tr>
<tr>
<td>B31</td>
<td>1.7</td>
<td>2.5</td>
<td>2.8</td>
<td>4.1</td>
</tr>
<tr>
<td>B24</td>
<td>2.1</td>
<td>3.0</td>
<td>3.4</td>
<td>4.9</td>
</tr>
<tr>
<td>B34</td>
<td>2.4</td>
<td>3.5</td>
<td>4.0</td>
<td>5.7</td>
</tr>
<tr>
<td>O2.05</td>
<td>4.8</td>
<td>6.7</td>
<td>7.7</td>
<td>10.6</td>
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<tr>
<td>O3.05</td>
<td>4.9</td>
<td>6.8</td>
<td>7.8</td>
<td>10.7</td>
</tr>
<tr>
<td>O2.2</td>
<td>5.0</td>
<td>6.9</td>
<td>7.9</td>
<td>10.9</td>
</tr>
<tr>
<td>O3.2</td>
<td>5.2</td>
<td>7.2</td>
<td>8.3</td>
<td>11.4</td>
</tr>
</tbody>
</table>

**Effects of combination of additives**

Figure 3.7 shows the degree of nitridation of β and O-SiAlONs when using combinations of additives. The combinations of additives in β-SiAlONs generally led to increased nitridation but there was no apparent synergistic effect. The enhancement in nitridation appears to be cumulative since it was close to that obtained by adding the effects observed for single additives. I.e. the YAG and DyAG alone both enhanced nitridation whilst the CaO and ZrO\textsubscript{2} alone had no effect, and therefore combinations of additives had a similar degree of enhancement as the garnet phases on their own.
Figure 3.7: Effects of combination of the additives investigated earlier on the nitridation of $\beta$-SiAlONs ($z=1$ and 4) and O-SiAlONs ($x=0.05$ and 0.2) prepared by reaction bonding (2) and silicothermal reduction (3) routes.

In O-SiAlONs the additions of ZrO$_2$, which had a positive effect when added alone, combined with either YAG or DyAG, which also had positive effects, resulted in the highest degrees of nitridation of any of the O-SiAlON materials. The nitridation with these combinations was greater than any of the additives used singularly but was not strictly cumulative. Combinations of CaO with YAG also appeared to behave similarly to the sum of these additives added individually. I.e. the nitridation behaviour was a combination of the positive effects of the YAG when added alone and the negative effects of CaO when added alone. The behaviour of CaO/DyAG combinations again followed this same trend for the low substitution O-SiAlONs but not in those with higher degrees of substitution (O2.2 and O3.2).

These two samples showed very low degrees of nitridation with this combination of additives, which could not be explained as a sum of the effects of the two additives individually. The total percentage nitridation of these samples were more than 17 points lower than the expected value if the effects were to be cumulative, whereas in all other systems the difference between actual nitridation and that calculated assuming cumulative effects was much less, typically less than 7 points.

**Effects of the starting composition**

The high substitution $\beta$-SiAlONs, B34, systematically achieved lower degrees of nitridation than the other $\beta$-SiAlON compositions. However XRD analysis did not show any evidence of any Si or Si-containing crystalline phases in any of the materials (see Figure 3.14). This lower degree of nitridation was consistent across all additive types, but also in the sample with no additives and therefore it could not be attributed to a reaction between silicon and the additives to form a crystalline phase.
TGA analysis of a powder composition the same as B31 (see Figure 4.9) shows that there was an initial rapid increase in nitridation as the temperature was raised from 1250°C to 1350°C, but that it slowed down after a relatively short time during the hold at 1350°C. This temperature is close to the melting point of Si (1410°C) and therefore part of the Si that was not yet nitrided was susceptible to being lost by volatilization during the 6-h hold.

Note that the TGA analysis was carried out on powders rather than on pressed pellets and was also conducted in an atmosphere of flowing nitrogen, such that the absolute degrees of nitridation are not necessarily the same as those measured for the pellets under a static gas pressure. The mass of Si that evaporated may not significantly affect the calculated degree of nitridation in samples that contained a large amount of Si but could have a major impact on the calculation of the degree of nitridation for those that only have a small amount of Si, such as B34, assuming the total amount of Si lost by evaporation is similar.

Table 3.6 shows the measured degree of nitridation for the samples based on the average of all eleven additive combinations along with the number of moles of Si in the starting powder which need to be nitrided to form 1 mol of SiAlON based on equations (3.1) to (3.8). The samples with higher amounts of Si in the starting mixture lead to higher apparent degrees of nitridation but the maximum measured nitridation was only 86%. If it is assumed that all of the Si in the body is nitrided, and the difference between the measured value and 100% nitridation is due to evaporation, then the number of moles of Si lost per mole of SiAlON can be determined. These estimated losses varied from 0.38 to 0.98 mol Si / mol SiAlON (column 4) and can be used to determine the range of theoretically achievable degree of nitridation (column 5). In samples where there was no measurable Si remaining the measured nitridation was close to the maximum theoretical, therefore indicating that evaporation was responsible for the less than 100% nitridation. In samples where residual Si was detected, the difference between the measured and the theoretical maximum nitridation was greater (column 7). This analysis shows that care must be taken when describing apparent degrees of nitridation. Although B34 had only a 50% degree of nitridation, all of the Si that is in the sample at the end of the nitriding step is actually nitrided and losses are due to evaporation. Conversely, although B21 showed a higher degree of nitridation (over 80%), not all of the un-nitrided Si was lost by evaporation and some remained in the sample. Therefore this analysis explains why the average measured degree of nitridation was smaller in O-SiAlONs than in β-SiAlONs and why it was only 50% in B34. In summary, this analysis shows that the composition of the starting mixture was the main parameter that influenced the measured
degree of nitridation when SiAlONs were nitrided for a long time at temperatures below the main nitrogen pick-up temperature of about 1370°C.

Table 3.6: Effect of mass losses on the maximum degree of nitridation based on the average of all 11 additive systems.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Average degree of nitridation</th>
<th>Moles of Si required to form 1 mol of SiAlON</th>
<th>Estimated losses in mol Si / mol SiAlON</th>
<th>Range of theoretical degree of nitridation</th>
<th>Samples with remaining Si *</th>
<th>Difference between maximum and average degree of nitridation</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21</td>
<td>80.5%</td>
<td>5.00</td>
<td>0.98</td>
<td>80.5-92.4%</td>
<td>5</td>
<td>11.9%</td>
</tr>
<tr>
<td>B31</td>
<td>86.8%</td>
<td>4.69</td>
<td>0.62</td>
<td>79.1-91.9%</td>
<td>0</td>
<td>5.1%</td>
</tr>
<tr>
<td>B24</td>
<td>80.6%</td>
<td>2.00</td>
<td>0.39</td>
<td>51.0-81.0%</td>
<td>0</td>
<td>0.4%</td>
</tr>
<tr>
<td>B34</td>
<td>50.4%</td>
<td>0.77</td>
<td>0.38</td>
<td>-27.3-50.6%</td>
<td>0</td>
<td>0.2%</td>
</tr>
<tr>
<td>O2.05</td>
<td>64.3%</td>
<td>1.46</td>
<td>0.52</td>
<td>32.9-74.0%</td>
<td>2 (&gt;20%)</td>
<td>9.7%</td>
</tr>
<tr>
<td>O3.05</td>
<td>72.1%</td>
<td>1.46</td>
<td>0.41</td>
<td>32.9-74.0%</td>
<td>2</td>
<td>1.9%</td>
</tr>
<tr>
<td>O2.2</td>
<td>65.3%</td>
<td>1.35</td>
<td>0.47</td>
<td>27.4-71.9%</td>
<td>3</td>
<td>6.6%</td>
</tr>
<tr>
<td>O3.2</td>
<td>69.4%</td>
<td>1.35</td>
<td>0.41</td>
<td>27.4-71.9%</td>
<td>3</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

* Where XRD shows > 5%.

3.4.1.2 Effects of additives and initial compositions on densification

Effects on shrinkage

The density of β and O-SiAlONs increased during nitridation (see Figure 3.9 and Figure 3.11) whereas there was typically no, or only a small, shrinkage as seen in Table 3.7. This was in agreement with Moulson’s work [62] that showed that whilst nitridation of Si is accompanied with a volume increase, it is almost entirely accommodated within the pore structure. Table 3.7 shows the shrinkage in β and O-SiAlON compositions after nitridation along both the height and the diameter of the pellets. The uncertainty of the measuring technique (±0.1 mm) led to an uncertainty in the calculation of the shrinkage of ±1.6% making it difficult to estimate which samples actually underwent shrinkage. However the combination of the two tables (a) and (b) erased any doubt. Therefore it could be drawn from Table 3.7 that there was no shrinkage in B21, B31 and B24 in any case and in O2.05, O3.05 and O2.2 when single additive systems were used. A small shrinkage was observed (about 2-3% in height and diameter) in all the β-SiAlONs B34 and in O-SiAlONs O3.2 nitrided with single additives. All O-SiAlONs with a combination of two additives also displayed shrinkage.
Table 3.7: Shrinkage in β and O-SiAlONs after nitridation: (a) linear shrinkage along the height of the cylindrical pellets and (b) linear shrinkage along their diameter. Coloured cells represent pellets with significant changes in their linear dimensions that can be considered as actual shrinkage.

<table>
<thead>
<tr>
<th>Additives</th>
<th>B21</th>
<th>B31</th>
<th>B24</th>
<th>B34</th>
<th>O2.05</th>
<th>O3.05</th>
<th>O2.2</th>
<th>O3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0%</td>
<td>1.2%</td>
<td>0.2%</td>
<td>2.2%</td>
<td>0.1%</td>
<td>0.7%</td>
<td>0.1%</td>
<td>1.8%</td>
</tr>
<tr>
<td>CaO</td>
<td>0.6%</td>
<td>1.2%</td>
<td>0.0%</td>
<td>4.2%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>0.8%</td>
<td>3.1%</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-0.4%</td>
<td>0.5%</td>
<td>-0.4%</td>
<td>2.0%</td>
<td>0.6%</td>
<td>0.6%</td>
<td>0.4%</td>
<td>3.2%</td>
</tr>
<tr>
<td>YAG</td>
<td>-0.1%</td>
<td>0.6%</td>
<td>-1.2%</td>
<td>2.8%</td>
<td>-0.9%</td>
<td>0.6%</td>
<td>0.3%</td>
<td>4.2%</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.2%</td>
<td>1.1%</td>
<td>1.6%</td>
<td>2.9%</td>
<td>0.1%</td>
<td>0.5%</td>
<td>-0.9%</td>
<td>2.8%</td>
</tr>
<tr>
<td>DyAG</td>
<td>0.2%</td>
<td>1.0%</td>
<td>0.0%</td>
<td>2.0%</td>
<td>-0.9%</td>
<td>0.2%</td>
<td>0.0%</td>
<td>3.3%</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>0.3%</td>
<td>0.5%</td>
<td>0.3%</td>
<td>1.9%</td>
<td>-0.3%</td>
<td>-0.1%</td>
<td>-0.3%</td>
<td>2.0%</td>
</tr>
<tr>
<td>CaO/YAG</td>
<td>-0.6%</td>
<td>1.2%</td>
<td>0.5%</td>
<td>2.1%</td>
<td>3.5%</td>
<td>4.9%</td>
<td>4.4%</td>
<td>7.6%</td>
</tr>
<tr>
<td>CaO/DyAG</td>
<td>0.0%</td>
<td>1.4%</td>
<td>1.4%</td>
<td>2.7%</td>
<td>2.0%</td>
<td>2.2%</td>
<td>3.2%</td>
<td>5.3%</td>
</tr>
<tr>
<td>ZrO₂/YAG</td>
<td>-0.3%</td>
<td>0.3%</td>
<td>0.0%</td>
<td>1.4%</td>
<td>1.0%</td>
<td>1.7%</td>
<td>2.8%</td>
<td>5.8%</td>
</tr>
<tr>
<td>ZrO₂/DyAG</td>
<td>-0.2%</td>
<td>0.8%</td>
<td>0.9%</td>
<td>1.4%</td>
<td>1.8%</td>
<td>3.7%</td>
<td>3.3%</td>
<td>6.0%</td>
</tr>
</tbody>
</table>

The samples that showed appreciable shrinkage, B34 and O3.2, were targeted to form β and O-SiAlON with respectively z=4 and x=0.2, and were produced by silicothermal reduction. They both contained the largest amount of halloysite respectively among the β and O-SiAlON compositions and the collapse of the halloysite structure above 1000°C [67, 68] is thought to be the reason for the shrinkage observed whereas the small amount of halloysite present in B31 and O3.05 was not sufficient to have a noticeable effect on the shrinkage.

The shrinkage may also be affected by the presence of any liquid phase formed during heating which promotes primary grain rearrangement [56, 57]. For instance, the presence of a liquid phase in the O3.2 samples was indicated from SEM images as shown in Figure 3.8a, and EDS analysis showed that the additives were homogeneously distributed in these samples (see Appendix B). The only materials where this liquid phase could not be inferred from the SEM images were those that contained single
additions of ZrO\textsubscript{2} where Zr element was still observed in discrete regions (bright regions in Figure 3.8b). With the exception of ZrO\textsubscript{2}, all of the other additives can form a eutectic liquid in the respective SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-additive system at temperatures below 1390°C, whereas in the SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} system this eutectic temperature is 1710°C. Since the nitridation was carried out at 1350°C it is therefore not surprising that no liquid was observed in the single additive ZrO\textsubscript{2} system.

![Image](image.png)

Figure 3.8: ESEM micrographs of O-SiAlON (O3.2) nitrided at 1350°C with 2 mol% of (a) YAG, (b) ZrO\textsubscript{2}.

In the case of the additions of two additives, no shrinkage was observed in β-SiAlONs. This was probably due to the low SiO\textsubscript{2} content of the starting β-SiAlONs mixtures which did not allow to form enough liquid to enhance the densification. On the other hand, in O-SiAlON compositions which contain larger amounts of SiO\textsubscript{2}, more shrinkage was observed with two compared to one additive since more liquid could be formed. The highest shrinkages were seen for systems where both decomposition of halloysite and presence of a larger volume of liquid phase could take place (i.e. O3.2 with two additives).

**Effects on density and open porosity**

The bulk density of β-SiAlON pellets before and after nitridation is shown in Figure 3.9. None of these samples showed any shrinkage following the nitriding, and therefore increases in density are directly related to the amount of N\textsubscript{2} entering the structure. The similar increase in density after nitridation for the low substitution materials (B21 and B31) can be explained in terms of similar degrees of nitridation (see Table 3.6) and similar amounts of Si in the starting powders (equations (3.1) and (3.3)). On the other hand, although the nitridation of B31 and B24 were similar, the higher increase in density for B31 is attributed to the larger amount of Si in the starting mixture. Similarly, the low increase in density for B34 is attributed to the low initial Si content. Figure 3.10 shows an example of this behaviour. B21 and B31 have very similar microstructures when the same additives are used and their open porosity and nitridation are similar, thus indicating no real effect of processing route. On the other hand, B31 and B34 have very different densities whereby the lower amount of Si in B34 results in less pore filling by nitrogen and therefore a more porous structure, also shown in Figure 3.10.
Optimisation of the nitridation, formation and densification of β and O-SiAlONs

Figure 3.9: Effects of CaO, ZrO₂, YAG, DyAG and combination of these additives on the bulk density before (grey) and after (colours) nitridation and on the open porosity of β-SiAlONs (z=1 and 4) prepared by reaction bonding (2) and silicothermal reduction (3) routes.

Figure 3.10: ESEM micrographs of β-SiAlONs with 2 mol% YAG produced by (a) reaction bonding with z=1 and by silicothermal reduction with (b) z=1 and (c) z=4.

The bulk density of O-SiAlON pellets before and after nitridation is shown in Figure 3.11. In a manner similar to the β-SiAlONs, the increase in density after nitridation in O-SiAlONs was related to the amount of N₂ entering the structure. For instance, the addition of ZrO₂/DyAG led both to higher degrees of nitridation and to higher increase in density. However the difference in increase in density between the different O-SiAlONs was smaller than between the β-SiAlONs. Indeed, the difference in the amount of Si in these powders (1.35 to 1.46 mol Si / mol SiAlON) is much smaller than the difference in the β-SiAlONs (0.77 to 5.00 mol Si / mol SiAlON). Hence the increase in density in O-SiAlONs was not as dependent on the degree of nitridation as the β-SiAlONs were. The density was dependent on the starting compositions (processing routes and the levels of substitution). For comparable levels of substitution, samples that contained halloysite (silicothermal) had higher density, greater shrinkages and lower open porosities than those without (reaction bonding) and the difference
was greater for the higher levels of substitution. Of the silicothermal samples the ones with greater halloysite content achieved higher densities, than those with a lower halloysite content.

Figure 3.11: Effects of CaO, ZrO$_2$, YAG, DyAG and combination of these additives on the bulk density before (grey) and after (colours) nitridation and on the open porosity of O-SiAlONs (x=0.05 and 0.2) prepared by reaction bonding (2) and silicothermal reduction (3) routes.

The density and open porosity were dependent on the type of additive used, and their effects were consistent across all of the O-SiAlON compositions. When used singularly, CaO, YAG or DyAG systematically led to higher densities and lower open porosities than without additive, ZrO$_2$, Y$_2$O$_3$ or Dy$_2$O$_3$. This was thought to be due to the possibility of forming a liquid with the first three additives since the nitriding temperature was above the eutectic point of the CaO-SiO$_2$-Al$_2$O$_3$ system [105] and close to the one in the Re$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ systems [106, 107] (see Table 3.2). The nitriding temperature was below the eutectic point in the ZrO$_2$-SiO$_2$-Al$_2$O$_3$ system [104], and the amount of Al$_2$O$_3$ was too low when Y$_2$O$_3$ and Dy$_2$O$_3$ were added alone. Figure 3.12 shows the effect of additives on the microstructure after nitridation, and supports the porosity data. The samples with CaO had a higher density despite lower nitridation (and therefore less pore filling by nitrogen) since in the CaO system a liquid phase was formed. With ZrO$_2$ the liquid phase was not formed and despite higher nitridation the porosity was greater.
Optimisation of the nitridation, formation and densification of β and O-SiAlONs

The combinations of additives led to lower open porosities and greater densities but also greater shrinkage than the individual systems. This was probably due to the possibility of forming a larger volume of liquid in the quaternary systems than in the ternary ones.

3.4.1.3 Effects of additives and initial compositions on the crystalline phase composition

β and O-SiAlONs have been analysed by XRD, and semi-quantitative analysis was carried out to determine the crystalline phases present in the samples after the nitridation stage. The mass percentage of these phases, as a function of the starting compositions and of the additives employed, is described in Figure 3.13 to Figure 3.17. Note that all the subsequent figures demonstrating phase assemblages determined by XRD are intended to illustrate the major and minor phases present, rather than representing absolute amounts of each phase.

Phase assemblage of β-SiAlONs after nitridation

The amount of residual Si in β-SiAlONs produced by silicothermal reduction (B31 and B34) after nitridation was typically very low, if not undetectable as seen in Figure 3.13 and Figure 3.14. For reaction bonded samples, Si was only detected in significant amounts in B21, which correlates well with this sample having the lowest degrees of nitridation in comparison with the maximum achievable, as shown in Table 3.2. In addition, β-SiAlONs with z=1 (B21 and B31) both had similar phase assemblages independently of the type of additive used. They were comprised of two main phases of β-SiAlON and α-Si3N4 and two minor phases of Al2O3 and AlN. All of the compositions containing rare-earth oxides had a higher β-SiAlON content than the three compositions without it (namely the ones with no additive and with single additions of CaO and ZrO2), which instead had higher AlN and α-Si3N4 contents. This indicates that the rare-earth additions promoted the formation of β-SiAlON by enhancing the incorporation of AlN and Al2O3 into the Si3N4 structure.
Figure 3.13: Effects of CaO, ZrO$_2$, YAG, DyAG and combination of these additives on the crystalline phase assemblage of β-SiAlONs (z=1) prepared by reaction bonding (white) and silicothermal reduction (green) routes.

The main phases in β-SiAlONs with z=4 (B24 and B34) were β-SiAlON, Al$_2$O$_3$ and AlN as shown in Figure 3.14. These compositions initially contained a larger amount of Al$_2$O$_3$ and AlN than the β-SiAlONs with z=1 and these two phases were not able to be fully incorporated in to the Si$_3$N$_4$ structure during the nitriding stage and therefore remained in the samples at the end of nitriding, even when rare-earth oxides were used.
Optimisation of the nitridation, formation and densification of β and O-SiAlONs

Figure 3.14: Effects of CaO, ZrO₂, YAG, DyAG and combination of these additives on the crystalline phase assemblage of β-SiAlONs (z=4) prepared by reaction bonding (white) and silicothermal reduction (green) routes.

An equimolar amount of AlN and Al₂O₃ was used in the powder mixture of the high substitution β-SiAlON produced by reaction bonding (B24) according to equation (3.2). The mass ratio of Al₂O₃/AlN in this sample was therefore equal to 2.49 when no Al₂O₃ was included as an additive and 2.58 for the samples with the garnet additions. Table 3.8 gives the Al₂O₃/AlN mass ratio after the nitridation for all additive systems calculated from the results of the semi-quantitative analysis. The ratio was relatively similar for all systems after nitridation, despite containing different total amounts of the SiAlON phase, and close to that of the starting mixture. Thus the formation of β-SiAlON with z=4 by reaction bonding can be written as a progressive incorporation of these two phases into the Si₃N₄ structure:

\[
\begin{align*}
5\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3 + \text{AlN} & \rightarrow 3\text{Si}_5\text{AlON}_7 \\
4\text{Si}_5\text{AlON}_7 + 2\text{Al}_2\text{O}_3 + 2\text{AlN} & \rightarrow 5\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 \\
3\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 + 2\text{Al}_2\text{O}_3 + 2\text{AlN} & \rightarrow 4\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5 \\
2\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5 + 2\text{Al}_2\text{O}_3 + 2\text{AlN} & \rightarrow 3\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4
\end{align*}
\]

Peak shifts in XRD analysis of these samples after nitridation did indeed indicate that β-SiAlONs with low level of substitution (0 < z < 1) were formed whereas subsequent sintering of these samples did result in β-SiAlONs with high level of substitution (z=4). Since the measurements were only taken at two temperatures, the intermediate β-SiAlON phases could not be identified.
Table 3.8: Mass ratio of $\text{Al}_2\text{O}_3$ and $\text{AlN}$ in $\beta$-$\text{SiAlON}$ with $z=4$ produced by reaction bonding (B24) and silicothermal reduction (B34) routes determined by XRD semi-quantitative analysis. The ratio is slightly higher when additives containing $\text{Al}_2\text{O}_3$ are employed.

<table>
<thead>
<tr>
<th>Ratio in starting mixtures</th>
<th>B24</th>
<th>B34</th>
</tr>
</thead>
<tbody>
<tr>
<td>without garnet precursor phase</td>
<td>2.49</td>
<td>0.00</td>
</tr>
<tr>
<td>with garnet precursor phase</td>
<td>2.58</td>
<td>0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio after nitriding stage</th>
<th>No additive</th>
<th>CaO</th>
<th>ZrO$_2$</th>
<th>YAG</th>
<th>DyAG</th>
<th>Y$_2$O$_3$</th>
<th>Dy$_2$O$_3$</th>
<th>CaO/YAG</th>
<th>CaO/DyAG</th>
<th>ZrO$_2$/YAG</th>
<th>ZrO$_2$/DyAG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.00</td>
<td>2.41</td>
<td>2.32</td>
<td>2.25</td>
<td>2.89</td>
<td>2.37</td>
<td>2.29</td>
<td>2.19</td>
<td>2.21</td>
<td>2.53</td>
<td>2.57</td>
</tr>
</tbody>
</table>

The $\text{Al}_2\text{O}_3$/AlN ratio in the high substitution sample produced by silicothermal reduction (B34) was similar to that in the reaction bonded sample for all the compositions that contained the rare-earth oxides as seen in Table 3.8. This is despite the fact that the B34 samples contain no or very little alumina in the starting mixture ($\text{Al}_2\text{O}_3$/AlN = 0.04 with garnet additives) since halloysite was used instead of $\text{Al}_2\text{O}_3$.

Above $1000^\circ\text{C}$ halloysite decomposes into mullite and $\text{SiO}_2$ [67] according to equation (2.7). The XRD analysis and Figure 3.14 show that these rare-earth containing $\beta$-$\text{SiAlONs}$ B34 had no mullite or $\text{SiO}_2$ and contained a major phase of $\text{Al}_2\text{O}_3$. Rare-earth silicates were detected in small amounts, therefore it could be suggested that the rare-earth oxides reacted with mullite according to:

$$\text{Re}_2\text{O}_3 + 2\text{SiO}_2\cdot3\text{Al}_2\text{O}_3 \rightarrow \text{Re}_2\text{Si}_2\text{O}_7 + 3\text{Al}_2\text{O}_3$$

Such reactions destroyed the mullite structure and formed $\text{Al}_2\text{O}_3$ that can react with other phases or enter the $\text{Si}_3\text{N}_4$ structure to form $\beta$-$\text{SiAlON}$. Indeed the amount of $\beta$-$\text{SiAlON}$ present in these samples was higher than the corresponding ones without the rare-earth additives. This behaviour was also observed in the low substitution samples ($z=1$) prepared by silicothermal reduction. Any alumina that does not take part in $\text{SiAlON}$ formation remains as $\text{Al}_2\text{O}_3$ and is the reason for the $\text{Al}_2\text{O}_3$/AlN ratios observed. On the other hand in the three compositions without rare-earth oxide, the $\beta$-$\text{SiAlONs}$ produced by silicothermal reduction did not contain this remaining $\text{Al}_2\text{O}_3$ but they did contain between 20-30% in mass of mullite as well as about 5% in mass $\text{SiO}_2$ (not shown in Figure 3.14 for clarity purposes).
It appears then that the presence of the rare-earth catalysts the decomposition of mullite. However even for the B34 samples with rare-earth, even if all the Al$_2$O$_3$ contained in the initial halloysite was transformed into free Al$_2$O$_3$, the Al$_2$O$_3$/AlN ratio should still only be 0.42, which is 5-6 times less that observed. This suggests that some AlN was also transformed into Al$_2$O$_3$ which could correspond to the oxidation of AlN by the SiO$_2$ formed from the dissociation of halloysite according to:

$4\text{AlN} + 3\text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + \text{Si}_3\text{N}_4$

This would also lead to the formation of Si$_3$N$_4$ without picking up N$_2$ from the atmosphere. Table 3.9 shows the estimated composition after nitridation based on the 50% degree of nitridation measured for this sample. This shows that the nitride phase (low level substitution β-SiAlIONs and/or Si$_3$N$_4$) should only represent 6.8 mass% although the amount determined from the semi-quantitative XRD analysis was much higher (34.3%).

However if additional Si$_3$N$_4$ is formed according to reaction (3.19), then assuming that all of the SiO$_2$ contained in the halloysite is transformed to nitride, the calculated total amount of nitride phases (from nitridation of Si plus reaction (3.19)) is much closer to that determined from XRD analysis. Reaction (3.19) would also explain why the amount of nitride phases (β-SiAlION and Si$_3$N$_4$) seen in Figure 3.14 was much higher in B34 containing rare-earth oxides (34.3% in mass on average) than in those without it (9.3% in mass on average).

Table 3.9: Comparison of the measured crystalline phase composition in mass percentage to two calculated phase compositions: one taking into account only the Si$_3$N$_4$ formed from the Si reacting with the atmosphere and another one including both the nitridation reaction and the oxidation of AlN by SiO$_2$ according to reaction (3.19).

<table>
<thead>
<tr>
<th>Phases</th>
<th>M (g mol$^{-1}$)</th>
<th>If 50% of Si is converted to Si$_3$N$_4$ according to Table 3.6</th>
<th>Mass% measured from XRD semi-quantitative analysis (average of the 8 samples containing rare-earth additions)</th>
<th>If 50% of Si is converted to Si$_3$N$_4$ and if all SiO$_2$ is consumed in reaction (3.19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>140.28</td>
<td>5 701.4 6.8%</td>
<td>34.3%</td>
<td>26 3647.4 31.5%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>101.96</td>
<td>20 2039.2 19.6%</td>
<td>45.6%</td>
<td>52 5302.0 45.8%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>60.08</td>
<td>48 2884.1 27.8%</td>
<td>0.0%</td>
<td>0 0.0 0.0%</td>
</tr>
<tr>
<td>AlN</td>
<td>40.99</td>
<td>116 4754.6 45.8%</td>
<td>20.1%</td>
<td>64 2623.2 22.7%</td>
</tr>
</tbody>
</table>

A reaction path for the formation of β-SiAlION z=4 by silicothermal reduction can be suggested as follows. Following the decomposition of halloysite into mullite and SiO$_2$, the SiO$_2$ and AlN reacted with the nitrided Si to form β-SiAlION according to:

$9\text{Si}_3\text{N}_4 + 3\text{SiO}_2 + 6\text{AlN} \rightarrow 10\text{Si}_3\text{N}_4 + 2\text{Al}_2\text{O}_3 + 2\text{AlN} \rightarrow 6\text{Si}_5\text{AlION}_7$
After decomposition of mullite into Al$_2$O$_3$ and SiO$_2$, which was catalysed in presence of rare-earth oxides, the formation of $\beta$-SiAlON proceeded as SiO$_2$ and AlN were integrated into the SiAlON structure:

\[(3.21) \quad 2\text{Si}_{15}\text{AlON}_7 + 2\text{SiO}_2 + 4\text{AlN} \rightarrow 3\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6\]

The reaction can progress further as long as SiO$_2$ is available:

\[(3.22) \quad \text{Si}_3\text{Al}_2\text{O}_2\text{N}_6 + 2\text{SiO}_2 + 4\text{AlN} \rightarrow 2\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5\]

Once all of the SiO$_2$ is incorporated into the SiAlON structure, the remaining AlN and Al$_2$O$_3$ phases were present in the samples at an equimolar amount and the reaction occurring was the same as with reaction bonding:

\[(3.17) \quad 2\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5 + 2\text{Al}_2\text{O}_3 + 2\text{AlN} \rightarrow 3\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4\]

**Phase assemblage of O-SiAlONs after nitridation**

As seen previously in Figure 3.5, in O-SiAlON materials the nitridation, measured by mass losses, was hindered by CaO and enhanced by ZrO$_2$ additives. These effects are corroborated in Figure 3.15 and Figure 3.17 which show the phase assemblage based on XRD analysis where it can be seen that there is more Si detected in O-SiAlONs with CaO, and less with ZrO$_2$, in comparison to the samples without additives. The presence of ZrO$_2$ led to a major phase of $\alpha$-Si$_3$N$_4$ and to minor phases of O-SiAlON and SiO$_2$. For the high substitution materials, additional minor phases were observed depending on the processing route used, with Al$_2$O$_3$ being detected in reaction bonded samples (O2.2) and mullite being detected in O-SiAlON (O3.2) produced by the silicothermal reduction route. The presence of the SiO$_2$ and Al$_2$O$_3$ (or mullite) indicate that they were not able to be incorporated in to the Si$_3$N$_4$ structure to form O-SiAlON at 1350°C in these samples and therefore the amount of O-SiAlON is low whilst the $\alpha$-Si$_3$N$_4$ was high. The presence of a large amount of $\alpha$-Si$_3$N$_4$, the low content of O-SiAlON and the presence of SiO$_2$ in the low substitution materials suggests that similar reaction paths occurred in O-SiAlON $x=0.05$ and $x=0.2$ although the minor Al$_2$O$_3$ phase could not be detected presumably because of its much lower content in the starting mixture.
Figure 3.15: Effects of CaO, ZrO$_2$, YAG, DyAG and combination of these additives on the crystalline phase assemblage of O-SiAlONs ($x=0.05$) prepared by reaction bonding (white) and silicothermal reduction (green) routes.

In the presence of single additions of CaO, smaller amounts of Si$_3$N$_4$ and SiO$_2$ were observed in the O-SiAlONs compared to the sample without additives whereas a major phase of O-SiAlON was formed. Although CaO actually hindered the nitridation (see Figure 3.5) this result suggests that it did promote the formation of O-SiAlON by enhancing the incorporation of SiO$_2$ and Al$_2$O$_3$ into the Si$_3$N$_4$ structure of any nitride that had formed. The difference in the behaviour between the CaO and ZrO$_2$ additions is thought to be due to their eutectic temperatures and ability to form a liquid phase at the nitriding temperature (see Table 3.2). The nitriding temperature was above the eutectic temperature in the CaO-SiO$_2$-Al$_2$O$_3$ system whilst it was below that in the ZrO$_2$-SiO$_2$-Al$_2$O$_3$ one. Therefore ZrO$_2$ was able to enhance nitridation as described earlier but was not able to form a liquid phase in which O-SiAlION grains could precipitate. On the other hand, by forming a liquid phase at lower temperature, CaO additions promoted the formation of O-SiAlON but, as a consequence, the nitridation was hindered by this liquid phase which contributed to isolating Si from the nitrogen by hastening pore closure or by wetting the Si grains. The presence or absence of a liquid phase and its effect on densification was indicated in the ESEM images shown in Figure 3.12. This figure indicated not only density differences, but also the presence of high contrast particles for the sample containing ZrO$_2$. Figure 3.16 shows EDS elemental distribution of the additive elements of these same samples. The Ca (Figure
Chapter 3

3.16a) was much more homogeneously distributed due to formation of the liquid phase whereas the Zr was still present as discrete particles since no liquid phase was formed (Figure 3.16b).

Figure 3.16: EDS mapping of (a) Ca and (b) Zr in O-SiAlONs O3.2 with 2 mol% of CaO and ZrO₂ respectively. These elemental maps correspond to the ESEM micrographs given in Figure 3.12.

In the case of the O-SiAlON (x=0.2), nitrided with rare-earth oxide or garnet additions, high levels of O-SiAlON were produced (~80%). These high substitution materials contained Al₂O₃ in the starting mixture (either as oxide or through successive decompositions of halloysite and mullite) and therefore even in samples which only have single additions of rare-earth oxide, there is sufficient Al₂O₃ available to form the SiAlON phase.

However, in the O-SiAlONs (x=0.05), there was a difference in the phase assemblage of samples with additions of rare-earth oxide and garnet phases. The amount of O-SiAlON was twice as high in samples with YAG and DyAG additions (about 80% in mass) compared with Y₂O₃ and Dy₂O₃ (about 40% in mass) as shown in Figure 3.15. In these materials the amount of alumina in the starting mixture is lower and with single rare earth oxide additions the SiAlON phase cannot be formed to the same extent. The extra Al₂O₃ provided with the garnet phases is thought to be the reason for the enhanced formation of the O-SiAlON phase with this additive, which occurs in the presence of a liquid phase by dissolution/precipitation [3, 21]. This correlates well with the results on the open porosity as O-SiAlONs with Y₂O₃ and Dy₂O₃, which had higher open porosities than the ones with YAG and DyAG (see Figure 3.11).

Almost all of the O-SiAlONs with rare-earth garnet additions, either alone or in combination, led to the same phase assemblage composed of a major phase of O-SiAlON (around 80% in mass) and minor phases of Si₃N₄ as shown in Figure 3.17. Only the O-SiAlONs (x=0.2) with CaO/DyAG additions had a phase assemblage significantly different. The XRD analysis showed that these samples contained the most Si, which was in good agreement with their degree of nitridation being the lowest among all additive systems (about 28% as shown in Figure 3.7) and they also both contained mullite. However, while the mullite in the O-SiAlONs (x=0.2) produced by silicothermal reduction was issued from the
decomposition of halloysite, the presence of mullite in the samples produced by reaction bonding can only come from reaction between SiO$_2$ and Al$_2$O$_3$. This could occur since the Si was not yet nitrided and therefore these phases could not be incorporated into the Si$_3$N$_4$ structure. The SiO$_2$ and Al$_2$O$_3$ phases would be susceptible to react and form mullite at this temperature [109] according to:

$$3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$$

Contrary to the β-SiAlONs, in this case the rare-earth oxide was not able to decompose the mullite presumably because it had preferentially reacted with the greater amount of SiO$_2$ present in the starting mixtures to form phases such as Dy$_2$Si$_2$O$_7$. The formation of either mullite or the rare earth silicates (both detected by XRD analysis) explains why no SiO$_2$ was observed in this sample even though it was major component of the starting mixture and the amount of O-SiAlON formed was low.

Figure 3.17: Effects of CaO, ZrO$_2$, YAG, DyAG and combination of these additives on the crystalline phase assemblage of O-SiAlONs ($x=0.2$) prepared by reaction bonding (white) and silicothermal reduction (green) routes.

3.4.1.4 Conclusions
A study of the starting compositions and processing routes on the nitridation stage of β and O-SiAlONs with different additives both added singularly and in combination, has led to the following conclusions:
• ZrO$_2$ and CaO additions had no significant influence on the nitridation of $\beta$-SiAlONs. However they respectively enhanced and hindered nitridation in O-SiAlONs.

• In O-SiAlONs, the enhancing effect of ZrO$_2$ was probably due to the formation of ZrN that provided an internal source of nitrogen. CaO did not have the expected enhancing effect since, instead of reacting with the SiO$_2$ layer at the surface of the Si powder to expose free Si, it reacted with the initial SiO$_2$ powder to form a liquid phase that reduced the interface area between Si and N$_2$ by wetting the Si grains and enhancing the pore closure.

• The presence of the liquid phase formed with CaO additives led to the formation of O-SiAlON at the nitriding temperature, whereas additions of ZrO$_2$, which led to higher conversion of Si to Si$_3$N$_4$, could not form O-SiAlON at the same temperature since no liquid phase was formed.

• Additions of rare-earth oxides typically enhanced the nitridation of Si in SiAlONs. In SiAlONs with low level of substitution, the extra Al$_2$O$_3$ provided with the garnet phase additives (YAG or DyAG) enhanced the formation of the SiAlON phase compared to single additions of Y$_2$O$_3$ or Dy$_2$O$_3$.

• In high substitution $\beta$-SiAlONs ($z=4$) prepared by silicothermal reduction with rare-earth oxides, a large amount of nitride phase observed, about 34% in mass, which could not be achieved if the nitridation of Si was the only source of Si$_3$N$_4$. It is thought the oxides catalysed the decomposition of mullite produced from the original halloysite, and that the subsequent SiO$_2$ reacted with AlN to form Al$_2$O$_3$ and Si$_3$N$_4$. Without rare-earth oxides, the mullite was not decomposed, and the lower amount of nitride phase corresponded to calculations where nitridation of Si was the only source of Si$_3$N$_4$.

• Long dwelling times at temperatures close to the melting point of Si led to losses of Si by evaporation. This explains why degrees of nitridation for low Si containing samples appear to be low.

3.4.2 Effects of additives, initial composition, temperature and nitrogen pressure on the sintering stage

The influence of different factors on the sintering of SiAlON samples was assessed by designing an orthogonal experimental design based on the Taguchi method with 4 factors each of 3 levels as described in Section 3.2. The nitriding enhancers and sintering additives, where used, were added at 2 mol%. The 8 SiAlON powders described in Table 3.4 and mixed with the additives described in Table 3.3 were fired in a two-step process:
The nitriding schedule, which ended after the 6 h hold at 1350°C under 0.4 MPa of nitrogen, was designed to investigate the effects of additives and initial compositions on the nitridation and formation of SiAlONs. The results drawn from it have been described in the previous section.

The sintering step includes a final hold of 2 h at the temperatures and nitrogen pressures described in Table 3.3.

The experimental methodology developed was used to optimise the sinterability of β and O-SiAlONs and to study the influence of a wide set of variables during the gas pressure sintering of these materials.

3.4.2.1 Phase composition

XRD spectra of SiAlONs with CaO additions produced by reaction bonding and sintered at 1700°C under 0.1 MPa of nitrogen (corresponds to run 4 described Table 3.3) are presented in Figure 3.18. They show that the sample targeted at z=1 was fully converted to β-SiAlION but that the one targeted at z=4 was comprised of about 90% β-SiAlION, plus minor phases of Al₂O₃ and 15R-AlN polytype. The O-SiAlON samples (x=0.05 and 0.2) were converted into O-SiAlON (≈90-95%) and either β-Si₃N₄ or β-SiAlON with a very low substitution (≈5-10%). These XRD spectra were representative of the phase assemblage of all the SiAlONs sintered in this experiment.

Different traces of other phases could be detected depending on the type of additive used but the relative amount of the minor phases shown in Figure 3.18 was similar at 1600°C and 1700°C. At 1800°C the same phases were observed but their relative amounts varied with the level of
decomposition of the sample as will be detailed in Section 3.4.2.3. All these results and observations were similarly obtained for the samples prepared by silicothermal reduction. The processing route employed had therefore no significant influence on the final crystalline phase assemblage of SiAlONs and this applied to all the sintering conditions and additive systems used in this experiment.

3.4.2.2 Densification
In order to study the effects of the 4 factors on the densification of SiAlONs all containing different additives it would be best to investigate the relative density of the samples. However, the relative density, which is calculated from the ratio bulk/theoretical density, was likely to be inaccurate since it is difficult to estimate the theoretical density of SiAlONs (see Section 3.3.3.3). Reporting the results in terms of bulk density did not make sense either: samples containing additives with heavy elements, such as Y or Dy, would tend to give higher bulk densities than those containing lighter elements or no additive at all. Higher bulk densities are therefore not necessarily representative of samples with higher relative density.

Since it may not be accurate to use the relative density, two other properties, open porosity and shrinkage were employed in complement to investigate the densification. Indeed the densification process consists of pore elimination which results in shrinkage. Therefore, in general, samples that displayed the lowest open porosity as well as the highest shrinkage could be considered as achieving the highest density. In this experiment, some samples decomposed, which led to further shrinkage but higher open porosities. Since this could be a source of misinterpretation, shrinkage could not be used alone to evaluate the extent of densification. Similarly, a sample may have a low open porosity but a high closed porosity, meaning that a sample which is not dense could be considered as such. Open porosity which is in general high when samples are not dense and/or when they have decomposed, could not be used alone either to observe the densification state of the samples.

The goal of this experiment was to be able to identify which factor had the most influence on densification and which level was the most appropriate to produce the most dense samples. Combining the information given by the three properties – relative density, shrinkage and open porosity – could give a reliable estimate of the behaviour of the samples regarding densification. Furthermore, the results obtained for all three properties were coherent: in general samples with high relative density showed low open porosity and large shrinkage. This means that the potential sources of errors may not have a large effect in this experiment. Results from the experimental design, in terms of open porosity and shrinkage, are shown in Figure 3.19 and Figure 3.20 respectively. Results in terms of relative density are only given in Appendix D due to the potential inaccuracy of the values reported. Open
porosity and shrinkage may not always be representative of the densification process, but the values reported are accurate.

The data are presented in Figure 3.19 to Figure 3.21 in terms of the effects of temperature (1600, 1700 and 1800°C), nitrogen pressure (0.1, 0.4 and 0.7 MPa), nitriding enhancers (none, ZrO₂ and CaO) and sintering additives (none, YAG and DyAG). Note that the Taguchi method of experimental design used in this work means that the data are plotted in such a way that all combinations are included as a single point. For example, the data plotted against ZrO₂ in Figure 3.19 represent those samples where ZrO₂ was used as the nitriding enhancer in combination with any other parameters: i.e. ZrO₂ + 1600°C + 0.7 MPa + none, ZrO₂ + 1700°C + 0.4 MPa + YAG and ZrO₂ + 1800°C + 0.1 MPa + DyAG.

As expected, the sintering aids had the greatest influence on the density. Without sintering aids, all samples achieved higher open porosities and smaller shrinkages with the exception of O3.2. This may be due to the fact that the data point representing the average effect of DyAG on the open porosity includes the O3.2 samples containing DyAG and CaO. These samples achieved by far the lowest degree of nitridation among all the other compositions represented in the sintering additives section (i.e. they had a degree of nitridation of 30% in comparison with between 50 and 80% for all the other combinations of that section). This lower degree of nitridation would have lead to less pores being filled by nitrogen, hence a higher open porosity after the nitridation step that translated in a higher porosity after sintering.

![Image](image-url)
Although the density reached by the samples with YAG and DyAG were similar, YAG seemed to increase the density slightly more in O-SiAlON, whereas DyAG produced the highest density for β-SiAlON.

The temperature was the second most influential factor in the densification of SiAlON. Generally the open porosity decreased and shrinkage increased when the temperature was raised from 1600°C to 1700°C. However the increase from 1700°C to 1800°C led to further shrinkage whereas the open porosity increased. Temperature was the only factor where open porosity and shrinkage did not give very similar results: this was due to the fact that samples kept shrinking with the increasing temperature while they underwent a significant decomposition at 1800°C as will be described in the following section. In overall, the density did not seem to increase from 1700°C to 1800°C due to this decomposition. The effects of temperature on both open porosity and shrinkage were larger in the O-SiAlONs than in the β-SiAlONs.

Nitrogen pressure had no significant effect on the densification of SiAlONs with a low level of substitution produced by both routes (B21, B31, O2.05 and O3.05) as both open porosity and shrinkage did not vary significantly. However, for higher substitution (B24, B34, O2.2 and O3.2), the density decreased with increasing nitrogen pressure.

![Figure 3.20: Influence of design parameters on the shrinkage of the samples along their diameter.](image)

The addition of nitriding enhancers had the smallest influence on density: in general the presence of CaO led to comparable or slightly higher densities, whereas ZrO₂ had a negative effect on density. The
eutectic temperature in the SiO$_2$-Al$_2$O$_3$-ZrO$_2$ system, which is above 1700°C [104], was higher than any of the other corresponding additive systems. This means that it was the only additive with which it was not possible to form a eutectic liquid at anything other than the highest sintering temperature when it was used alone.

3.4.2.3 Mass loss during the sintering

Densification is not the only property to take into account when sintering SiAlONs. Indeed while high temperatures and long dwelling times are necessary to densify SiAlONs, these two parameters may also enhance the decomposition (i.e. phase change generally accompanied by mass losses) of these materials. It is of importance to limit decomposition as it may alter the chemistry and the structure of the surface of the samples. Nitrogen pressures and powder beds have already been used and shown to limit Si$_3$N$_4$ and SiAlONs decomposition [42, 88, 94]. In this work, powder beds have been used as an invariant parameter while nitrogen pressures have been changed, along with temperature and additives, according to the experimental design. Results from this experiment, in terms of mass loss, are shown in Figure 3.21.

Temperature was the most influential factor as an increase in temperature led to greater mass losses. For the low substitution β-SiAlONs, the mass loss, even at 1800°C, was not excessive (1-3%), but was slightly higher in the high substitution samples (6-8%). The mass loss at the highest temperature was much higher in the O-SiAlONs (10-19%). These results correspond with the densification data in that greater mass loss produced samples with lower density, presumably due to gaseous evaporation leaving behind porosity. In fact, for the O-SiAlON samples there was a similar correlation between open porosity and mass loss for most of the parameters studied. The only exception was gas pressure, where increase in pressure resulted in lower decomposition but not necessarily in lower open porosities, probably because the pressure of the gas entrapped in the pores hindered their elimination.
The decomposition was also in general much lower in β-SiAlONs than in O-SiAlONs for all parameters. Figure 3.22 shows representative XRD spectra for β and O-SiAlONs sintered at 1700°C and 1800°C, and the mass losses of these samples. The decomposition was much smaller in β-SiAlONs showing that they were more stable at higher temperatures than O-SiAlONs. Moreover, the higher mass losses for the O-SiAlON samples were associated with a transformation to β-SiAlON, suggesting that the mass losses were SiO, and that the overall decomposition reaction of O-SiAlON could be:

\[
6\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.95}\text{N}_{1.95} \rightarrow \text{Si}_{5.7}\text{Al}_{0.3}\text{O}_{0.3}\text{N}_{7.7} + 6\text{SiO(g)} + 2\text{N}_2(g)
\]

O-SiAlON \( (x = 0.05) \)  \( \rightarrow \)  β-SiAlON \( (z = 0.3) \)

A white cloud was observed above the O-SiAlON samples that had decomposed and XRD analysis showed that it was made of \( \alpha \)-Si\(_3\)N\(_4\) confirming that SiO was probably lost from the sample since it has been shown that reaction of N\(_2\) and Si in gas state leads to the formation of \( \alpha \)-Si\(_3\)N\(_4\) [62, 64].
3.4.2.4 Validation

This last step of the experimental design used the previous results to determine optimum sintering conditions and additives to produce dense SiAlONs.

As seen in Figure 3.19 and Figure 3.20, open porosity and shrinkage correlated well to give a good estimate of the densification of a sample. However in the case of a sample undergoing large decomposition, these two parameters did not match. High open porosity could be measured in a sample that did not densify and also in a sample that did densify but was subject to large decomposition. In both cases, the samples would not be dense and this would be shown through the measured open porosity. This would not be true regarding the shrinkage: a high shrinkage may be caused by a large decomposition; therefore it was not appropriate to take shrinkage into account to determine the set of optimal conditions.

Based on the results from these statistical design experiments, the conditions that should lead to maximum density and minimum decomposition were determined and are given in Table 3.10. Only the open porosity (not the shrinkage) was taken into account to evaluate the conditions that led to the highest density. Note that the optimum conditions leading to the lowest open porosity were the same that led to the highest relative density.
Table 3.10: Summary of optimum configurations for highest densities and smallest mass losses.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Temperature (°C)</th>
<th>N₂ pressure (MPa)</th>
<th>Nitriding Enhancers</th>
<th>Sintering Aids</th>
<th>Temperature (°C)</th>
<th>N₂ pressure (MPa)</th>
<th>Nitriding Enhancers</th>
<th>Sintering Aids</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21</td>
<td>1700</td>
<td>0.7</td>
<td>ZrO₂</td>
<td>DyAG</td>
<td>1600</td>
<td>0.7</td>
<td>CaO/ZrO₂</td>
<td>none</td>
</tr>
<tr>
<td>B31</td>
<td>1600/1700</td>
<td>0.1/0.4</td>
<td>CaO/ZrO₂</td>
<td>YAG/DyAG</td>
<td>1600</td>
<td>0.1</td>
<td>CaO/ZrO₂</td>
<td>DyAG</td>
</tr>
<tr>
<td>B24</td>
<td>1700</td>
<td>0.1</td>
<td>none/CaO</td>
<td>DyAG</td>
<td>1600</td>
<td>0.7</td>
<td>ZrO₂</td>
<td>YAG/DyAG</td>
</tr>
<tr>
<td>B34</td>
<td>1600</td>
<td>0.1</td>
<td>CaO</td>
<td>DyAG</td>
<td>1600</td>
<td>0.1</td>
<td>ZrO₂</td>
<td>DyAG</td>
</tr>
</tbody>
</table>

The optimum conditions leading to the highest densities and smallest mass losses were not the same therefore the conditions selected for the validation run represent a compromise to achieve dense samples with low decomposition in most of the SiAlONs. As a consequence, validation runs were conducted at 1700°C under 0.7 MPa of nitrogen using CaO + DyAG for β-SiAlONs and CaO + YAG for O-SiAlONs. Figure 3.23 shows the densities and mass loss for these validation runs compared with the data from all of the original experiments.

Figure 3.23: Validation data (▲) compared with averages (●) and range (▬) from original runs.

As can be seen from this figure, even though the optimum conditions for densification and mass loss were not the same, for most of the samples the conditions used for the validation trials resulted in open porosities lower than average and comparable to the best data from the original runs. All of the samples had effectively zero mass loss using these conditions. These results show that the Taguchi
analysis is suitable for optimising a range of sintering parameters and the optimised conditions can be used as the basis for further development. All the samples did not have the same relative density therefore it was not possible to study the effects of the factors on mechanical or chemical properties since they both depend on the porosity of the samples.

3.4.2.5 Conclusions
The study of the effects of four factors – temperature, nitrogen pressure, nitriding enhancers and sintering aids – through the design of a Taguchi experimental plan has led to the following conclusions:

• The sintering aids had the greatest influence on the density; their presence improved the final density.
• The temperature had the greatest influence on the decomposition of the samples. A critical decomposition had been observed at 1800°C when the lowest densities are achieved.
• The nitrogen pressure had a smaller influence on the densification and the decomposition than the previous 2 factors. High pressures typically tended to reduce the decomposition of SiAlON but they did not necessarily lead to higher densities.
• In general the nitriding enhancers had a smaller influence on the densification and the decomposition than the first two factors. In general ZrO$_2$ additions led to the lowest densities because ZrO$_2$ does not form a eutectic liquid below 1700°C.
• Reaction bonding and silicothermal reduction routes had a similar behaviour in all the configurations that have been investigated: the four factors had the same influence on samples produced by either routes.
• $\beta$ and O-SiAlIONs did not have the same behaviour with respect to temperature. Indeed O-SiAlIONs greatly decomposed at 1800°C by losing SiO from the surface which led to the formation of a porous outer layer of $\beta$-SiAlION. $\beta$-SiAlIONs also decomposed at this temperature but its extent was more limited showing that they were more stable than O-SiAlIONs at high temperatures.

3.5 Summary
The traditional route employed to produce SiAlIONs involves Si$_3$N$_4$ as a starting powder, but the chemical process required to obtain this powder is expensive. Therefore alternative routes that do not require this powder have been developed to produce SiAlIONs. The effects of additives on the nitridation of Si in SiAlION compositions produced by reaction bonding and silicothermal reduction
routes was different from the effects of such additives on the nitridation of pure Si powder. Some of the additives reacted with mullite to enhance the formation of SiAlONs produced by the silicothermal reduction route. A catalytic effect of rare-earth oxides on the decomposition of mullite appears to occur in the β-SiAlONs but did not take place in O-SiAlON compositions, where SiO$_2$ is present in larger amounts. The amount of SiO$_2$ in the starting mixture played an important role since it greatly influenced the way the nitridation and SiAlON forming reactions evolved. For instance, the quaternary systems created by the combination of additives in O-SiAlONs seemed to have a eutectic temperature lower than the nitriding temperature as they led to more shrinkage and lower open porosity without a significantly different degree of nitridation. Utilising the nitriding enhancing effect of two additives as well as their lower eutectic point, should make it possible to nitride, form and sinter SiAlONs at lower temperatures. However the densification of the pellets before the end of nitridation could hinder the nitridation.

For both routes, the effects of the chosen parameters during the sintering stage were similar although the magnitude of these effects was larger in O-SiAlONs than in β-SiAlONs; sintering aids had the greatest effect on densification and temperature had the largest influence on decomposition. It was possible to select optimised parameters that led to dense materials with minimum decomposition in all samples which provides a basis for further improvement. Since no major difference was observed between the two production routes, most of the further research will be focused on the silicothermal reduction as it presents advantages for the forming of the products due to the plasticity of halloysite. The nitriding schedule employed here, which was inspired from pressureless sintering techniques, were long and required powder beds. In view to broaden the use of such SiAlONs, these schedules must be shortened and simplified, for instance by suppressing the need for powder beds, since it is not yet ideal to transfer such techniques to the industry.

One of the nitriding enhancers, CaO, hindered the nitridation in O-SiAlON since it could form a low eutectic temperature in the CaO-SiO$_2$-Al$_2$O$_3$ ternary system which could lead to simultaneous nitridation and densification. On the other hand, in β-SiAlONs with DyAG, it was not possible to form a eutectic liquid during the nitriding stage, therefore nitridation and densification occurred consecutively. The next chapter studies the influence of nitrogen pressures on the nitridation stage of SiAlONs with various porosities during this stage, such that the possibility of forming and densifying SiAlONs at low temperatures can be investigated.
CHAPTER 4
EFFECTS OF NITROGEN PRESSURE ON THE NITRIDATION OF $\beta$ AND O-SiAlONs

4.1 Introduction

The previous chapter has shown that most of the additives used were efficient at enhancing the nitridation of almost all of the eight different starting mixtures; only CaO had a negative effect on the nitridation of O-SiAlON pellets. Nitrogen pressure, sintering temperature and additives had the same effects on $\beta$ and O-SiAlONs independently of the processing routes used. Besides the following experiments carried out with SiAlONs produced by both reaction bonding and silicothermal reduction routes, the rest of the thesis will essentially deal with SiAlONs produced by the silicothermal reduction route since this method presents, in addition to being a less expensive alternative to $\text{Si}_3\text{N}_4$, the advantages of the halloysite clay in terms of forming.

This chapter investigates the relationship between the nitridation and the pore closure, or densification, during the nitridation stage. Several SiAlON compositions which were susceptible to have different porosities were nitrided: $\beta$-SiAlONs that should not densify during the nitridation and O-SiAlONs that were expected to do so. Since the effects of CaO on the nitridation were thought to be due to the formation of a low temperature eutectic liquid, O-SiAlON compositions with $x=0.05$, where these effects were limited (for an addition of 2 mol%), were compared to O-SiAlON compositions with $x=0.2$, where the same addition had a drastic influence on the extent of the nitridation reaction due to the larger amount of $\text{Al}_2\text{O}_3$. The purpose of this chapter is to demonstrate that low nitrogen overpressures, typically 0.4-1.0 MPa, are sufficient to significantly improve the extent of the nitridation reaction such that a mild pore closure does not impede the overall reaction. This would also
justify the use of nitrogen overpressure as an alternative to additives to enhance the nitridation of SiAlON which would have the advantage to limit the amount of additive to the minimum required to densify the material.

4.2 Initial observations of the effects of powder bed and processing steps on the nitridation and sintering of SiAlONs

The experimentation plan designed in Chapter 3 consisted of studying 4 factors – temperature, nitrogen pressure, nitriding enhancers and sintering additives – each at 3 different levels while all the other factors were arbitrarily determined and kept constant. This section investigates the influence of those other parameters in order to further enhance formation and sintering of SiAlONs. The effect of the immediate environment, the nitriding schedule and the different processes will be discussed.

4.2.1 Effects of powder bed

In the previous chapter, SiAlONs were fired in a BN crucible and covered by a powder bed of a composition similar to that of the sample, e.g. a β-SiAlON powder bed was used for the β-SiAlON samples. This section investigates the effects of the presence of powder bed during consecutive nitriding and sintering of β and O-SiAlONs produced under 0.4 MPa by both reaction bonding and silicothermal reduction as described in Section 3.3.

Powder beds and nitrogen pressures have been used to reduce the decomposition of SiAlONs and Si$_3$N$_4$ [42, 88, 94] at elevated sintering temperatures. However previous results (see Section 3.4.2) have shown that nitrogen pressures did not have a significant influence on the decomposition in the presence of a powder bed, which may have actually hindered the effect of the gas pressure by modifying the local partial pressure at the surface of the samples. For the same reason, the powder bed may also have an influence on the nitridation. All the samples in this experiment were nitrided under 0.4 MPa without additives following the heating schedule described in Figure 3.3.

4.2.1.1 Effects of powder bed on the nitridation

The degrees of nitridation of SiAlONs nitrided in BN crucibles with and without powder bed are shown in Figure 4.1. Pellets nitrided without powder bed systematically achieved a higher degree of nitridation than the ones nitrided with a powder bed regardless of the composition of the SiAlON. Typically, powder beds are used to minimise depletion of Si and O from SiAlONs during pressureless sintering. However, powder beds actually hindered nitridation as they made the access of nitrogen to the sample more difficult.
Effects of N\textsubscript{2} pressure on the nitridation of β and O-SiAlONs

4.2.1.2 Effects of powder bed on the composition after nitridation

The XRD patterns of β-SiAlON (z=1) prepared by reaction bonding under 0.4 MPa with and without powder bed are presented in Figure 4.2. The two samples had similar patterns and contained crystalline phases of α and β-Si\textsubscript{3}N\textsubscript{4} (with α dominant) as well as Al\textsubscript{2}O\textsubscript{3} and AlN which composed the original mixture.

![Figure 4.2: Influence of powder bed on the nitridation of β-SiAlON (z=1) prepared by reaction bonding. JCPDF file numbers are given in Appendix C.](image)

The major difference between these samples was the amount of remaining Si, which was consistent with the calculated degree of nitridation. Indeed the sample with the lowest amount of remaining Si was the one that displayed the highest degree of nitridation. Besides differences in phase structure due to the different starting mixtures, similar results were observed in β and O-SiAlONs with high and low levels of substitution and produced by either reaction bonding or silicothermal reduction routes. Under 0.4 MPa of nitrogen pressure, nitridation was clearly hindered by the presence of powder bed.
4.2.1.3 Effects of powder bed on mass losses at sintering temperature

The samples nitrided in the previous section were fired following the sintering schedule described in Figure 3.4 at 1800°C under 0.4 MPa of nitrogen pressure. Figure 4.3 shows the mass loss of samples sintered with and without powder bed.

![Figure 4.3: Influence of powder bed on mass losses in β and O-SiAlONs after 2 h at 1800°C. Note that this figure shows the result of single measurements.](image)

When SiAlONs are fully formed, they are susceptible to decompose at the sintering temperatures and powder beds are often used to try and reduce or eliminate this decomposition [42]. This section focuses on the effect of powder bed on the overall process of production of SiAlON. The mass losses represented in Figure 4.3 are the mass losses of SiAlONs occurring between the nitriding and the end of the sintering stage. It should be noted that these are samples that were made from identical compositions and then sintered with and without powder beds following the nitridation step. Powder beds were shown to hinder nitridation (see Section 4.2.1.1), which means that the samples already had a difference in their phase composition before the sintering was carried out. The effects of powder bed that are investigated here are therefore not solely on the decomposition of SiAlONs. The reported mass losses can have two origins, one being the decomposition of a SiAlON phase and the other being the loss of any un-nitrided Si at high temperatures.

Powder beds are typically used to limit mass losses under pressureless sintering. However when powder beds were used in consecutive nitriding and sintering under nitrogen overpressures, they had the opposite effect. The smallest mass losses were observed when no powder bed was used. This effect was actually more significant than it appears in Figure 4.3 since all of the samples had lower degrees of nitridation under powder bed, and that some samples – B21, O2.05, O3.05 and O2.2 (see Figure 3.13 to Figure 3.17) – still had significant amounts of Si after the nitridation step in comparison to the samples nitrided without powder bed. This remaining Si, if not lost by evaporation, was likely to pick
up N\textsubscript{2} during the sintering stage, leading to a mass increase which virtually compensated the mass loss measured for these samples (due to decomposition of a SiAlON phase and to the loss of un-nitrided Si). Considering that the samples with lower degrees of nitridation and higher amounts of remaining Si after the nitridation stage (i.e. SiAlONs nitrided under powder beds) already displayed similar or higher mass losses than the samples sintered without powder beds, it is clear that the mass losses were reduced when only nitrogen overpressure was used, i.e. without powder beds.

In summary, Figure 4.3 shows that without powder bed, β-SiAlONs did not suffer mass losses while O-SiAlONs had great mass losses. This highlights the difference of stability at high temperature between β and O-SiAlONs which will be discussed later in Section 6.4.

### 4.2.1.4 Effects of powder bed on the composition after sintering

Figure 4.4 shows the XRD patterns of β and O-SiAlONs with respectively z=4 and x=0.2 both prepared by reaction bonding and subsequently sintered at 1800°C with and without powder bed. These patterns were representative of samples prepared by both silicothermal and reaction bonding routes. Figure 4.5 shows how the different phases detected by XRD analysis can be formed on a SiAlON behaviour diagram.

![XRD patterns of β and O-SiAlONs](image)

Figure 4.4: Influence of powder bed on the sintering of β-SiAlON (z=4) and O-SiAlONs (x=0.2) prepared by reaction bonding. JCPDF file numbers are given in Appendix C.

For β-SiAlONs sintered in the absence of powder bed, mass losses were negligible (see Figure 4.3) and all the samples were composed of a single β-SiAlON phase. The level of substitution of these samples, calculated according to Ekström’s method [110], was close to the targeted value. In β-SiAlONs (aimed
at z=1 and 4) fired under powder bed, the z values were lower than the targeted values. Although the powder bed had no other influence on the final composition of β-SiAlON (z=1), minor phases of 8H and 15R AlN-polytypes were observed by XRD in β-SiAlON (z=4) sintered under powder bed (Figure 4.4). In β-SiAlON (z=4) fired under powder bed, which had higher mass losses than the ones sintered without powder bed (see Figure 4.3), AlN-polytype phases could be formed following a loss of SiO as shown in Figure 4.5. Since the compositions targeted at z=4 were close to the highest level of substitution that can be achieved in β-SiAlONs, the loss of SiO led to an excess of AlN that could not be incorporated into the SiAlON structure and therefore AlN-rich phases, such as 8H and 15R AlN-polytypes, could be formed.

Figure 4.5: Influence of mass losses on the composition of β and O-SiAlONs shown on the SiAlON behaviour diagram at 1700°C [8].

O-SiAlON compositions were comprised of a major O-SiAlON phase and of a minor β-Si₃N₄ phase as shown in Figure 4.4. This phase assemblage was similar for both levels of substitution and both processing routes. However X-SiAlON was detected in compositions targeted at x=0.2 while it was not present in the ones targeted at x=0.05. X-SiAlON is a Al₂O₃-rich SiAlON and its presence was probably due to the fact that x=0.2 is close to the highest level of substitution that can be achieved in O-SiAlONs. The loss of Si during the nitridation provoked a deviation from the intended stoichiometry, therefore Al₂O₃ could not be incorporated in the O-SiAlON structure which led to the formation of this Al₂O₃-rich SiAlON as shown in Figure 4.5. This minor phase was present in both O-SiAlON x=0.2 sintered with and without powder bed whereas X-SiAlON was not detected in the O-SiAlONs targeted at x=0.05. Indeed this composition, which is not located at the limit of solubility of Al₂O₃ into O-SiAlON, could incorporate the excess of Al₂O₃. The compositions sintered with a powder bed possessed a higher relative amount of β-Si₃N₄ (see Figure 4.4) than the ones sintered without powder bed, indicating that the loss of SiO from O-SiAlONs led to the formation of β-SiAlON/β-Si₃N₄ as shown in Figure 4.5.
In contrast to pressureless methods, powder beds are not required to limit decomposition and form single phase SiAlONs under 0.4 MPa of nitrogen pressure. They actually hinder the effect of nitrogen pressure as they lead to higher decomposition.

4.2.1.5 Conclusions
The study of the effect of the environment on the nitridation and sintering of β and O-SiAlONs has led to the following conclusions:

• Under 0.4 MPa of nitrogen pressure, both β and O-SiAlONs have shown higher degrees of nitridation and lower mass losses when nitrided without a powder bed.
• None of the β-SiAlONs showed any decomposition during the sintering stage when sintered without powder bed. They were also fully converted to a single β-SiAlON phase with a level of substitution close to the targeted value.
• In β-SiAlONs that showed decomposition (those sintered under a powder bed), the presence of minor phases rich in AlN suggests that the mass lost from the samples was due to volatilisation of SiO.
• All O-SiAlON compositions have shown mass losses and contained a minor phase of β-Si$_3$N$_4$ at 1800°C. Furthermore the samples that had the lowest mass losses also had the smallest amount of β-Si$_3$N$_4$ suggesting that mass losses are associated with evaporation of SiO.
• For O-SiAlONs targeted at $x=0.2$ which is close to the highest level of substitution achievable at this sintering temperature [30], the loss of Si during nitridation caused a deviation from the intended stoichiometry leading to an excess of Al$_2$O$_3$ which could not be incorporated into the O-SiAlON structure. This led to the formation of a minor phase of X-SiAlON, a Al$_2$O$_3$-rich SiAlON. In O-SiAlONs targeted at lower level of substitution, i.e. $x=0.05$, it was still possible to incorporate this extra Al$_2$O$_3$, and therefore no X-SiAlON was formed.

4.2.2 Determination of a new nitriding schedule
The extent of the nitridation reaction was relatively low in most of the SiAlONs nitrided so far. The absence of powder bed has already been shown to enhance nitridation, and since it presents an obvious advantage not to use powder beds, all new heating schedules were carried out without it. This section investigates the evolution of nitridation in different conditions and materials in order to develop a new nitriding schedule that will further improve the nitridation.
The purpose of the nitridation step is to nitride as much Si as possible and to start forming SiAlONs. In order to know how to modify the current nitriding schedule, a series of thermogravimetric analysis (TGA) were carried out.

4.2.2.1 Stepwise nitridation of pure Si

Figure 4.6 shows the TGA of a pure Si powder under flowing nitrogen. In pure Si, mass change is directly related to the nitridation hence the mass change has been converted to degree of nitridation. The nitriding schedule was the same as described in Figure 3.3, however the nitridation was carried out without powder bed and under flowing nitrogen instead of static nitrogen pressure.

![Figure 4.6: Evolution of the degree of nitridation in a Si powder nitrided under flowing nitrogen gas.](image)

A rapid and substantial mass gain was observed in the first hours of each hold, at 1250°C and 1350°C. When temperature was held for longer, the rate at which the nitridation increased decreased significantly. For instance, when the temperature reached 1350°C, the degree of nitridation was 17.5%. In the following 3 h at 1350°C, it increased up to 81.9%, but during the last 3 h of the hold, the increase was only 5.7% to achieve a final degree of nitridation of 87.6%. The experiment was repeated with an increase to 1400°C after the hold at 1350°C and it showed that it was possible to achieve full nitridation and therefore that the nitridation reaction was indeed not complete after the hold at 1350°C (see Appendix E).

Based on these observations, another heating profile was developed: the hold at 1350°C was shortened to 3 h and an extra step of 3 h at 1400°C was added. Figure 4.7 shows the evolution of the nitridation in a Si pellet lightly pressed (about 8 MPa) with this new profile. Up until the end of the 3 h at 1350°C, the heating schedule was the same as used previously. At this point, the degree of nitridation in the Si powder (81.9%, Figure 4.6) was higher than in the pellet (56.6%, Figure 4.7). However after a short time at 1400°C, the nitridation was completed in the pellet. It should therefore be possible to enhance...
the nitridation by increasing the temperature of the final hold. A 6-h hold at 1400°C was not necessary to nitride all the Si, hence a 3-h hold will be used instead so the overall time of the nitriding schedule remains similar to the one used previously in Chapter 3.

![Figure 4.7: Evolution of the degree of nitridation in a Si pellet nitrided under flowing nitrogen gas with a shorter hold at 1350°C.](image)

4.2.2.2 Halloysite behaviour

It has been shown that water has an influence on the nitridation [62]. Consequently, SiAlONs were heated up to 1000°C under vacuum before nitrogen gas was introduced. However, the nitridation actually begins below 1000°C, at about 840°C as shown in Figure 4.6 and Figure 4.7. In order to determine how early nitrogen gas can be introduced, a TGA was carried out on halloysite powder and is shown in Figure 4.8.

![Figure 4.8: Water losses in a halloysite powder.](image)

As reported in literature [67], the loss of adsorbed water was observed at about 150°C and the loss of the constitution water occurred between 450°C and 600°C. Above 800°C, there were no more mass
changes in the halloysite and all the water was considered eliminated. It was therefore not necessary to heat up under vacuum until 1000°C. Nitrogen gas can already be introduced at 800°C.

4.2.2.3 Example of nitridation of a SiAlON powder containing halloysite
Si is only one of the constituents used to form SiAlONs and therefore its nitridation may be influenced by the other surrounding powders. The TGA shown in Figure 4.9 has been carried out on a powder designed to produce a β-SiAlON (z=1) by silicothermal reduction. The water loss characteristic of the halloysite was observed at temperatures below 600°C. The mass gain above this temperature corresponds to the nitridation of Si. The steps observed in Figure 4.6, even though still identifiable here, did not have the same shape: at each dwelling time, 1250°C and 1350°C, instead of having a fast mass gain followed by a slightly increasing plateau, there was a more constant rate of mass gain. This led to higher degrees of nitridation at low temperatures than in the Si powder, and to a slightly higher final degree of nitridation (87.6% and 93.5% respectively in Figure 4.6 and Figure 4.9). The experiment was repeated with an increase to 1400°C after the hold at 1350°C but, in contrast to pure Si, it was not possible to achieve full nitridation in the β-SiAlON powder (see Appendix E). This illustrates the difference between the nitridation of pure Si, where full nitridation could be achieved at 1400°C, and that of a SiAlON mixture, where the Si can potentially react with SiO₂ and be lost as gaseous SiO before it can be nitrided. A shorter dwelling time at 1350°C (which should reduce mass losses) followed by a hold at a higher temperature of 1400°C (which should enhance the nitridation reaction) may lead to overall higher degrees of nitridation in nitriding more Si before it can be lost by volatilisation.

![Figure 4.9: Evolution of the nitridation of Si in a β-SiAlON powder under flowing nitrogen.](image)

4.2.2.4 Conclusions
The study of the evolution of nitridation and mass changes in Si and SiAlONs powders and pellets has led to the following conclusions:
The final holding temperature used in the nitriding schedule employed in Chapter 3, 1350°C, was too low to achieve full nitridation for all SiAlONs. 3 h at this temperature were sufficient to complete the main nitrogen pick up and longer times were not beneficial since after 3 h the nitridation reaction became sluggish. The last 3 hours of the nitriding schedule can therefore be carried out at a higher temperature, nonetheless still below the melting point of Si.

The nitrogen pick-up did not occur at a constant rate for a set temperature. Consequently the nitriding schedule can be planned stepwise: the temperature can be increased after the main nitrogen pick up has occurred at a given temperature. Carrying out the last 3 h of the heating schedule at 1400°C instead of 1350°C was sufficient to complete the nitridation in Si pellets.

Heating under vacuum until 800°C was sufficient to make sure that any water had been removed from the samples before the beginning of the nitridation.

A new nitriding schedule, that will be used in future experiments, has been designed to improve the nitridation and is shown in Figure 4.10.

![Figure 4.10: New heating schedule and nitrogen pressure profile of the nitridation stage.](image)

Degrees of nitridation achieved in Si powders were higher than in Si pellets after the hold at 1350°C. However the increase to 1400°C led to full nitridation in both cases. The influence of the time when the pellets are pressed, i.e. before or after nitridation, is investigated in the following section for several SiAlION mixtures.

### 4.2.3 Effects of processing steps

Nitridation occurred more readily in Si powders than in pellets up to 1350°C under flowing nitrogen due to an easier access to N\(_2\) (i.e. loosely packed material and greater surface area), indicating that it may be of interest to nitride powders before pressing them. However, higher nitriding temperatures still led to full nitridation in both cases under flowing nitrogen. Nitrogen overpressure might have a
different influence on the nitridation behaviour because overpressure can help N$_2$ penetrate the packed material and provide more N$_2$ to the reaction site more quickly. A comparison of the two methods (i.e. nitriding the SiAlON powders before or after they have been pressed) has been conducted on 8 SiAlON mixtures under the nitriding schedule described in Figure 4.10 to establish which process should be used in future experiments.

SiAlONs have been produced, as described in Section 3.3, according to the following process: powders were prepared then pressed into pellets, nitrided and finally sintered. A single firing schedule presents the advantages of saving the cooling down time after the nitridation and all the preparation of the furnace before sintering, which includes the time to make the vacuum in the furnace. In Chapter 3, nitriding and sintering were carried out separately to observe SiAlONs after nitridation; otherwise they would have been realised consecutively in a single step. This method may however present a drawback in the case of thick products since the core of the product may be more difficult to nitride.

The alternative method consists of nitriding the loose powder first, then to press and sinter it. Although this method may facilitate nitridation, it will not allow to benefit from the properties of the raw materials regarding the forming of the products, e.g. halloysite clay will have been decomposed into mullite and SiO$_2$. It also requires two distinct firing schedules making the overall process much longer.

These two methods have been carried out to produce SiAlON pellets (ø12 mm x 5 mm) from 8 mixtures – 4 β and 4 O-SiAlONs (see Table 3.4). The experimental plan conducted in Chapter 3 showed that the combination of additives achieving the best results in terms of densification and decomposition was 2 mol% of CaO plus 2 mol% of DyAG or YAG. β and O-SiAlONs have therefore been nitrided and sintered with an addition of 2 mol% of CaO plus 2 mol% of YAG in β-SiAlON and with an addition of 2 mol% of CaO plus 2 mol% of DyAG in O-SiAlON.

4.2.3.1 Influence of the nitriding schedule and processing steps on the nitridation

The degree of nitridation of SiAlONs nitrided as pellets and as powders under the nitriding schedule described in Figure 4.10 is shown in Figure 4.11. In order to observe the efficiency of the new nitriding schedule, results obtained in Chapter 3 are plotted on the same figure. Figure 4.12 and Figure 4.13 give additional information about the differences between the two nitriding schedules in terms of densification during the nitridation.
Effects of $N_2$ pressure on the nitridation of $\beta$ and O-SiAlONs

SiAlONs nitrided with the new schedule achieved similar or higher degrees of nitridation than the ones nitrided with the schedule described in Chapter 3 as shown in Figure 4.11. Figure 4.12 shows that after both nitriding schedules, $\beta$-SiAlONs did not have a significant shrinkage. Therefore, the slightly higher bulk densities and lower open porosities observed in $\beta$-SiAlONs in Figure 4.13 could be attributed to the slightly higher degrees of nitridation. Indeed the extra nitrogen picked up filled up the pore structure (conversion from Si to $Si_3N_4$ is accompanied with a volume expansion which is almost entirely accommodated within the pore structure [62]) and led to higher bulk densities.

O-SiAlONs nitrided with the new schedule had a greater shrinkage and achieved higher bulk densities and lower open porosities than the ones nitrided as in Chapter 3, as shown in Figure 4.12 and Figure 4.13 respectively. This cannot be only explained by the increase in nitridation since such an increase
should have led to the same slight differences in bulk densities and open porosities as observed in β-
SiAlONs.

Figure 4.13: Influence of the nitriding schedule on the densification during nitridation of β-SiAlONs
with 2 mol% of CaO and YAG, and of O-SiAlONs with 2 mol% of CaO and DyAG.

The main difference between the two schedules was the temperature of the last 3 h which was 50°C
higher in the new schedule. At this higher temperature, the liquid phase was less viscous, helping grain
rearrangement and therefore enhancing densification. However this densification was not observed in
β-SiAlONs. Although a liquid phase may be formed in those systems, it may have a higher viscosity at
this temperature due to the lower content of SiO2 in β-SiAlONs when compared with the O-SiAlONs.
The formation of these liquid phases and the difference between O and β-SiAlONs will be discussed in
Chapter 5.

Typically, the new nitriding schedule only slightly enhanced nitridation in all SiAlONs nitrided as
pellets. Its effect on β-SiAlONs was therefore limited. However it had a major effect on O-SiAlONs
since the higher temperature resulted in a less viscous liquid phase which greatly enhanced
densification.

In general, higher degrees of nitridation were obtained when SiAlONs were sintered as powders rather
than as pellets as seen in Figure 4.11. However the difference between β-SiAlONs nitrided as pellets
and as powders was rather small (around 5%) whereas the difference in O-SiAlONs was larger
(between 10% and 50%). Two main differences were expected to lead to higher degrees of nitridation
in powders than in pellets: the higher surface area of the powders and their loose packing make them
more prone to react with N2. Figure 4.12 and Figure 4.13 show that β-SiAlON pellets did not densify
during nitridation (shrinkage was below 1.5%) and that the open porosity remained large throughout
the nitridation (still above 25% at the end of nitridation). In this case, the penetration of nitrogen in the
Effects of N$_2$ pressure on the nitridation of β and O-SiAlONs

pellet was not impeded and nitrogen was able to diffuse into the pellet and react with Si. The long dwelling times used in the nitriding schedule did not allow observation of whether the time to nitride SiAlON was actually shorter in the powder. The O-SiAlON pellets densified much more than the β-SiAlON pellets as shown in Figure 4.12 and Figure 4.13. Their open porosity dropped below 15% which impeded the diffusion of nitrogen, leading to lower degrees of nitridation in the pellets than in the powders. In O-SiAlONs O3.2, the difference of degree of nitridation between the pellet and the powder (see Figure 4.11) was remarkable. These pellets had a very low open porosity (approximately 2.5%) which contributed to isolating Si from N$_2$ and led to the low degree of nitridation.

In summary, the difference between the nitridation of pellets and powders was more significant in the O-SiAlONs than in β-SiAlONs. This feature will be used in a later section to observe the effect of nitrogen pressure on SiAlONs with various porosities during the nitridation.

4.2.3.2 Influence of processing steps on the densification and phase composition

Both sets of samples were pressed under the same 200 MPa pressure and they had similar green density. However the samples nitrided as pellets had a higher density before sintering than those nitrided as powders since the N$_2$ that reacted with Si contributed to filling their porosity during the nitridation stage. These SiAlONs nitrided as pellets and as powder were sintered at 1600°C for 4 h under 0.4 MPa of nitrogen. Figure 4.14 shows their bulk density and open porosity. In general, the SiAlONs nitrided as pellets led to higher bulk densities and lower open porosities than the ones nitrided as powders and pressed afterwards. This is thought to be due to the fact that the porosity in the samples nitrided as pellets had been partially filled by Si$_3$N$_4$ formed from the reaction of Si and N$_2$.

![Figure 4.14: Influence of the process on the densification of β-SiAlONs with 2 mol% of CaO and YAG, and of O-SiAlONs with 2 mol% of CaO and DyAG sintered at 1600°C for 4 h under 0.4 MPa of nitrogen. Note that this figure shows the result of single measurements.](image-url)
While there were no differences in terms of bulk density between the β-SiAlONs targeted at \(z=4\) (B24 and B34) nitrided as pellets or as powders (Figure 4.14), the β-SiAlONs targeted at \(z=1\) (B21 and B31) and nitrided as pellets achieved higher bulk density than the ones nitrided as powders. None of these SiAlONs densified during nitridation as shown in Figure 4.12, therefore their porosity was only dependent on the amount of \(\text{N}_2\) entering their structure. In β-SiAlONs (\(z=4\)), the amount of Si was small and its nitridation did not eliminate a lot of pores. Conversely, in β-SiAlONs (\(z=1\)), a large amount of Si was present in the starting mixture; when all this Si was nitrided a large part of the porosity was filled by \(\text{Si}_3\text{N}_4\). The difference in bulk density between SiAlONs nitrided as pellets and the ones nitrided as powders was therefore exacerbated in SiAlONs that contained more Si (\(z=1\)), and remained limited for those with small amount of Si (\(z=4\)). There was also a difference between O-SiAlONs nitrided as pellets and as powders, with the samples nitrided as pellets achieving higher bulk density and lower degree of nitridation than the samples nitrided as powders. The amount of Si that was expected to be nitrided was similar in both O-SiAlONs with low and high levels of substitution (see Table 3.6). The difference in bulk density between SiAlONs nitrided as pellets and the ones nitrided as powders observed between β-SiAlONs with high and low levels of substitution was therefore not observed between O-SiAlONs with high and low levels of substitution.

Very low open porosities were obtained for all the β-SiAlONs (typically below 1%) and no differences were observed by XRD analysis in the crystalline phase composition between the two processes. β-SiAlONs (\(z=1\)) were all composed of a single β-SiAlON phase and the ones targeted to \(z=4\) were composed of a major phase of β-SiAlON, minor phases of \(\text{Al}_2\text{O}_3\) and 15R-AlN polytype and traces of YAG. These final compositions were very similar to the ones obtained in Chapter 3 (see Figure 3.18 and Figure 4.4).

O-SiAlONs did not convert to a single O-SiAlON phase. They were composed of a major O-SiAlON phase, a minor phase of either β-\(\text{Si}_3\text{N}_4\) or β-SiAlON with a very low substitution, and traces of \(\text{SiO}_2\). These final compositions were also very similar to the ones obtained previously. The only sample that was not consistent with the other O-SiAlONs was the O3.2 nitrided as pellet in which the two major phases were O-SiAlON and Si. This SiAlON had the greatest shrinkage (see Figure 4.12) and achieved the lowest open porosity (see Figure 4.13) after nitridation. This pellet densified so quickly that it probably isolated Si from the nitrogen atmosphere and left it unreacted.

Pressing SiAlONs into shape prior to nitriding, while not beneficial to nitridation, did not critically hinder it in most compositions such that the same final crystalline phase composition as with SiAlONs nitrided as powders could be achieved after sintering. The only exception was the O-SiAlONs
Effects of $N_2$ pressure on the nitridation of $\beta$ and O-SiAlONs produced by silicothermal reduction route and targeted to $x=0.2$ that had their nitridation significantly hindered due to an early densification. However the nitridation of SiAlONs as pellets enhanced their densification during sintering. This process presented another advantage: the overall shrinkage of $\beta$ and O-SiAlONs shown in Figure 4.15 was smaller (between 7.6% and 13% depending on the starting composition) than when the SiAlONs were pressed after nitridation (between 15% and 18.2%). This was due to the fact that conversion of Si to $Si_3N_4$ eliminates a part of the porosity without external volume change.

![Figure 4.15: Influence of the process on the shrinkage along the diameter of $\beta$-SiAlONs with 2 mol% of CaO and YAG, and of O-SiAlONs with 2 mol% of CaO and DyAG sintered at 1600°C for 4 h under 0.4 MPa of nitrogen. Note that this figure shows the result of single measurements.](image)

4.2.3.3 Conclusions

The nitriding schedule implemented in the previous section has been compared with the one used in Chapter 3. Powder beds were not used with the new schedule and the temperature during the last 3 h was increased by 50°C.

- The nitridation was not significantly improved with the new nitriding schedule. Its effect on $\beta$-SiAlONs was limited, however the higher temperature allowed the O-SiAlONs to densify and achieve higher bulk densities and lower open porosities after nitridation.
- The new nitriding schedule will be used for the next experiments since it gave similar or better results than the previous one, and that it did not require the use of powder beds.

The investigation of the influence of the order of the pressing/nitriding or nitriding/pressing sequence has led to the following conclusions:
• Pressing SiAlONs into shape before nitridation allows the products to achieve higher densities with smaller shrinkages in the subsequent sintering stage, than when they are nitrided as powders (about 10% and 15% on average when nitrided as pellets and as powders respectively).

• Although the nitridation of SiAlON powders generally led to higher degrees of nitridation than the nitridation of pellets, no significant difference in the phase composition have been found after sintering. The crystalline phase assemblage of these SiAlONs was also very similar to the phase assemblage found in the SiAlONs sintered in Chapter 3.

• No remaining Si was detected after sintering in most of the pellets. Even though the nitridation was not completed after the nitriding stage, it could be completed during the higher temperature sintering. This was valid as long as the porosity remained large enough after nitridation to allow nitrogen to diffuse into the pellets. The next sections investigate the possibility of improving nitridation by using higher nitrogen pressures for those compositions that densified at lower temperatures.

4.3 Experimental procedure based on the initial observations

The preliminary experiments have shown that it was possible to nitride and form SiAlONs without powder beds under 0.4 MPa of nitrogen pressure. Furthermore powder beds hindered nitridation and increased mass losses in comparison with the use of nitrogen pressure alone. A nitriding schedule with a higher final temperature was developed to further improve nitridation during this stage. Whereas it only slightly enhanced nitridation, it led to the formation of more dense O-SiAlONs following nitridation. Nitriding products that have already been pressed present a lot of advantages such as being able to regroup nitriding and sintering stages into one firing schedule, to benefit from the properties of the raw materials such as facilitating forming by pressing, slip casting and extrusion, and to obtain products with higher density while having smaller shrinkage. However this method is of interest only if the nitridation can be completed, which may not be possible if the open porosity drops too low too quickly and impedes penetration of N₂ within the pellets. Since nitrogen gas is a reactant, nitrogen pressures can be used to modify the time necessary to complete nitridation and therefore to be able to fully nitride SiAlONs even when they are rapidly densified. This would allow retention of the advantage of early densification (during the nitridation stage) while ensuring that nitridation has been completed.

SiAlONs prepared by silicothermal reduction and with a wide range of porosities were produced in order to investigate the relation between pore closure and nitridation under various nitrogen pressures. The previous section has shown that, under the new nitriding schedule, O-SiAlONs shrunk between
Effects of $N_2$ pressure on the nitridation of $\beta$ and O-SiAlONs

5% and 9% while the $\beta$-SiAlONs did not significantly shrink (below 1.4%). This was thought to be due to the formation of a liquid phase in the quaternary system CaO-Re$_2$O$_3$-SiO$_2$-Al$_2$O$_3$. This liquid phase was still too viscous at the nitriding temperature in $\beta$-SiAlONs because of the low SiO$_2$ content in their starting powder. No information was found on the quaternary systems CaO-Re$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ in the literature, therefore only one additive was employed in the following compositions so the results could be discussed in terms of well-known ternary systems [105, 107].

DyAG, which has been found to enhance nitridation in $\beta$-SiAlONs when added at 2 mol% (see Figure 3.6), has a eutectic point of 1389°C [106] in the Dy$_2$O$_3$-SiO$_2$-Al$_2$O$_3$ system. CaO, which has been found to hinder nitridation in O-SiAlONs when added at 2 mol% (see Figure 3.5), possesses a lower eutectic point, 1170°C [105], in the CaO-SiO$_2$-Al$_2$O$_3$ system. Furthermore, the liquid region in these two systems is located in the SiO$_2$ rich corner of the phase diagram at low temperatures and extends towards its centre at higher temperatures [105-107]. It is therefore possible to form a liquid at lower temperature in compositions containing larger amounts of SiO$_2$ (like in O-SiAlONs) with CaO additions than in compositions containing less SiO$_2$ (like in $\beta$-SiAlONs) with DyAG additions. DyAG and CaO have also been chosen since they had the largest beneficial effect on mass loss, shrinkage and open porosity after sintering respectively for $\beta$ and O-SiAlONs (see Figure 3.19 to Figure 3.21). Consequently, DyAG was added to $\beta$-SiAlONs and CaO was added to O-SiAlONs. Both additives were employed in several amounts (0, 1, 2, 4 and 8 mol%) to observe the effects of nitrogen pressures over a range of compositions that can form increasing amounts of intergranular phase.

These two configurations were used to investigate the effects of nitrogen pressures during the nitridation of pellets for two different cases. One was where nitridation should not be affected by pore closure since it was expected to be completed before the shrinkage began (i.e. $\beta$-SiAlONs with DyAG additions) and the other was pellets that were susceptible to rapidly densify before nitridation was completed (i.e. O-SiAlONs with CaO additions). The experimental procedure was the same as described in Section 3.3 with the exception that the pellets were only nitried and that the nitridation was carried out under the nitriding schedule described in Figure 4.10.
4.4 Results and discussions

This section describes the effects of nitrogen pressures in the two cases where SiAlON pellets prepared by silicothermal reduction do and do not densify during the nitridation. The different amounts of additives allowed gradual alteration of the densification rate so that the minimum open porosity required to reach full nitridation may be identified.

4.4.1 Straightforward nitridation in β-SiAlON

The purpose of this experiment was to investigate the effects of nitrogen pressure on the nitridation of SiAlONs without altering their porosity. In order not to modify the pore closure, an additive, DyAG, was chosen for its high eutectic temperature (1389°C [106]) in the Dy$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ ternary system which is close to the final nitriding temperature of 1400°C. Furthermore, a β-SiAlON (z=1) composition was selected rather than an O-SiAlON composition since only halloysite contained the SiO$_2$ necessary to form the eutectic liquid (β-SiAlON precursor mixture was composed of Si, AlN and halloysite, and was therefore poorer in SiO$_2$ than O-SiAlONs). It was therefore expected that a liquid phase might be formed but it would not help the densification of β-SiAlON during the early stages of the nitridation due to its high viscosity.

4.4.1.1 Effects of nitrogen pressure on β-SiAlONs (z=1) without densification during nitridation

Figure 4.16 shows the effects of DyAG additions on the open porosity and the shrinkage of β-SiAlON (z=1) nitrided under various nitrogen pressures. The additions of DyAG to β-SiAlONs did not have any influence on the open porosity and the shrinkage of the pellets as seen in Figure 4.16 suggesting that if a liquid phase was formed at 1400°C it must have possessed a high viscosity which did not allow primary grain rearrangement. Note that, while there seems to be an effect of DyAG additions on the shrinkage, particularly at 0.1 MPa, there is actually no significant difference between the values measured since the accuracy of the measurement was ±1.6% as detailed in Section 3.4.1.2 and the scale of the vertical axis in Figure 4.16b is ±2%.
Effects of $N_2$ pressure on the nitridation of $\beta$ and O-SiAlONs

Figure 4.16: Influence of DyAG additions on (a) the open porosity and (b) the shrinkage of $\beta$-SiAlONs ($z=1$) nitrided under various nitrogen pressures.

The influence of nitrogen pressures on the nitridation of $\beta$-SiAlONs is presented in Figure 4.17. Regardless of the amount of additives used, the degree of nitridation increased between the $\beta$-SiAlONs nitrided without nitrogen overpressure and under 0.4 MPa indicating that the presence of overpressure clearly had an enhancing effect on the nitridation. However there was no significant difference in the degree of nitridation between the $\beta$-SiAlONs nitrided under nitrogen overpressures (0.4 MPa, 0.7 MPa and 1.0 MPa), suggesting that higher overpressures were not necessary to achieve high degrees of nitridation.

Under both ambient conditions and nitrogen overpressures, there was no remaining Si in the $\beta$-SiAlON samples as shown in Figure 4.18 and Figure 4.19. The difference between 100% nitridation and the measured values (Figure 4.17) can thus be attributed to Si losses by volatilisation. Under ambient conditions, DyAG additions had an enhancing effect on the nitridation and allowed more Si to be nitrided before it was lost. The DyAG additions did not have such an effect under nitrogen overpressures because overpressures allowed full nitridation to be reached in a shorter time than under 0.1 MPa (see Chapter 5). Additives used to enhance nitridation may be of interest in the case of pressureless nitriding, however nitrogen pressures fulfil the same purpose. The amount of additive employed can therefore be reduced to the minimum amount required to densify the material during the final sintering stage.
Figure 4.17: Influence of nitrogen pressure on the nitridation of β-SiAlONs (z=1) with various amounts of DyAG.

While the dimensions of the β-SiAlON pellets did not change, independently of the nitrogen pressure and of the amount of additive (Figure 4.16b), the open porosity decreased (Figure 4.16a) and the degree of nitridation (Figure 4.17) increased with increasing nitrogen pressures. This indicates that the volume expansion associated with the nitridation reaction was entirely accommodated within the pore structure as described by Moulson in reaction bonded Si₃N₄ [62] and that this volume expansion could be used to eliminate pores and increase densification at the nitriding temperatures.

The crystalline phase compositions of β-SiAlONs (z=1) after nitridation under 0.1 MPa and 1.0 MPa of nitrogen with different amounts of DyAG are shown in Figure 4.18 and Figure 4.19 respectively. Note that these figures are intended to illustrate major and minor phases rather than absolute percentages. Under ambient conditions, the pellets were composed of a major β-SiAlON phase and of minor phases of α-Si₃N₄, AlN, O-SiAlON, Al₂O₃ or DyAG. The evolution of the crystalline phases observed in Figure 4.18 suggests that additions of DyAG facilitated the formation of β-SiAlON since α-Si₃N₄, AlN and O-SiAlON phases, present in the samples nitrided without additive, reacted to lead to higher relative amount of β-SiAlON in samples with higher amount of additive. Unreacted Al₂O₃ was always detected after nitridation suggesting that it could not yet be incorporated to the β-SiAlON structure.
Effects of N₂ pressure on the nitridation of β and O-SiAlONs

Figure 4.18: Crystalline phase composition of β-SiAlON (z=1) nitrided under 0.1 MPa of nitrogen with different amounts of DyAG.

Figure 4.19 is representative of the phase assemblage of the β-SiAlONs nitrided under all nitrogen overpressures (i.e. under 0.4, 0.7 and 1.0 MPa). The major difference with the β-SiAlONs nitrided under ambient conditions was that without DyAG the material nitrided under nitrogen overpressures was composed of a major phase of α-Si₃N₄ and of minor phases of β-SiAlON, AlN and O-SiAlON. The addition of 1 mol% of DyAG, sufficient to form a ternary eutectic phase, helped the formation of a major β-SiAlON phase by dissolving α-Si₃N₄, AlN and O-SiAlON and precipitating them into β-SiAlON grains. Higher additions of DyAG led to further dissolution of the α-Si₃N₄ phase which was the only minor phase remaining with 1 mol% of DyAG.

Another difference between the β-SiAlON nitrided under ambient conditions and under nitrogen overpressures was the presence of Al₂O₃. Si was not detected in any of the nitrided materials, however the degrees of nitridation of the β-SiAlON nitrided under 0.1 MPa were about 10 % lower than those
nitrided under overpressure (see Figure 4.17) indicating that more Si had been lost by volatilisation. Due to this loss, the chemical composition of the targeted β-SiAlON was modified and less Si₃N₄ was formed leaving this unreacted phase of Al₂O₃. Under nitrogen overpressures, the degrees of nitridation were higher and the smaller mass losses did not significantly affect the overall composition such that the Al₂O₃ could still be incorporated into the SiAlION structure.

4.4.1.2 Conclusions
The study of the influence of nitrogen pressure on the nitridation and formation of SiAlIONs has led to the following conclusions:

- The amount of DyAG did not have an influence on the densification of the samples at the nitriding temperatures. However the samples containing DyAG had higher β-SiAlON contents (in excess of 80% in mass) than the ones nitrided without additives (25-50%). The final nitridation temperature was very close to the eutectic point in the Dy₂O₃-Al₂O₃-SiO₂ ternary system therefore it is thought that if a liquid phase was formed it could enhance the formation of β-SiAlON through a dissolution/precipitation process but it would be too viscous to favour primary grain rearrangement.

- Higher nitrogen pressures led to higher degrees of nitridation by both enhancing the nitridation reaction and lowering mass losses. The influence of the volatilisation of Si on the final SiAlON composition was therefore reduced and it was possible to obtained a single phase β-SiAlON after the nitridation stage under nitrogen overpressures while it was not achievable under ambient conditions.

4.4.2 Competing nitridation and densification in O-SiAlONs
The O-SiAlON precursor mixture was composed of Si, SiO₂ and halloysite. With the addition of CaO to this powder, it was expected that a eutectic liquid could be formed in the CaO-Al₂O₃-SiO₂ system. The liquidus temperature for this system is the lowest of all the additives used so far, 1170°C [105], and since the nitriding temperature is over 200°C higher than the eutectic temperature, it was thought that in this case, unlike the Dy₂O₃-Al₂O₃-SiO₂ system described previously (see Section 4.4.1), the liquid would have a viscosity sufficiently low as to enhance the densification of O-SiAlON during the early stages of the nitridation. This early densification could lead to pore closure at temperatures below which all of the Si can be nitrided, hence hindering the nitridation by isolating Si from N₂. This section investigates the possibility of using nitrogen pressures to complete nitridation before the pore closure is too advanced.
Two O-SiAlON compositions, one with a low level of substitution (x=0.05) and one with a high level (x=0.2), produced by silicothermal reduction were nitrided with 0, 1, 2, 4, or 8 mol% of CaO under 0.1, 0.4, 0.7 and 1.0 MPa of nitrogen without powder bed in BN crucibles. The O-SiAlONs with x=0.2 contained more Al₂O₃ and SiO₂ in their starting mixture than the O-SiAlONs with x=0.05 and were therefore susceptible to form a greater amount of liquid. This should lead to a faster grain rearrangement and result in a lower porosity. Hence it should be possible to study the influence of the nitrogen pressures on the nitridation of SiAlONs that have a wide range of porosity: O-SiAlONs (x=0.05) should generate less liquid phase and have a moderate densification while O-SiAlONs (x=0.2) should generate greater amounts of liquid and have a quicker densification. In order to emphasise these effects, different amounts of CaO have been added to the starting mixtures to further alter the densification of the pellets during the nitridation stage. Indeed, greater amounts of CaO should increase the amount of liquid phase formed and therefore increase the densification of the SiAlONs.

4.4.2.1 Effects of nitrogen pressure on O-SiAlONs (x=0.05) with a moderate densification during nitridation

Figure 4.20 shows the effects of CaO additions on the porosity and the shrinkage of O-SiAlONs (x=0.05) nitrided under various nitrogen pressures. As expected, increasing amounts of CaO led to the formation of samples with decreasing open porosity and increasing shrinkage. This indicates that the CaO additions successfully enhanced the densification during the nitridation. It is then possible to investigate the influence of nitrogen pressure on the nitridation of SiAlONs that had different open porosity during the nitridation.

![Figure 4.20: Influence of CaO additions on (a) the open porosity and (b) the shrinkage of O-SiAlONs (x=0.05) nitrided under various nitrogen pressures.](image-url)
Typically the O-SiAlONs which had a high densification (for instance O-SiAlONs with 8 mol% CaO) during the sintering achieved a lower degree of nitridation than those that had a low densification (for instance O-SiAlONs without CaO) as shown in Figure 4.21. Therefore the greater the densification during the nitridation stage, the more the nitridation was hindered. The influence of nitrogen pressure on the degree of nitridation of these O-SiAlONs is shown in Figure 4.21. Although the degree of nitridation was still generally lower in O-SiAlONs with high amount of CaO additives than without CaO, the difference between the degree of nitridation of O-SiAlONs with 8 mol% and without CaO was reduced with increasing nitrogen pressures. This suggests that, under nitrogen overpressures, most of the Si was able to react with N$_2$ before the pore closure isolates Si from N$_2$. This was not the case under ambient conditions, and the Si that did not react with N$_2$ was lost (by evaporation upon reacting with SiO$_2$ and/or by melting out of the samples) and/or remained unreacted in the samples.

Under ambient conditions, XRD analysis shows that there was no remaining Si in β and O-SiAlON compositions with low amounts of additive (0 and 1 mol%) as shown in Figure 4.18 and Figure 4.22. This indicates that some Si had been lost but all of the Si remaining in these samples had been nitrided. In O-SiAlONs with higher CaO contents (2 to 8 mol%), the degrees of nitridation were extremely low (below 25%) as these samples both suffered mass losses and contained unreacted Si.

![Figure 4.21: Influence of nitrogen pressure on the nitridation of O-SiAlONs (x=0.05) with various amounts of CaO.](image)

Nitridation is a preliminary stage to the formation of O-SiAlON by silicothermal reduction. Additives may be used to enhance the nitridation, however in large amounts, on top of their detrimental effects on the properties of the final material presented in Section 2.2.1.6, they may have an adverse effect and actually hinder the nitridation due to an early pore closure resulting from the formation of a liquid phase. The formation of SiAlON, which occurs by a dissolution/precipitation mechanism [21], may therefore be influenced by both the amount of Si nitrided, dependent on the nitrogen pressures as
shown previously, and by the amount of liquid phase generated in which the Si\textsubscript{3}N\textsubscript{4} grains can dissolve and precipitate as O-SiAlION.

The crystalline phase compositions of O-SiAlIONs (x=0.05) nitried under 0.1 MPa of nitrogen are shown in Figure 4.22. Without overpressure, the pellets with low additions of CaO (≤ 2 mol% of CaO) were composed of a main phase of O-SiAlION and of minor phases of AlN, SiO\textsubscript{2} (quartz) and carbon. The carbon, not theoretically present in the initial composition, was probably due to a contamination of these specific powder mixtures. The O-SiAlION starting mixture was composed of Si, SiO\textsubscript{2} and halloysite (at 55%, 35% and 10% in mass respectively). With higher amounts of CaO (≥ 4 mol% of CaO), the quartz phase was not detected after nitridation, however two phases, Si and SiO\textsubscript{2} (cristobalite), were identified and the relative amount of O-SiAlION phase decreased from about 65% to 20%. Halloysite was expected to decompose into mullite (2SiO\textsubscript{2}:3Al\textsubscript{2}O\textsubscript{3}) but the latter was not detected. Instead AlN was identified, suggesting that the Al\textsubscript{2}O\textsubscript{3} from the mullite may have reacted, directly or indirectly, with N\textsubscript{2} to form AlN. Without nitrogen overpressure, the early pore closure, caused by the large amount of CaO, isolated the starting mixture in the core of the pellets from N\textsubscript{2}, leading to samples essentially unreacted. Si was not detected in O-SiAlIONs with additions of CaO below 2 mol%, however the calculated degrees of nitridation were low, suggesting that Si had been lost by volatilisation during the nitridation. This also explains the negative values obtained when the mass gain subsequent to the nitridation of Si was smaller than the mass loss.

![Figure 4.22](image_url)

**Figure 4.22:** Crystalline phase composition of O-SiAlON (x=0.05) nitried under 0.1 MPa of nitrogen with different amounts of CaO.

The crystalline phase compositions of O-SiAlION (x=0.05) nitried under 1.0 MPa of nitrogen described in Figure 4.23 are representative of all the O-SiAlIONs (x=0.05) nitried under nitrogen overpressure (i.e. under 0.4 and 0.7 MPa). Under these conditions, the pellets without additive and
with 1 mol% of CaO were composed of two major phases of $\alpha$-Si$_3$N$_4$ and O-SiAlON and of minor phases of $\beta$-Si$_3$N$_4$, SiO$_2$ and AlN. With higher amounts of CaO ($\geq$ 2 mol% of CaO), the composition of these minor phases did not change; however the amount of $\alpha$-Si$_3$N$_4$ decreased, while the O-SiAlON phase formed became the only major crystalline phase. Si was not detected in any of the O-SiAlONs nitrided under nitrogen overpressure suggesting that the Si had been nitrided or lost by evaporation. In this case, the main reaction was the nitridation reaction, however Si must still have been lost by volatilisation since the calculated degrees of nitridation were not equal to 100%.

![Figure 4.23: Crystalline phase composition of O-SiAlON (x=0.05) nitrided under 1.0 MPa of nitrogen with different amounts of CaO.](image)

In O-SiAlONs with 0 or 1 mol% of CaO, the degree of nitridation achieved under 0.1 MPa was lower than under overpressures (see Figure 4.21). Therefore more Si$_3$N$_4$ was formed under overpressures than under ambient conditions. There were no Si$_3$N$_4$ phases detected in these samples formed under 0.1 MPa (Figure 4.22) whereas the O-SiAlON phase was identified, suggesting that the amount of Al$_2$O$_3$ and SiO$_2$ present in the O-SiAlON compositions was sufficient to react with all of the Si$_3$N$_4$ formed during the nitridation stage. Under 1.0 MPa, the same amount of Al$_2$O$_3$ and SiO$_2$ (the initial compositions were identical) was not sufficient to react with the greater amount of Si$_3$N$_4$ formed under overpressures during the same dwelling time, explaining why both O-SiAlON and Si$_3$N$_4$ phases were detected in these samples (Figure 4.23).

In summary, it is thought that, under 0.1 MPa, the nitridation reaction was the limiting reaction while under nitrogen overpressures, the reaction of the Si$_3$N$_4$, Al$_2$O$_3$ and SiO$_2$ was the limiting reaction to the formation of O-SiAlON. Indeed Si$_3$N$_4$ phases were detected in samples with low amounts of CaO (0 and 1 mol%) nitrided under overpressures, which may lead to the formation of the lowest amount of liquid phase and which is probably not enough to dissolve and precipitate the all of the Si$_3$N$_4$ into O-SiAlON. With higher amounts of CaO, a major phase of O-SiAlON was observed with only traces of
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unreacted α and β-Si$_3$N$_4$ suggesting that the amount of liquid phase formed was sufficient to react with all of the Si$_3$N$_4$.

The densification of the pellets increased with the amount of CaO (see Figure 4.20), and the degrees of nitridation decreased (see Figure 4.21) since the access to nitrogen was reduced due to the pore closure. In this experiment, the open porosity varied from about 10 to 25% depending on the amount of additives. The nitrogen overpressures were able to compensate the effect of the pore closure such that nitridation was achieved to almost the same degrees as without significant pore closure. However the lowest open porosity achieved with these O-SiAlON compositions was about 10%, thus an O-SiAlON (x=0.2) composition, for which the open porosity was much lower, was investigated.

4.4.2.2 Effects of nitrogen pressure on O-SiAlONs (x=0.2) with a major densification during nitridation

This O-SiAlON composition was chosen because it has been observed that it tends to result in lower open porosities than the O-SiAlON with x=0.05 (see Figure 3.11). Also after the same isostatic pressing at 200 MPa they achieved higher compactions, about 75% compared to 65% in the O-SiAlONs with x=0.05. They were therefore more challenging to nitride since the access to Si was more difficult due to an early advanced densification that quickly closed the open pores. Figure 4.24 shows the effects of CaO additions on the open porosity and the shrinkage of O-SiAlONs (x=0.2) nitrided under various nitrogen pressures. In a similar manner as with O-SiAlON with x=0.05, increasing amounts of CaO led to the formation of O-SiAlONs (x=0.2) with decreasing open porosity and increasing shrinkage. The range of open porosities investigated with this O-SiAlON composition extends from approximately 15% to as low as 2%. In this case it was therefore possible to study the influence of nitrogen pressure on the nitridation of SiAlONs which underwent a major pore closure.
Figure 4.24: Influence of CaO additions on (a) the open porosity and (b) the shrinkage of O-SiAlONs (x=0.2) nitrided under various nitrogen pressures.

Figure 4.25 shows the nitridation of O-SiAlONs under various nitrogen pressures. In a similar manner as for O-SiAlONs with x=0.05, the degrees of nitridation obtained for O-SiAlON with x=0.2 under 0.1 MPa were lower than the ones achieved under nitrogen overpressures for a given amount of additive. The degree of nitridation also increased with nitrogen pressures for a given amount of additive but this increase was not sufficient to compensate the adverse effect of the pore closure on the nitridation of the pellets which had an open porosity below 10% (i.e. the O-SiAlONs with 2 mol% of CaO or more). The results obtained in Figure 4.21 and Figure 4.25 show that it was possible to nitride SiAlONs as long as their open porosity remained in excess of about 10% during the nitriding stage (see Figure 4.20 and Figure 4.24). Below this value, the nitrogen path was hindered, and it was not possible to complete the nitridation.

Figure 4.25: Influence of nitrogen pressure on the nitridation of O-SiAlONs (x=0.2) with various amounts of CaO.

While the degrees of nitridation increased with nitrogen pressures, the magnitude of the increase was much greater when nitrogen pressures were increased from 0.1 MPa to 0.4 MPa rather than from 0.4
Effects of N$_2$ pressure on the nitridation of $\beta$ and O-SiAlONs

MPa to 1.0 MPa in any of the O-SiAlONs (x=0.05 and x=0.2). Under nitrogen overpressure, O-SiAlONs with x=0.2 (O3.2) did not achieve higher degrees of nitridation than O-SiAlONs with x=0.05 (O3.05). If the nitrogen pick-up was the only phenomenon affecting the mass change, O3.2 should have also achieved lower degrees of nitridation without nitrogen overpressure. However under 0.1 MPa, they achieved higher degrees of nitridation than O3.05. The negative degrees of nitridation revealed that mass was lost from the pellets, and that O3.05 suffered greater mass losses than O3.2. O-SiAlONs (x=0.05) contained more free SiO$_2$ in their starting mixture (22.3 % in mass) than O3.2 (12.7% in mass) for an equivalent amount of Si (76.4% and 81.3% in mass respectively) and were therefore more prone to lose mass by evaporation of SiO according to the following equation:

\[(4.1) \quad \text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO(g)}\]

The nitrogen overpressures reduced this decomposition leading to much higher degrees of nitridation because Si could react with N$_2$ before it reacted according to reaction (4.1). The degree of nitridation increased with nitrogen overpressures but the effect was much smaller than between 0.1 and 0.4 MPa since only the amount of nitrided Si increased.

The O-SiAlONs with x=0.05 were representative of samples where the degree of nitridation remained in excess of 75% under nitrogen overpressures (see Figure 4.21). In the case of O-SiAlONs with x=0.2, the early pore closure prevented pellets with high amounts of CaO (CaO mol% $\geq$ 4) to be properly nitrided (Figure 4.25). Figure 4.26 and Figure 4.27 show the crystalline phase compositions of O-SiAlONs with x=0.2 after nitridation under 0.1 MPa and 1.0 MPa of nitrogen respectively.

Figure 4.26: Crystalline phase composition of O-SiAlON (x=0.2) nitrided under 0.1 MPa of nitrogen with different amounts of CaO.

The crystalline phase compositions of O-SiAlONs (x=0.2) nitrided without overpressure (Figure 4.26) were similar to the O-SiAlON (x=0.05) compositions nitrided under the same conditions (see Figure
4.22) with the exception of the presence of mullite, detected due to the greater initial amount of halloysite. As the amount of CaO was increased, the open porosity decreased and, with high amounts of CaO, the quantity of O-SiAlON formed decreased while the unreacted phases of mullite and Si became predominant. The addition of 1 mol% of CaO was not sufficient to provoke a rapid pore closure and hinder the nitridation while the small volume of liquid phase formed could enhance the formation of O-SiAlON. With CaO in excess of 2 mol%, the open porosities were lower (see Figure 4.24), leading to lower degrees of nitridation (Figure 4.25) and therefore less O-SiAlON was formed. In a similar manner as with O-SiAlON (x=0.05), the early pore closure, caused by the large amount of CaO, isolated the starting mixture in the core of the pellets from N\textsubscript{2}, leading to samples essentially unreacted.

![Figure 4.27](image.png)

**Figure 4.27:** Crystalline phase composition of O-SiAlON (x=0.2) nitrided under 1.0 MPa of nitrogen with different amounts of CaO.

The crystalline phase compositions of O-SiAlON (x=0.2) nitrided under 1.0 MPa of nitrogen described in Figure 4.27 are representative of all the O-SiAlONs (x=0.2) nitrided under nitrogen overpressure (i.e. under 0.4 and 0.7 MPa). From 0 to 2 mol% of CaO, the crystalline phase compositions were similar to that observed with O-SiAlON (x=0.05) (see Figure 4.23). Even though the degree of nitridation was lower with 2 mol% CaO than with less CaO, it was still around 70% (depending on the nitrogen overpressure, see Figure 4.25), and the composition of the pellet after nitridation was not significantly affected by the pore closure. With additions of CaO in excess of 4 mol%, the degrees of nitridation were much lower (below 55%, see Figure 4.25), unreacted Si was detected by XRD analysis and less O-SiAlON phase could be formed.

In both O-SiAlONs (with x=0.05 and 0.2) nitrided under 0.1 MPa of nitrogen, the optimal addition of CaO was 1 mol% since it led to the highest relative amount of O-SiAlON. Indeed the addition of CaO generated a liquid phase that enhanced the formation of O-SiAlON but also accelerated the pore
Effects of N\textsubscript{2} pressure on the nitridation of β and O-SiAlONs

closure. High amounts of O-SiAlON could not be achieved in the absence of CaO (due to the lack of liquid phase) while an excess of CaO (≥ 2 mol%) was detrimental to nitridation hence to the formation of O-SiAlON (due to the pore closure). Nitrogen overpressure shifted this optimum addition to 2 mol%. Almost all the pellets could be fully nitrided, and the greater amounts of liquid phase enhanced the formation of O-SiAlON as long as they did not lead to critically low open porosities (below 5%).

4.4.2.3 Conclusions

The study of the influence of nitrogen pressure on the nitridation and formation of SiAlONs designed to have different open porosities during the nitridation has led to the following conclusions:

- During the nitridation of SiAlONs, Si either reacted with N\textsubscript{2} to form a Si\textsubscript{3}N\textsubscript{4} or a Si\textsubscript{2}ON\textsubscript{2} phase or was lost by volatilisation. In comparison with ambient conditions, nitrogen overpressures greatly reduced the losses of Si since less time was required for nitridation. Higher nitrogen overpressures further enhanced the nitridation however the effect was not as great as between ambient pressure and the lowest overpressure.

- Without nitrogen overpressure, the nitridation reaction was the limiting reaction to the formation of O-SiAlON. With nitrogen overpressure the nitridation reaction occurred more readily and O-SiAlON could be formed providing there was a sufficient amount of liquid phase. In both cases, if the amount of liquid phase was too great, the amount of N\textsubscript{2} penetrating the pellets and reacting was not sufficient to complete the nitridation before the open porosity was closed, and therefore the pellets remained mainly composed of the unreacted initial components, with the exception of the high temperature transformations of such components (e.g. halloysite to mullite and quartz to cristobalite).

- Nitrogen overpressures reduced the influence of the pore closure during nitridation as long as the open porosity remained above 10% as shown in Figure 4.28. Below this value, the nitridation could not be completed and the detrimental effect of the pore closure could not be compensated with lower open porosity leading to a lower degree of nitridation.
Figure 4.28: Summary of the influence of the porosity on the nitridation of $\beta$ and O-SiAlONS with 0 mol% to 8 mol% (indicated on the graph) of DyAG or CaO respectively under nitrogen overpressures. Each data point is the average of the degree of nitridation and open porosity obtained for a given composition under all 3 nitrogen overpressures.

4.5 Summary

SiAlONS were first nitrided and sintered using the conventional method of powder beds to protect SiAlONS from decomposition during pressureless sintering. To produce SiAlONS by either reaction bonding or silicothermal reduction routes during a single firing schedule, powder beds were covering the green samples before the beginning of the nitridation. Since the powder beds were modifying the local environment around the pellets, they also hindered the beneficial effects (higher degrees of nitridation and lower mass losses) of nitrogen pressures on the nitridation. While the loss of Si by volatilisation did not have a significant influence on SiAlONS with a low level of substitution, the same loss of Si in SiAlONS with a high level of substitution (close to the limit of solubility of Al and O into the $\text{Si}_3\text{N}_4$ structure), which led to a lack of $\text{Si}_3\text{N}_4$, had a major influence on the final crystalline compositions since X-SiAlON and AlN-polytypes phases were formed along with SiAlON. The long time required to nitride Si at 1350°C was one of the reasons for its depletion from the samples since Si could react with $\text{SiO}_2$ to form SiO gas at this temperature. In order to reduce this phenomenon and improve the nitridation of SiAlONS, the temperature of the final 3 h of the nitridation stage was raised to 1400°C and powder beds were not used. Under these new conditions, SiAlONS were nitrided as powders and as pellets. While the nitridation was improved when SiAlONS were sintered as powders, there were no differences with the SiAlONS nitrided as pellets in the final, sintered, material. Since pressing the powders before nitriding presents many advantages such as utilising the plasticity of halloysite during the forming, the use of a single firing schedule or the reduced shrinkage, this method was employed for the remaining experiments.
Although the nitridation was only slightly improved with the new nitriding schedule, the higher temperature allowed the O-SiAlONs to densify and achieve higher bulk densities and lower open porosities after nitridation. This feature was used to produce SiAlONs with a wide range of open porosities (2% to 25%) during the nitridation. Nitrogen overpressure had a crucial effect on the nitridation, with the degrees of nitridation with overpressure being higher since the pressure both enhanced the nitridation and reduced the volatilisation of Si. While the pore closure had a great effect on SiAlONs sintered under ambient conditions, this effect was significantly reduced under overpressures as long as the open porosity did not drop below 10%. When the open porosity was below this value, the access of N\textsubscript{2} was impeded and the core of the pellets remained unreacted. The additives used to alter the porosity through the formation of a liquid phase, also enhanced the formation of SiAlONs.

Nitrogen overpressures have been shown to have a great influence on the nitridation and on the volatilisation of Si in comparison with ambient conditions. Since N\textsubscript{2} is a reactant in the nitridation and formation of SiAlON, nitrogen overpressures may have other effects on the final material other than increasing their degree of nitridation. Indeed, the time to nitride Si was reduced with nitrogen overpressures, therefore the shorter nitridation reaction may alter the formation and the growth of Si\textsubscript{3}N\textsubscript{4} grains, which are expected to react and form the final material. Ultimately nitrogen pressures are therefore susceptible to have an influence on the composition and microstructure of the final material.
CHAPTER 5
REACTION SEQUENCES OF FORMATION OF β AND O-SiAlONs

5.1 Introduction
Research has generally been aimed at finding additives suitable for promoting nitridation of Si to produce SiAlON. These additives are commonly designed to enhance nitridation by lowering the temperature of nitrogen pick-up and increasing the amount of converted Si at a given temperature. This method is relevant when the facilities do not allow to modify other parameters, for instance in the case of a furnace designed for pressureless sintering. The relatively little interest given in literature to the two processing routes used in this work is due to the very long time required to fully nitride and form SiAlONs. In the previous chapters, the nitriding schedule used was 15-h long, cooling down time excluded, and included a total dwelling time of 9 h at different temperatures.

Gas pressure furnaces are mainly used to benefit from the effects of gas pressure in order to sinter SiAlON at high temperatures, typically above 1800°C, without decomposition. However they could be of great interest at lower temperatures to enhance nitridation and formation of SiAlON phases formed by reaction bonding and silicothermal reduction routes. Indeed the effects of additives on nitridation under pressureless sintering are rather limited, or require a great quantity of additive which in turn is not optimal due to the large amount of intergranular phase that would be generated. On the other hand the effects of even small amounts of additives on the sintering stage are not negligible since they allow to densify the material at lower temperatures.
Since nitrogen gas is a reactant in SiAlONs produced by either reaction bonding or silicothermal reduction routes, overpressures are of importance not only at high temperatures to limit decomposition but also at lower temperatures during their formation. Therefore this chapter investigates the possibility of using gas pressure to promote conversion of Si to Si$_3$N$_4$ with a short nitriding schedule as a precursor to the formation of SiAlONs. The reaction sequences for formation of β and O-SiAlONs under different nitrogen pressures have been established in order to observe the influence of low gas overpressure on the nitridation and formation of these two SiAlON phases.

Chapter 3 has shown that SiAlONs produced by both reaction bonding and silicothermal reduction routes achieved comparable densities and porosities as well as final phase compositions. The current work focuses only on SiAlONs prepared by silicothermal reduction since this route offers the additional advantage of allowing manufacture of products not only by powder pressing but also by plastic forming routes such as slip casting or extrusion due to the use of halloysite [71].

5.2 Experimental procedure

It has been shown respectively in Chapters 3 and 4 that long dwelling times at 1350°C were not sufficient to fully nitride the Si present in the starting mixture, and that higher temperatures were beneficial to the nitridation. Therefore the possibility of using a faster nitriding schedule to nitride and form SiAlONs was investigated. A preliminary TGA experiment on Si pellets lightly pressed (about 8 MPa) was carried out. Figure 5.1 shows the mass change in these pellets under different nitriding schedules. The shape of the nitridation curves of the samples nitrided with a constant ramp was the same as observed by MacKenzie et al. [53]. The initial mass gain starting at about 1250°C and leading to approximately 10% conversion was described as corresponding to the conversion of the SiO$_2$ present at the surface of the Si particles and of some of the underlying Si into Si$_2$ON$_2$ [53]. At about 1350°C, a second mass increase which led to full nitridation at 1400°C was observed. As seen in the previous chapter, 1350°C was not sufficient to rapidly lead to full nitridation and only a temperature increase to 1400°C allowed the full conversion of Si to Si$_3$N$_4$. Figure 5.1 also shows that the start of the first small nitrogen pick-up and of the main reaction occurred at the same temperatures, respectively 1250°C and 1350°C, independently on how long had been spent at lower temperatures. The two steps of the reaction were therefore only dependent on temperature and not on the heating schedule. Consequently two significantly shorter nitriding schedules were designed.
Chapter 5

Figure 5.1: Mass change in Si pellets heated under flowing nitrogen at 5°C.min⁻¹ (solid line), 0.85°C.min⁻¹ (dotted line) and under the nitriding schedule described in Chapter 4 (dashed line).

For both schedules, SiAlON pellets were placed in BN crucibles and heated in a graphite furnace with graphite heating elements under vacuum until 800°C at approximately 4.3°C.min⁻¹ (fixed ramp that cannot be controlled below 800°C), and then up to 1400°C at 5°C.min⁻¹. One heating schedule was set with a 1-h hold at this temperature before further heating at 5°C.min⁻¹ to the final temperature as shown in Figure 5.2. The second schedule did not have a dwell time at 1400°C and the ramp was kept constant at 5°C.min⁻¹ until the desired temperature was reached. The two heating sequences were both carried out under atmospheric pressure (0.1 MPa) and under 0.7 MPa of nitrogen pressure. The heating schedules were stopped every 200°C at low temperatures and at shorter intervals at higher temperatures (Figure 5.2). Once heating had been stopped or reached its final temperature, samples were immediately cooled down at 10°C.min⁻¹ to 1000°C, and the rest of the cooling down was done at the natural rate of the furnace.

Figure 5.2: Heating schedule with the 1-h hold at 1400°C.
The two heating schedules achieved the same effects but without the holding time a higher temperature was required: 1500°C instead of a 1-h hold at 1400°C. Therefore the results and discussions bear only upon the heating schedule with the 1-h hold at 1400°C.

The raw material preparation and the characterisation of the sintered products were identical to those described in Sections 3.3.1 and 3.3.3. β and O-SiAlONs with low levels of substitution (respectively z=1 and x=0.05) were employed as they contain a high amount of Si. 2 mol% of DyAG and YAG were added in β and O-SiAlON respectively according to their effect on densification seen in Chapter 3. DyAG (or YAG) was still added as a mixture of Dy$_2$O$_3$ (or Y$_2$O$_3$) and Al$_2$O$_3$.

5.3 Results and discussions

5.3.1 Effect of nitrogen pressure on the nitridation during a short nitriding schedule

Figure 5.3 shows the degree of nitridation for β and O-SiAlON with and without nitrogen overpressure. β and O-SiAlONs exhibited the same behaviour under both 0.1 and 0.7 MPa of nitrogen until 1200°C. Above this temperature, for O-SiAlON under 0.1 MPa, the negative degrees of nitridation seen in Figure 5.3b show that more mass was lost from the samples than was gained due to nitridation. At high temperatures, Si can react with SiO$_2$ to form SiO gas [111]. This could occur more readily in O-SiAlON which contained more SiO$_2$ in their starting powder than β-SiAlION.

Figure 5.3: Effects of nitrogen overpressure on the degree of nitridation of (a) β-SiAlON z=1 and (b) O-SiAlON x=0.05 produced by silicothermal reduction.
Without nitrogen overpressure (0.1 MPa), Si could not be fully converted to Si$_3$N$_4$ in either β or O-SiAlONs. The conversion was only about 50% in β-SiAlONs at 1500°C while O-SiAlONs had already suffered mass losses preventing proper calculations of their degree of nitridation. The O-SiAlON experiments without nitrogen overpressure were stopped 1500°C as the decomposition and creep behaviour at 1500°C indicated that it would not be possible to gather results at higher temperatures. This phenomenon was one of the reasons why temperatures below 1500°C and long dwelling times [30] or powder beds [42] were typically used to produce pressureless sintered O-SiAlONs.

The use of nitrogen pressure was clearly beneficial to nitridation of Si in SiAlON samples. At 0.7 MPa almost all of the Si was converted – degree of nitridation in excess of 90% – in both β and O-SiAlONs after 1 h at 1400°C (Figure 5.3). Furthermore under 0.7 MPa, the nitridation plots of β and O-SiAlON had a similar profile as described for pure Si by MacKenzie [53]: nitrogen pick-up started between 1200°C and 1350°C and led to the same 12% of Si nitrided. By 1400°C, the nitridation reaction had converted more than half the Si present in both SiAlONs, and after the 1-h hold at 1400°C almost all the Si had been nitrided. These results show that the nitridation reaction can progress readily in SiAlONs fired under 0.7 MPa.

The main nitridation reaction occurring above 1350°C therefore achieved completion faster when nitrogen overpressures were used. Above this temperature and below the melting point of Si there are actually two phenomena occurring simultaneously: the main one is the nitridation and the second one is the volatilisation of Si. The maximum degree of nitridation reached depends on how fast full nitridation can be achieved. Two cases can be observed in Figure 5.3: a nitridation reaction that did not lead rapidly to full nitridation (under 0.1 MPa) and one that did (under 0.7 MPa).

In the first case when no nitrogen overpressures (0.1 MPa) were used, longer times were required to achieve full nitridation allowing evaporation of the Si before it could be nitrided; this in turn lowered the maximum amount of nitrogen which could react, hence the low mass gain achieved.

In the second case, under 0.7 MPa of nitrogen pressure, Si was almost fully nitrided to form Si$_3$N$_4$ in a short period of time thus limiting mass losses from the samples since Si$_3$N$_4$ decomposes at a much higher temperature than Si.

The term “degree of nitridation” actually encompasses both mass gain due to nitridation and mass loss due to evaporation. The use of “degree of nitridation” allows comparison between the actual mass gain with that expected in the absence of any evaporative mass losses. A value of 100% would indicate that the samples have been fully nitrided and that they did not suffer any mass losses during the nitridation. A lower value coupled with an XRD analysis showing that there is no elemental Si in the sample,
Reaction sequences of formation of β and O-SiAlONs reflects the extent of the mass losses. For the samples sintered under 0.7 MPa of nitrogen pressure, it can be seen from Figure 5.3 that the nitridation was essentially complete at 1400°C and did not decrease at higher temperatures thus implying no mass losses. For the β-SiAlON samples sintered without overpressure, the nitridation was incomplete at 1400°C, and although it increased above this temperature, it did not reach 100%. There was no remaining Si detected in the XRD analysis (see Figure 5.8) which indicates that both mass gain and mass loss occurred simultaneously. I.e. there was a net mass increase but lower than that which would be expected if all of the initial Si was nitride.

Nitrogen overpressure has a significant influence on nitridation of both β and O-SiAlONs. It allows the use of short nitriding schedules (faster heating rates until the start of nitridation and shorter hold times at the nitridation temperature) which limits mass losses at temperatures above 1350°C. Its effect on nitridation is also greater than the effects observed with additions of different additives [11].

5.3.2 Effect of nitrogen pressure on the densification of β and O-SiAlONs during the nitriding schedule

Densification in SiAlONs produced by silicothermal reduction can have two origins: incorporation of nitrogen into the sample pore structure, and shrinkage. Bulk density, open porosity and shrinkage were used to determine the sequence in which these two phenomena occurred in both β and O-SiAlONs and how they were affected by nitrogen pressures.

5.3.2.1 Consecutive nitridation and densification in β-SiAlONs

Figure 5.4 shows the effects of nitrogen pressures on bulk density, open porosity and shrinkage of β-SiAlON and indicates that up to 1200°C, there were no changes regarding these three properties. Most changes occurred above this temperature when nitridation takes place. Figure 5.4a and Figure 5.4b show, under 0.7 MPa of nitrogen, an increase in bulk density from 1.75 to 2.47 g.cm⁻³ and a decrease in open porosity from 32% to 20.3% when comparing samples at 1200°C and following 1 h at 1400°C. These changes can only be attributed to the nitridation reaction since up to 1500°C, the β-SiAlON samples did not shrink (Figure 5.4c). Measurements of open porosity in samples where the nitridation reaction is the overwhelming factor affecting mass change were in good agreement with the theoretical decrease in open porosity if the volume expansion is considered to be entirely accommodated within the pore structure [62] (e.g. measured and theoretical decreases in open porosity between β-SiAlONs at 1200°C and 1500°C are 11.1% and 10.1% respectively). This, plus the bulk density increase due to the formation of a more dense material (Si₃N₄ has a density of 3.2 g.cm⁻³ whereas density of Si is only 2.3 g.cm⁻³) led to the higher bulk density without shrinkage.
Figure 5.4: Effects of nitrogen overpressure on (a) bulk density, (b) open porosity and (c) shrinkage of β-SiAlON z=1 produced by silicothermal reduction.

The only phenomenon that occurred during the hold at 1400°C was therefore the nitrogen pick up. Under 0.7 MPa of nitrogen pressure, the nitridation reaction could be considered almost completed after 1 h at 1400°C (see Figure 5.3), and up to 1500°C the samples did not shrink (Figure 5.4c). This explains why there were no differences between the end of the hold at 1400°C and 1500°C in terms of bulk density and open porosity and why the same results could be achieved at 1500°C without the hold at 1400°C in the case of the second heating schedule used. The 5°C.min⁻¹ ramp employed from 1400°C to 1500°C had the same effect as 1 h at 1400°C.

Without nitrogen overpressure, only about 43% of the Si was nitrided following 1 h at 1400°C (see Figure 5.3a). Up to this point the bulk density increased up to 2.10 g.cm⁻³ (Figure 5.4a) which is slightly less than half way between 1.75 g.cm⁻³ (no Si converted) and 2.47 g.cm⁻³ (above 90% of Si nitrided), while there was still no shrinkage (Figure 5.4c). However, there was only a slight decrease in open porosity from 32% at 800°C to 30.6% following 1 h at 1400°C which did not match the theoretical decrease of about 4.5% that should be observed due to the degree of nitridation of 43%. In summary, above 1350°C the measurements did not correlate with the calculations (see Appendix F) and between 1400°C and 1500°C, the open porosity did not decrease even though degrees of nitridation are higher. This discrepancy revealed that mass change was not only affected by nitrogen pick-up but also by mass losses, by both SiO volatilisation and Si melting out of the sample above its melting point. There are then two competing phenomena occurring simultaneously: pore filling with Si nitridation and pore creation caused by SiO gas volatilisation. Long dwelling times below 1400°C are typically required to form β-SiAlONs without nitrogen overpressure to avoid melting Si before it is nitrided but this does not eliminate mass losses by evaporation.
Nitrogen overpressure allowed more rapid and higher degree of nitridation and formation of β-SiAlONs. Once a liquid was formed above 1500°C, samples densified due to grain rearrangement and pore elimination represented by the shrinkage. Bulk densities above 2.9 g.cm\(^{-3}\) with open porosities below 2% were reached at 1700°C. Without overpressure, mass was lost by evaporation and the longer time required to complete nitridation did not allow full nitridation of the Si before reaching its melting point, leading to further mass losses and consequently to samples with higher porosity.

5.3.2.2 Partially overlapping nitridation and densification in O-SiAlON

In a similar manner to β-SiAlONs, the nitridation reaction in O-SiAlONs could be considered almost complete after 1 h at 1400°C under 0.7 MPa. Figure 5.5 shows the effects of nitrogen pressures on bulk density, open porosity and shrinkage of O-SiAlON. Up to 1350°C, about 12.5% of the Si was nitrided. As for β-SiAlONs, this led to an increase in bulk density (Figure 5.5a) – in this case from 1.63 g.cm\(^{-3}\) at 800°C to 1.72 g.cm\(^{-3}\) – related to the amount of Si that had reacted with nitrogen, and to a decrease in open porosity (Figure 5.5b) since there was no shrinkage in O-SiAlON samples up to this temperature (Figure 5.5c).

![Figure 5.5: Effects of nitrogen overpressure on (a) bulk density, (b) open porosity and (c) shrinkage of O-SiAlON x=0.05 produced by silicothermal reduction.](image)

In summary, up to 1350°C under 0.7 MPa, the nitridation of Si was the only phenomenon occurring in O-SiAlONs. Contrary to β-SiAlON’s, O-SiAlON samples started shrinking above 1350°C and until nitridation was completed, both nitridation and densification were occurring simultaneously. The onset of shrinkage at lower temperatures in this material is thought to be due to the presence of more SiO\(_2\) in the initial mixture of O-SiAlONs, which can result in the formation of a eutectic liquid at lower temperatures as described in more detail later. This explains the rapid increase in bulk density (Figure 5.5a) and decrease in open porosity – from 33% to below 15% (Figure 5.5b) – between 1350°C and
following 1 h at 1400°C. Above 1500°C, there was further shrinkage but with the nitridation being already completed, this was attributed to densification only: bulk density reached up to 2.73 g.cm\(^{-3}\) (approximately 96% of relative density) while open porosity dropped below 2%.

At 1350°C without nitrogen overpressure, shrinkage and bulk density were higher and open porosity was lower than under 0.7 MPa. However the degree of nitridation (see Figure 5.3) was lower (only about 5% at 0.1 MPa in comparison with 12% at 0.7 MPa). At higher temperatures, the latter actually tended to decrease and reached negative values. This means two things: the nitridation did not progress as quickly as under 0.7 MPa and that mass was lost from the samples. At these temperatures, Si and SiO\(_2\) are susceptible to react and form SiO [111] according to:

\[
(4.1) \quad \text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO(g)}
\]

Under 0.7 MPa, the nitridation reaction was rapidly completed and the samples could be nitrided without detectable mass losses. The reaction of formation of O-SiAlON proceeded readily according to:

\[
(2.10) \quad 3\text{Si} + 2\text{SiO}_2 + 2\text{N}_2(g) \rightarrow 2\text{Si}_2\text{ON}_2 \quad (\text{O-SiAlON } x=0)
\]

O-SiAlON was detected at 1350°C (see later section) and was quickly formed at higher temperatures. On the contrary, without nitrogen overpressure, the time to complete nitridation was longer and reaction (2.10) could progress further. In this case mass was lost from the sample through volatilisation of SiO possibly according to reaction (4.1) or:

\[
(5.1) \quad 2\text{Si} + \text{SiO}_2 + \text{N}_2(g) \rightarrow \text{Si}_2\text{ON}_2 + \text{SiO(g)}
\]

Without overpressures O-SiAlON was not detected by XRD until higher temperatures when compared to samples sintered under 0.7 MPa (see later section) since nitridation is inhibited by lower availability of nitrogen.

Above 1200°C without overpressure, O-SiAlON pellets had already started shrinking while this did not occur until above 1350°C under 0.7 MPa. This suggested a difference in the reaction path that will be detailed in the next section.

As the temperature increased, shrinkage led to an increase in bulk density (Figure 5.5a) and to rapid pore closure (Figure 5.5b). The low open porosity, typically around 2%, isolated Si from the nitrogen atmosphere, preventing completion of the nitridation reaction and leaving pure Si remaining in the samples at 1400°C (see Figure 5.13). When the temperature was raised to 1500°C, Si still present melted and the pellets crept. This creep was obvious at 1500°C as a sudden expansion was measured along the diameter (Figure 5.5c). This expansion across the diameter correlated with further shrinkage observed in the height of the pellets, not represented here.
Again nitrogen overpressures were beneficial for rapid nitridation and densification of O-SiAlON. It was more important than for β-SiAlON since it did not only enhance nitridation but also prevented decomposition and major creep behaviour of O-SiAlON at temperatures above 1350°C. This difference between β and O-SiAlON is thought to be mainly due to the greater amounts of Si and SiO\textsubscript{2} in the O-SiAlON starting mixture and their likeliness to react and form gaseous SiO. Under nitrogen overpressure, the reactant nitrogen was in sufficient quantity to complete reaction (2.10). Without overpressure, nitrogen was not available to fully complete reaction (2.10) and therefore SiO was lost by evaporation according to reaction (5.1).

Even though pore closure and shrinkage began before nitridation was completed, this did not prevent full nitridation when nitrogen overpressures were used since the nitridation reaction was completed before the open porosity dropped too low, here below 15%.

5.3.3 Effect of nitrogen pressure on the reaction sequence for the formation of β and O-SiAlONs produced by silicothermal reduction

Nitrogen pressures have a major influence on the nitridation for both β and O-SiAlONs. Since Si\textsubscript{3}N\textsubscript{4} is formed more readily under nitrogen overpressures, and the presence of Si\textsubscript{3}N\textsubscript{4} is a requirement for the formation of SiAlONs, the reaction path may therefore be affected by nitrogen pressures. The formation of the SiAlONs was studied by analysis of the phase constituents and their relative amounts at different temperatures, determined by semi-quantitative analysis of XRD patterns. This analysis was also carried out on the starting powders and showed that the relative amounts of the phases determined by XRD were in good agreement with the actual mixed composition as shown in Table 5.1. Therefore the weight percentages determined by the XRD semi-quantitative analysis of the sintered samples can be considered to be a fair representation of the crystalline phase assemblages.
Table 5.1: Comparison of the crystalline phase assemblages obtained by XRD semi-quantitative analysis with those obtained from the published compositions for the as received halloysite powder and the prepared β-SiAlON precursor powder.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Theoretical mass%</th>
<th>XRD semi-quantitative analysis mass%</th>
<th>Theoretical mass%</th>
<th>XRD semi-quantitative analysis mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>-</td>
<td>60.3%</td>
<td>60.3%</td>
<td>64%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10.0%</td>
<td>9.0% (Quartz α)</td>
<td>2.6%</td>
<td>2% (Quartz α)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>3% (Cristobalite)</td>
<td>2.7%</td>
<td>3%</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>-</td>
<td>5.3%</td>
<td>5.3%</td>
<td>2%</td>
</tr>
<tr>
<td>Halloysite 7A</td>
<td>90.0%</td>
<td>88%</td>
<td>15.1%</td>
<td>14%</td>
</tr>
<tr>
<td>AlN</td>
<td>-</td>
<td>-</td>
<td>14.0%</td>
<td>15%</td>
</tr>
</tbody>
</table>

5.3.3.1 Reaction sequence for the formation of β-SiAlON produced by silicothermal reduction under different nitrogen pressures

Under 0.7 MPa of nitrogen, single phase β-SiAlONs were fully formed at temperatures above 1500°C. However they only reached densities of 2.95 g.cm⁻³ (approximately 92% of relative density) and open porosities of 3.4% at 1700°C. Figure 5.6 shows the evolution of the crystalline phase assemblage that led to this single crystalline phase β-SiAlON. Again, the following and subsequent figures describing crystalline phase assemblages are intended to illustrate major and minor phases rather than absolute percentages. Figure 5.7 shows the ESEM micrographs and EDS elemental mapping of β-SiAlON at 1200°C, 1400°C and 1600°C.

![Figure 5.6: Crystalline phase composition of β-SiAlON nitrided under 0.7 MPa of nitrogen overpressure.](image-url)
Up until 1200°C, there was no significant change in the main crystalline phase assemblage: all the starting crystalline phases were detected by XRD with the exception of crystalline halloysite which was not observed at 800°C and above, after its dehydroxylation at 600°C [67].

Below 1200°C, in addition to the onset of the nitridation reaction, decomposition of halloysite into mullite and SiO₂ takes place and there was also a decrease in the amount of crystalline Dy₂O₃ (Figure 5.6). The halloysite when fired independently at 1400°C formed crystalline mullite and SiO₂ (as cristobalite, quartz α and β) as detected by XRD shown in Table 5.2. However in the SiAlON mixture, these phases were only detected as traces at 1200°C and were not detected at higher temperatures because they were involved in the SiAlON formation.

Table 5.2: Composition of halloysite after firing at 1400°C according to XRD semi-quantitative analysis and theoretical values.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Theoretical mass%</th>
<th>XRD Semi-Quantitative analysis mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mullite</td>
<td>57.7%</td>
<td>62%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3% (α-quartz)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.3%</td>
<td>9% (β-quartz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26% (cristobalite)</td>
</tr>
</tbody>
</table>

At 1350°C, crystallised SiO₂ disappeared and the relative amount of AlN decreased while Si₂ON₂ and β-SiAlON appeared. At this stage, the nitridation reaction had converted about 14% of the Si (see Figure 5.3). The formation of Si₂ON₂ was due to the reaction of Si with the surrounding SiO₂ and nitrogen [53] according to reaction (2.10). Since the amount of Al₂O₃ did not vary, the formation of β-SiAlON and the decrease of AlN were explained by both the reactions of SiO₂ and AlN and of mullite and AlN with the newly formed Si₃N₄ respectively according to:

(5.2) \[3\text{Si}_3\text{N}_4 + \text{SiO}_2 + 2\text{AlN} \rightarrow 2\text{Si}_5\text{AlON}_7\]
(5.3) \[21\text{Si}_3\text{N}_4 + 2\text{SiO}_2.3\text{Al}_2\text{O}_3 + 7\text{AlN} \rightarrow 13\text{Si}_5\text{AlON}_7\]

The SiO₂ involved in the reactions came partially from the crystalline SiO₂ observed up to 1200°C, a component of the raw halloysite, and partially from the SiO₂ generated from the halloysite decomposition. Only the original Al₂O₃ added was not yet involved in these reactions.

When the temperature reaches 1400°C (300 min), the nitridation reaction was more advanced and about half the Si had been converted into Si₃N₄. A further decrease in AlN and increase in β-SiAlON suggested that reactions (5.2) or (5.3) were still occurring. More Si₂ON₂ was formed and a minor phase of α-Si₃N₄ was detected suggesting that these reaction intermediates formed readily at this
temperature but the nitrided Si is not immediately converted to $\beta$-SiAlON. The EDS analysis at 1200°C (see Figure 5.7a) showed that the Si, Al and Dy elements were all observed in discrete regions, whereas at 1400°C (see Figure 5.7b) they were all more homogeneously distributed, although there are still some areas of Al and Si enrichment corresponding to the $\text{Al}_2\text{O}_3$ and Si phases still observed in the XRD pattern at this temperature. These results, combined with the decrease in AlN, $\text{Dy}_2\text{O}_3$ and Si/$\text{SiO}_2$ crystalline phases from XRD analysis, may suggest the formation of a liquid phase at this temperature (eutectic temperature in the $\text{SiO}_2$-$\text{Al}_2\text{O}_3$-$\text{Dy}_2\text{O}_3$ ternary system is 1389°C [106]). The Al in this liquid is thought to come from the AlN and possibly the $\text{Al}_2\text{O}_3$ resulting from the decomposition of the halloysite, rather than the additional $\text{Al}_2\text{O}_3$ used as an additive, which is thought to be the origin of the remaining regions of high Al content shown in the EDS mapping. Although there may be a liquid phase present at this temperature, there was no effect on density since the liquid is probably close to its eutectic temperature and therefore has a high viscosity.

After 1 h at 1400°C, all intermediate phases had disappeared and only $\beta$-SiAlON and Si were detected. $\text{Si}_2\text{ON}_2$ reacted with AlN to give $\beta$-SiAlON according to:

\[(5.4) \quad \text{Si}_2\text{ON}_2 + \text{AlN} + \text{Si}_3\text{N}_4 \rightarrow \text{Si}_5\text{AlON}_7\]

The remaining $\text{Si}_3\text{N}_4$ reacted with $\text{Al}_2\text{O}_3$ and AlN to form $\beta$-SiAlON:

\[(3.14) \quad 5\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3 + \text{AlN} \rightarrow 3\text{Si}_5\text{AlON}_7\]

It should be noted that whilst the above chemical formula are stoichiometric expressions, actual determination of the degree of substitution based on lattice parameters calculated from shifts in the SiAlON peak positions and using the expression reported by Ekström [110] showed that the material formed was a $\beta$-SiAlON with a $z$ value close to 1.

At 1600°C, $\beta$-SiAlON was the only crystalline phase detected and the calculated degree of nitridation indicated that all the Si had been nitrided. The EDS analysis shows a homogeneous distribution of Si, Al and Dy elements. There was no longer any of the Al enrichment which was still observable at 1400°C, and the incorporation of the additional $\text{Al}_2\text{O}_3$ into a liquid phase based on the $\text{Dy}_2\text{O}_3$-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$ ternary system helps densification at this higher temperature since it is now considerably above its melting point and therefore likely to be less viscous.
Without nitrogen overpressure (Figure 5.8), the time to complete nitridation was longer and therefore the reaction path was similar to that under 0.7 MPa only until 1350°C, when the main nitrogen pick-up began.

Since the nitridation took more time to achieve completion, the α-Si₃N₄ phase formed under 0.7 MPa was not detected without nitrogen overpressure as seen in Figure 5.8. While the reaction limiting the formation of β-SiAlON was the incorporation of AlN, SiO₂ and Al₂O₃ into the Si₃N₄ structure under
0.7 MPa of nitrogen, the formation of Si$_3$N$_4$ was limiting the formation of β-SiAlON under 0.1 MPa. This was also seen in the fact that the Si$_2$ON$_2$ phase remained longer in the sample as it required Si$_3$N$_4$ to form β-SiAlON as shown in equation (5.4). After 1 h at 1400°C and under 0.7 MPa, a major β-SiAlON phase and a minor phase of Si were observed by XRD (see Figure 5.6). After the same hold at this temperature but without nitrogen overpressure, Si$_2$ON$_2$, and AlN were still present in the samples.

Figure 5.8: Crystalline phase composition of β-SiAlON nitrided without nitrogen overpressure (0.1 MPa).

In contrast to samples sintered under 0.7 MPa, it was not possible to obtain a single β-SiAlON crystalline phase without overpressure, even at 1700°C. At this temperature, Si was not detected but the degree of nitridation was only about 57% (see Figure 5.3). All of the remaining Si had therefore been nitrided but only after some of it had already been lost by volatilisation and/or by melting out. A Dy-α-SiAlON phase was observed by XRD along with remaining AlN, which suggests the incomplete formation of β-SiAlON leading to the formation of Dy-α-SiAlON according to:

\[
\begin{align*}
5/3(2\text{SiO}_2\cdot3\text{Al}_2\text{O}_3) + (26/3)\text{SiO}_2 + 183\text{Si} + 122\text{N}_2(g) + 29\text{AlN} + \text{Dy}_2\text{O}_3 \\
\rightarrow 3\text{Dy}_2\text{Si}_9\text{Al}_3\text{ON}_{15} + 30\text{AlN} + 39\text{SiO}(g) + 129\text{Si} + 99\text{N}_2(g)
\end{align*}
\]

instead of fully leading to β-SiAlON with an intergranular phase containing Dy$_2$O$_3$:

\[
\begin{align*}
5/3(2\text{SiO}_2\cdot3\text{Al}_2\text{O}_3) + (26/3)\text{SiO}_2 + 183\text{Si} + 122\text{N}_2(g) + 29\text{AlN} \rightarrow 39\beta-\text{Si}_3\text{AlON}_7
\end{align*}
\]

The formation of β-SiAlON depends on the formation of Si$_3$N$_4$ whose reaction rate is enhanced by nitrogen overpressures. Therefore the formation of β-SiAlON is controlled by nitrogen pressures. Higher nitrogen pressures would probably not be necessary, as at 0.7 MPa α-Si$_3$N$_4$ is already detected showing that the nitridation reaction proceeds more readily than the reaction of formation of β-SiAlON.
5.3.3.2 Reaction sequence for the formation of O-SiAlON produced by silicothermal reduction under different nitrogen pressures

Under 0.7 MPa, O-SiAlONs were fully formed at temperatures above 1500°C. However they only reached densities of 2.73 g.cm\(^{-3}\) (approximately 96% of relative density) and open porosities of 2% at 1700°C. Figure 5.9 shows the evolution of the crystalline phase assemblage that led to this major crystalline phase of O-SiAlON.

![Graph showing phase composition evolution](image)

Figure 5.9: Crystalline phase composition of O-SiAlON nitrided under 0.7 MPa of nitrogen overpressure.

Up to 1000°C, there was no significant change in the main crystalline phase assemblage. Between 1000°C and 1200°C mullite is expected to be formed, but only traces of crystalline mullite were detected by XRD. At a temperature of 1350°C, the crystalline phases of Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\) had both disappeared and the amount of SiO\(_2\) had decreased suggesting the formation of a liquid phase based on Y\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-SiO\(_2\). This is supported by the EDS mapping presented in Figure 5.10 which shows analysis of samples sintered at 1200°C and 1400°C. In the lower temperature sample the Y and Al elements coming from the rare-earth and the aluminium oxides are visible as discrete particles between the Si grains. On the other hand, in the higher temperature sample, although there are still some Si rich regions from the original Si powder, the Si, Al and Y elements all show a more uniform distribution.
Figure 5.10: ESEM of O-SiAlONs at 1200°C (a) and 1400°C (b) and EDS mapping of Si (a1 and b1), Al (a2 and b2) and Y (a3 and b3).

Figure 5.9 shows that at 1350°C, an increase in Si was observed but this does not actually represent an actual increase in Si in the sample. Figure 5.9 represents the crystalline phase assemblage in weight percentage and, since there were less crystalline phases (Y₂O₃ and Al₂O₃ had disappeared and there was less quartz), the relative Si weight percentage increased. Figure 5.11 shows the actual XRD patterns on which the semi-quantitative analyses have been based and there was not more Si in the samples at 1350°C than at 1200°C: the XRD patterns were all obtained under the same conditions and the intensities of the Si peaks were similar at 1000°C, 1200°C and 1350°C. Si₂ON₂ started to be detected at 1350°C and it corresponded to the nitrided Si reacting with SiO₂ according to:

\[ \text{Si} + \text{SiO}_2 \rightarrow \text{Si}_2\text{ON}_2 \]
Reaction sequences of formation of $\beta$ and O-SiAlONs

(5.7) \[ \text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{ON}_2 \]

Figure 5.11: XRD of O-SiAlON formed under 0.7 MPa of nitrogen. The semi-quantitative analyses that led to Figure 5.9 are based on these results. JCPDF file numbers are given in Appendix C.

The formation of a rare-earth containing liquid phase is similar to that seen in the $\beta$-SiAlON sintered with Dy$_2$O$_3$ although in that case the source of Al was thought to be the Al$_2$O$_3$ from the halloysite, and the AlN since the amount of Al$_2$O$_3$ from the additives did not change. In O-SiAlON at 1350°C, the Al$_2$O$_3$ from the additive had also completely disappeared as shown in Figure 5.9.

In the sample sintered at 1400°C crystalline YAG was observed which could possibly have crystallised from the liquid during cooling. At this temperature, more Si$_2$ON$_2$ was formed from reaction (5.7) as Si and quartz continued to decrease. The traces of mullite detected until 1350°C had disappeared, suggesting they had dissolved and started to react to form O-SiAlON. Figure 5.9 only legends O-SiAlON since Si$_2$ON$_2$ can be considered as an O-SiAlON with $x=0$. There is no structural transformation between the two phases, only a substitution of Al and O respectively for Si and N.

A large amount of crystalline $\beta$ quartz was detected at 1400°C but this did not correlate with the decrease in $\alpha$ quartz that started at 1200°C. This showed that other sources of SiO$_2$ crystallised to $\beta$ quartz. Besides the starting quartz phase, the other SiO$_2$ phase susceptible to lead to $\beta$ quartz was the SiO$_2$ issued from the decomposition of halloysite according to:

(5.8) \[ 3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2.2\text{H}_2\text{O}) \rightarrow 2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3 + 4\text{SiO}_2 + 6.6\text{H}_2\text{O}(g) \]

EDS elemental mapping in Figure 5.10 showed that Si particles were still present at 1400°C whereas after 1 h at this temperature Si is homogeneously distributed (Figure 5.12). This correlates well with
the XRD analysis seen in Figure 5.9 where Si is detected at 1400°C and is not after 1 h at this temperature and with the calculated degree of nitridation that shows that the Si had been fully nitrided (see Figure 5.3) after 1 h at 1400°C but not before. XRD does not show Si₃N₄ after 1 h at this temperature therefore the nitrided Si had reacted with SiO₂ (from quartz and mullite) and Al₂O₃ (from mullite) to form O-SiAlON according to:

\[(5.9) \quad \frac{5}{3}(2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3) + 26/3\text{SiO}_2 + 85.5\text{SiO}_2 + 97.5\text{Si}_3\text{N}_4 \rightarrow 200\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95}\]

After 1 h at 1400°C, traces of β-SiAlON were detected by XRD. This was probably formed from the decomposition of O-SiAlON at high temperatures according to:

\[(3.23) \quad 6\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} \rightarrow \text{Si}_{5.7}\text{Al}_{0.3}\text{O}_{0.3}\text{N}_{7.7} + 6\text{SiO}(g) + 2\text{N}_2(g) \quad \text{O-SiAlON} (x = 0.05) \quad \beta\text{-SiAlON} (z = 0.3)\]

Up to 1700°C, a major phase of O-SiAlON and traces of β-SiAlON were still detected. Semi-quantitative analysis (Figure 5.9) showed that the amount of β-SiAlON increased with temperature. This also corresponded to the slight decrease in degree of nitridation observed in Figure 5.3 for the O-SiAlON samples sintered above 1500°C. However the decompositions observed under 0.7 MPa were limited in comparison with that observed under lower nitrogen pressures.

\[\text{Figure 5.12: ESEM of O-SiAlONs after 1 h at 1400°C and EDS mapping of Si (a1), Al (a2) and Y (a3).}\]

Under 0.7 MPa, it was possible to obtain samples essentially composed of O-SiAlON, about 97% of the crystalline phases, after only 1 h at 1400°C.
Without nitrogen overpressure, only traces of O-SiAlON, about 6% of the crystalline phases, were obtained at the same temperature as shown in Figure 5.13. Up to 1200°C, nitrogen pressure did not have an influence on the reaction path of formation of O-SiAlON. This was expected since at this temperature Si had not started to be nitrided (see Figure 5.3). At 1350°C, less Si was nitrided without nitrogen pressure than with 0.7 MPa (4.6% and 12.4% respectively) hence the O-SiAlON phase that was formed under 0.7 MPa was not detected by XRD under 0.1 MPa.

![Figure 5.13: Crystalline phase composition of O-SiAlON nitrided without nitrogen overpressure (0.1 MPa).](image)

Without nitrogen overpressures, shrinkage started at 1350°C whereas it was not observed to begin until 1400°C in the samples sintered with 0.7 MPa as seen in Figure 5.5c. This is thought to be due to the above differences in the amount of SiAlON formed and the effects of this on the composition of the liquid phase. Y\(_2\)O\(_3\), Al\(_2\)O\(_3\) and SiO\(_2\) form a liquid phase by 1350°C which favours the rearrangement of particles and therefore samples begin shrinking. However this rearrangement and shrinkage is dependent on the viscosity of the liquid present at a given temperature which in turn is affected by its composition. The liquid region in the Y\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-SiO\(_2\) ternary system is located in the SiO\(_2\) rich corner of the phase diagram at low temperatures and extends towards the centre of the phase diagram at higher temperatures as shown in Figure 5.14 [112]. In the samples with nitrogen overpressure the SiO\(_2\) had already started to react with the nitrided Si to form O-SiAlON and therefore the composition of the liquid phase would be deficient in SiO\(_2\) which would move its melting point to a higher temperature, and compared to a SiO\(_2\) rich composition, result in a more viscous liquid at a given temperature.
Between 1200°C and 1350°C, some of the quartz that did not go into the liquid phase started to be converted to cristobalite. This transformation proceeded until only cristobalite remained after 1 h at 1400°C. At 1500°C cristobalite was also dissolved in the liquid phase.

From between 1200°C and 1350°C to 1 h at 1400°C, the liquid phase formed promoted densification of samples until shrinkage reached about 10% (see Figure 5.5c) and open porosity dropped to less than 1% (see Figure 5.5b). Without nitrogen overpressure it was not possible to convert Si into Si$_3$N$_4$ before pore closure. Therefore, when the temperature was raised to 1500°C, the Si melted and the samples showed a significant creep represented by the sudden drop in shrinkage from 10% to less than 0% (a negative shrinkage corresponds to an expansion) along the diameter of the pellets as seen in Figure 5.5c.

Since only a small amount of Si had been nitrided, only a small amount of O-SiAlON could be formed. At 1500°C, the samples were composed of Si (which melted and recrystallized), O-SiAlON, and a glassy phase which was formed on cooling from the liquid phase formed in the Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ system. The O-SiAlON samples were not nitrided without overpressure above 1500°C to avoid destroying the crucibles through melt attack.
5.3.4 Conclusions

A study of the influence of nitrogen pressures on the formation of β and O-SiAlONs produced by silicothermal reduction has been carried out and led to the following specific conclusions:

- Nitrogen overpressures are beneficial to the formation of SiAlONs as they greatly enhance the conversion of Si into Si$_3$N$_4$. Under 0.7 MPa of nitrogen overpressure, the degree of nitridation in β and O-SiAlON compositions at 1400°C with no holding time was 50.5% and 65.5% respectively. Without overpressure at this temperature the nitridation was only 27% complete in β and was not measurable in O due to mass losses, caused by formation and volatilisation of SiO. Under 0.7 MPa of nitrogen overpressure, essentially fully formed β and O-SiAlONs were produced after only 1-h hold at 1400°C, or at 1500°C without any hold. Without overpressures only around 60% and 6% of the β and O-SiAlON phases were formed at this temperature.

- The enhanced nitridation and SiAlON formation observed under 0.7 MPa makes it possible to employ shorter heating schedules than those traditionally designed for pressureless sintering. The shorter time spent at the nitriding temperature also limits mass losses by evaporation and full nitridation can be achieved even when a liquid phase is formed before the nitridation is completed.

- Although full β and O-SiAlON formation could be achieved following 1-h hold at 1400°C using nitrogen overpressure, their density was only 2.47 g.cm$^{-3}$ and 2.39 g.cm$^{-3}$ respectively (relative density ~ 77% and 84% respectively). In samples sintered at 1700°C following the nitriding step, and with only 2 mol% of additive, β and O-SiAlONs reached bulk density of 2.95 g.cm$^{-3}$ and 2.73 g.cm$^{-3}$ respectively (~ 92% and 96%) with open porosity of 3.4% and 2%.

5.4 Summary

The materials investigated in this work could potentially find application as refractories where the chemical and thermal properties are of interest as well as their cost of production. The silicothermal reduction technique by which SiAlONs were produced possesses advantages of being both a cheaper alternative to traditional sintering of SiAlONs and of facilitating plastic forming due to the presence of halloysite clay in the raw material. In this work β and O-SiAlONs were formed after 1 h at 1400°C under 0.7 MPa of nitrogen pressure, whereas this could not be achieved under ambient nitrogen conditions (0.1 MPa). Similar results were also achieved at 1500°C without holding (see Appendix G), although the holding time may be beneficial for larger products to ensure all of the Si is nitried before raising temperature above its melting point.
The samples obtained were not fully dense – the maximum relative density was approximately 92% and 96% at 1700°C for β and O-SiAlONs respectively – since no dwelling time was employed once the final temperature had been reached. However, since both β and O-SiAlONs already began to shrink above 1600°C, it should be possible to produce SiAlONs dense enough to be used for refractory applications with a short dwelling time at this temperature. Chapter 6 investigates improved densification through the use of holding times at the final temperature. SiAlONs produced by this technique using affordable raw powders and a short sintering schedule should be of interest for refractory applications.
CHAPTER 6
EFFECTS OF NITROGEN PRESSURES ON THE MICROSTRUCTURE AND DECOMPOSITION OF β AND O-SiAlONs

6.1 Introduction

In all ceramic materials, SiAlONs included, mechanical properties are strongly dependent on the microstructure and the density of the product. Consequently, studies have been conducted on the grain growth of these materials in view to tailor their mechanical properties. Such experiments have typically been carried out on α-SiAlONs produced by the traditional liquid phase reaction sintering route (see Section 2.3.2) since they display the highest intrinsic hardness amongst SiAlONs and that elongated grains would improve their fracture toughness. These works focused mainly on modifying parameters such as sintering temperatures [46], holding time [28], heating rate [23, 43], characteristics and composition of the starting powder [28, 41, 44], and composition and amount of additives [45, 113] in order to control nucleation and grain growth.

While outstanding mechanical properties are critical in SiAlONs designed for high performance applications, both excellent mechanical and chemical properties are required for refractory purposes. Nitridation of both β and O-SiAlONs has been shown to be greatly influenced by nitrogen pressures, with higher degrees of nitridation obtained when SiAlONs were nitrided under overpressures. Thus the nitridation stage, which generally led to the formation of an intermediate Si₃N₄ phase, is likely to have an influence on the microstructure of the sintered material and consequently on its mechanical properties.
6.2 Effects of nitrogen pressure on the overall firing process: same nitrogen pressures during nitriding and sintering

The reaction sequences of formation of both β and O-SiAlONs have been described in Chapter 5 under both ambient conditions and nitrogen overpressures. It was shown that the latter clearly had a significant beneficial effect on the formation and the final phase assemblage of the material. However, the alteration of the reaction sequence with nitrogen overpressures is likely to have an influence on the microstructure and therefore on the mechanical properties. As a consequence, SiAlONs were produced under different nitrogen pressures to investigate their effect on the microstructure of the final product.

6.2.1 Experimental procedure

6.2.1.1 Firing schedule

Under the short nitriding schedule described in Chapter 5 (see Figure 5.2), the decomposition of SiAlONs sintered under ambient pressure was so great that it led to the destruction of both the samples and the crucible. In order to obtain data under all the nitrogen pressures, it was necessary to use a different schedule which allowed O-SiAlONs sintered under ambient conditions to be characterised. The longer nitriding schedule used in Chapter 4 (see Figure 4.10) led to much higher degrees of nitridation under ambient conditions than the short nitriding schedule, hence these samples were less likely to destroy the crucibles since more Si was converted into Si₃N₄ before the beginning of the sintering stage, which reduced the risk of Si melting out or decomposing above 1410°C.

β and O-SiAlONs were nitrided in Chapter 4 with respectively various amounts of DyAG and CaO. In order to obtain products of sufficient density to be used as refractory materials, these samples were subsequently sintered at 1600°C for 4 h (with a 5°C.min⁻¹ ramp). The nitrogen pressures during the sintering were kept identical to the one used during the nitridation (e.g. a β-SiAlON nitrided under 0.4 MPa of nitrogen was also sintered under 0.4 MPa) in order to investigate the effects of nitrogen pressures on the overall firing process of β and O-SiAlONs.

In addition to the β-SiAlONs (z=1) nitrided in Chapter 4, β-SiAlONs (z=3) were similarly nitrided and sintered (i.e. in two steps, with cooling down to room temperature after the 3-h hold at 1400°C). This additional composition was designed to investigate the effects of nitrogen pressures on β-SiAlONs which contain significantly less Si. After nitridation, these two β-SiAlONs were comprised of a major phase of β-SiAlON, representing about 80% and 50% in mass of the crystalline phase assemblage in β-SiAlONs targeted to z=1 (see Figure 4.19) and to z=3 (see Appendix H) respectively. The O-
SiAlONs compositions (x=0.05 and x=0.2) were comprised of a major crystalline phase of O-SiAlON (typically in excess of 60% in mass) or of α-Si₃N₄ after nitridation, with the exception of the samples containing a large amount of additives which did not achieve high degrees of nitridation (see Figure 4.23 and Figure 4.27). During the sintering stage, all these compositions were expected to be fully converted to a single SiAlON phase and to achieve high densities.

6.2.1.2 Characterisation

In addition to the characterisations systematically carried out so far on SiAlONs, i.e. phase identification, bulk density, open porosity, mass losses measurements and ESEM analyses, mechanical tests have been realised. The silicothermal reduction route is used to reduce production costs of SiAlION but it typically leads to products with higher porosity than the SiAlONs produced by traditional liquid phase reaction sintering, which in turn leads to lower mechanical properties. Even though mechanical properties are not the main reason why β and O-SiAlONs are used for refractory applications, they still need to display properties high enough to be able to sustain the constraints of their use. Therefore Vickers hardness and indentation fracture toughness were carried out to observe whether or not it was possible to produce SiAlONs by cost efficient processes that were able to achieve mechanical properties similar to those obtained with the traditional method.

Vickers indentations were realised by applying pressure to a Vickers diamond indenter for a given time on a polished plane surface. In this work the indentation fracture toughness was sought to be determined at the same time as the micro-hardness, therefore the load applied to the diamond was chosen to be high enough to generate radial-median cracks [55]. The Vickers indentations were realised under a load of 98.1 N (10 kgF) applied for 10 seconds. A schematic of the indent and cracks generated is given in Figure 6.1.

The Vickers hardness was determined according to:

\[ H_V = 2 \sin \left( \frac{\theta}{2} \right) \times \frac{F}{(d)^2} \]  [114]

with \( F \), the applied load in kilogram-force, and \( d \), length of the diagonal, in millimetre. By replacing \( \theta \), the angle between the opposite faces of Vickers’ pyramid (136°), and expressing \( F \) and \( d=2a \) respectively in gram-force and micrometre, (6.1) becomes:

\[ H_V = 1854.4 \times \frac{F}{(2a)^2} \]

The Vickers hardness is expressed by a number without units. In order to compare these results with other sources, Vickers hardness was therefore expressed in gigapascal according to:
\[ H_V = 18.19 \times \frac{F}{(2a)^2} \]

with \( F \) in gram-force and \( a \) in micrometre.

![Figure 6.1: Schematic idealised plan view of a Vickers indent with radial-median crack system.](image)

Indentation fracture toughness is a simple, fast and non-destructive method to measure the fracture toughness. However it does not offer the same accuracy as other techniques [54] such as single edge notched beam (SENB) and there is a great diversity of equations available in the literature. These equations can be sorted in two groups depending on which one of the radial-median or Palmqvist crack geometries is considered [55]. In the case of SiAlONs, the more appropriate equation when \( c/a \geq 2 \) seems to be a radial-median equation such as:

\[ K_{lc} = 0.016 \left( \frac{E}{H_V} \right)^{1/2} \left( \frac{P}{c^{3/2}} \right) \]

with Young’s modulus \( E \) in GPa, Vickers hardness \( H_V \) in GPa, applied load \( P \) in N and crack length \( c \) in m.

Optical microscopy was used to measure indent and crack lengths generated by Vickers indentations, and environmental scanning electron microscopy (ESEM) to observe grain size and morphology. With heavy element as additives, the intergranular phase appeared bright while the SiAlON grains were dark.

### 6.2.2 Results and discussions

The effects of nitrogen pressures on the formation, densification and microstructure of \( \beta \) and O-SiAlONs produced by a two-step firing process are discussed in the following sections. These sections report the results obtained after the second step of the process (the sintering), the results regarding the first step (the nitridation) having already been discussed in Chapter 4.
6.2.2.1 Formation, densification and microstructure of β-SiAlONs

Figure 6.2 and Figure 6.3 show the bulk density and the open porosity of respectively β and O-SiAlONs. Nitrogen gas pressures ranging from 0.1 MPa to 1.0 MPa did not have a significant effect on the bulk density and on the open porosity of β-SiAlONs (with z=1 and 3) produced by silicothermal reduction with various amounts of DyAG as shown in Figure 6.2 and Figure 6.3. All the β-SiAlONs achieved relative density in excess of 90% with the exception of the ones sintered without additives (Table 6.1). Since for a given composition, the β-SiAlONs sintered with additives had comparable high bulk densities and low open porosities, it was possible to compare their mechanical properties, and expect that the variations of the porosity would not have an overwhelming effect on such properties.

![Figure 6.2](image1.png)

Figure 6.2: Effects of nitrogen pressure on the bulk density (a) and open porosity (b) of β-SiAlONs (z=1) with various amount of additives.

![Figure 6.3](image2.png)

Figure 6.3: Effects of nitrogen pressure on the bulk density (a) and open porosity (b) of β-SiAlONs (z=3) with various amount of additives.
The main crystalline phase assemblage and the relative density (bulk density measured by Archimedes’ method divided by theoretical density) of β-SiAlONs (z=1 and 3) are summarised in Table 6.1. The theoretical density was calculated for a material composed of a crystalline SiAlON phase and a crystalline intergranular phase. Any difference with this theoretical composition introduced an error in the relative density that could potentially lead to values above 100%, for instance in presence of a phase more dense than the expected ones. Moreover, XRD analysis does not allow to determine the composition of amorphous phases, hence if an amorphous phase possessed a different composition than expected, it may result in a deviation of the relative density from its actual value. Relative densities are therefore only given as a rough guide.

Table 6.1: Crystalline phase composition and relative density of β-SiAlON with (a) z=1 and (b) z=3.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Nitrogen pressure (MPa)</th>
<th>Main crystalline phases (in mass%)</th>
<th>Relative density**</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-SiAlON</td>
<td>α-Si₃N₄</td>
<td>DyAG*</td>
<td></td>
</tr>
<tr>
<td>0 mol% DyAG</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>82</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>84</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>75</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>1 mol% DyAG</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 mol% DyAG</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>4 mol% DyAG</td>
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<td>-</td>
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<td>10</td>
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</tr>
<tr>
<td>1.0</td>
<td>90</td>
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<td>-</td>
</tr>
<tr>
<td>8 mol% DyAG</td>
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<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>85</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>85</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
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<td>15</td>
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<table>
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<tr>
<th>Additives</th>
<th>Nitrogen pressure (MPa)</th>
<th>Main crystalline phases (in mass%)</th>
<th>Relative density**</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-SiAlON</td>
<td>α-Si₃N₄</td>
<td>DyAG*</td>
<td></td>
</tr>
<tr>
<td>0 mol% DyAG</td>
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<td>4</td>
</tr>
<tr>
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<td>5</td>
<td>-</td>
</tr>
<tr>
<td>1 mol% DyAG</td>
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<td>94</td>
<td>6</td>
</tr>
<tr>
<td>0.4</td>
<td>94</td>
<td>6</td>
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</tr>
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<td>100</td>
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<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>-</td>
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<td>2 mol% DyAG</td>
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</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>98</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>4 mol% DyAG</td>
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<td>100</td>
<td>-</td>
</tr>
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<td>98</td>
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<td>1.0</td>
<td>90</td>
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</tr>
<tr>
<td>8 mol% DyAG</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
</tr>
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<td>85</td>
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<td>1.0</td>
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</table>

<table>
<thead>
<tr>
<th>Additives</th>
<th>Nitrogen pressure (MPa)</th>
<th>Main crystalline phases (in mass%)</th>
<th>Relative density**</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-SiAlON</td>
<td>α-Si₃N₄</td>
<td>DyAG*</td>
<td></td>
</tr>
<tr>
<td>2 mol% DyAG</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

N/A: data not available. *the amount of these phases was roughly estimated as a lack of data in the XRD database did not allow to take them into account in the semi-quantitative analysis, **the theoretical density used in the calculation was based on a material composed of a single phase SiAlON and a DyAG crystalline intergranular phase.

The β-SiAlONs sintered with additives were composed of a major β-SiAlON phase and of an intergranular phase containing the additives. A crystalline intergranular phase was detected in compositions containing a large amount of additive and sintered under nitrogen overpressures. This intergranular phase was not detected by XRD analysis in compositions with low amounts of additives.
or under low nitrogen pressures, because the amount of crystalline phase was either below the detection threshold of the XRD equipment (2-3%) or because it remained mainly as an amorphous phase. The compositions sintered without additive were not fully converted to β-SiAlION due to the lack of liquid phase from which β-SiAlION grains can precipitate.

On one hand, the β-SiAlONs sintered without additive did not achieve high relative densities (typically below 80% of the theoretical density) and were not only comprised of a β-SiAlON and an intergranular phase but also contained other crystalline phases, indicating incomplete formation of the SiAlON, hence they were not considered for microstructural and mechanical characterisations. On the other hand for a given starting composition, β-SiAlONs sintered with additives had comparable relative densities and compositions under the various nitrogen pressures. It was therefore possible to study the influence of nitrogen pressure on their microstructure and mechanical properties.

β-SiAlONs were reported to be made of elongated grains with an aspect ratio varying from 4 to 10 [4] and whose size increases with increasing $z$ values [11]. β-SiAlONs with $z=1$ and $z=3$ were prepared in order to investigate the influence of nitrogen pressure on the grain growth and mechanical properties of compositions containing a large and a small amount of Si respectively that typically lead to different grain size. ESEM was used to observe grain size and morphology while Vickers hardness and indentation fracture toughness were carried out to characterise the mechanical properties.

Figure 6.4 shows the effects of nitrogen pressure on the Vickers hardness and the fracture toughness of β-SiAlONs ($z=1$). While nitrogen pressures did not have a significant influence on the fracture toughness of β-SiAlONs ($z=1$), their hardness seemed to slightly increase with increasing pressures as shown in Figure 6.4. In ceramics, mechanical properties are closely related to the microstructure and density of the material. Since densities and open porosities were similar in β-SiAlONs, the differences in hardness were probably due to microstructural changes.
Figure 6.4: Effects of nitrogen pressure on the Vickers hardness (a) and the fracture toughness (b) of β-SiAlON (z=1) with various amount of additives.

ESEM micrographs of β-SiAlONs with 4 mol% of DyAG and with 1 mol% of DyAG are respectively shown in Figure 6.5 and in Appendix I. They show that the average grain size decreased with increasing nitrogen pressures. The grain size analysis presented in Figure 6.6 (and later Figure 6.8) shows the average diameter of the projected area of the grains, considering they were spherical. The β-SiAlON grains were not spherical, therefore this was not intended to describe the actual size distribution of the grains in the material, but to support the visual observations that could be drawn from the micrographs in Figure 6.5 (and Figure 6.7). The data represented in these graphs corresponds to the measurements realised on more than 500 grains.
Effects of N₂ pressure on the microstructure and decomposition of β and O-SiAlONs

In this experiment, the only difference between two firing schedules was the nitrogen pressure. Independently of the amount of additive employed, the grain size in β-SiAlONs (z=1) decreased with increasing nitrogen pressures. Although the grain size distribution (Figure 6.6) does not reflect the actual size of the grains, the decrease of the average grain size between β-SiAlONs sintered under 0.1 MPa and 1.0 MPa was significant. The observed D₅₀ dropped from 0.19 µm to 0.13 µm which represented a 30% decrease. The fracture toughness did not significantly vary indicating that neither the grain morphology nor the composition of the intergranular phase had significantly changed when increasing nitrogen pressures.

Figure 6.5: ESEM micrographs of β-SiAlONs (z=1) sintered with 4 mol% of DyAG under (a) 0.1 MPa, (b) 0.4 MPa, (c) 0.7 MPa and (d) 1.0 MPa.
Figure 6.6: Grain size distribution in β-SiAlONs (z=1) with 4 mol% of DyAG after sintering under different nitrogen pressures.

The β-SiAlONs that achieved the highest hardness were the ones comprised of the smaller grains. With the exception of the grain size, no other significant changes in the grain morphology were observed: the grains were mainly equiaxed (there were a few elongated grains) independently of the nitrogen pressure. This latter feature alone differed from Hyuga’s observations that β-SiAlON grains were mainly elongated with an aspect ratio varying from 4 to 10 [11]. In that work, the author used a pressureless nitridation process followed by an 8-h hold at 1800°C and therefore both nitrogen pressures and dwelling times may have had an effect on the grain growth. Since the nitridation reaction requires a longer time to be completed under ambient pressure than under overpressures (see Chapter 5), fewer Si grains can react with nitrogen under low pressure during a given amount of time in comparison to a nitridation carried out under overpressures. In Hyuga’s work, the pressureless nitridation schedule may have led to the formation of fewer Si₃N₄ seeds which grew into larger elongated β-SiAlON grains after 8 h at 1800°C. Under nitrogen overpressure more Si₃N₄ seeds could be formed and by impeding on each other growth, they led to smaller grains than under pressureless sintering. The sintering at lower temperature and shorter dwelling time (4 h at 1600°C) may also have reduced the grain growth by coalescence. In summary, the higher nitrogen pressures during the nitridation stage led to the formation of a greater number of seed crystals that hindered the grain growth while the shorter dwelling time and lower temperature limited their growth by coalescence explaining the discrepancy between Hyuga’s results and the present ones.

Figure 6.7 shows the effects of nitrogen pressure on the Vickers hardness and the fracture toughness of β-SiAlON (z=3). In contrast to β-SiAlON (z=1), nitrogen pressures did not have a significant effect on either the hardness or the fracture toughness of β-SiAlONs (z=3) as shown in Figure 6.7. Figure 6.8 shows the grain size distribution in β-SiAlON (z=3) with 4 mol% of DyAG. In agreement with
literature [11], the microstructure of β-SiAlONs (z=3) was comprised of larger grains than β-SiAlON (z=1), with the observed $D_{50}$ more than 2 times greater with z=3 than with z=1. Nitrogen pressures did not have the same effect on these larger β-SiAlON (z=3) grains as they had on β-SiAlON (z=1). Neither the density, the porosity (see Figure 6.3) nor the grain size (Figure 6.8) were affected by nitrogen pressures, and the mechanical properties remained therefore similar under the various conditions as seen in Figure 6.7.

Figure 6.7: Effects of nitrogen pressure on the Vickers hardness (a) and the fracture toughness (b) of β-SiAlON (z=3) with various amount of additives.

Figure 6.8: Grain size distribution in β-SiAlONs (z=3) with 4 mol% of DyAG after sintering under different nitrogen pressures.

The microstructure of β-SiAlONs (z=3) presented in Figure 6.9 shows the presence of elongated grains in a matrix of smaller equiaxed grains. Whilst elongated grains are a necessary requirement for improved fracture toughness, they are only effective if the advancing crack path is diverted along the grain boundary, and this requires a grain/grain boundary bonding strength that is sufficiently weak to allow crack deflection [15]. The ESEM micrograph of the sample sintered under high overpressure
(Figure 6.9e) shows that the cracks propagated through the elongated grains rather than intergranularly, indicating that the intergranular phase was too strong and did not offer a preferential path to the propagation of the cracks, leading to an average fracture toughness which was not higher than that of \( \beta \)-SiAlON \((z=1)\).

![ESEM micrographs of \( \beta \)-SiAlONs \((z=3)\) sintered with 4 mol\% of DyAG under (a) 0.1 MPa, (b) 0.4 MPa, (c) 0.7 MPa, and (d) and (e) 1.0 MPa.](image)

The same phenomenon was also observed in \( \beta \)-SiAlONs with 1 mol\% of DyAG and ESEM micrographs of their microstructure are shown in Appendix I. \( \beta \)-SiAlONs \((z=3)\) contained less Si in their starting mixture than the ones aimed at \( z=1 \) explaining the greater effects of nitrogen pressures on \( \beta \)-SiAlONs \((z=1)\). \( \beta \)-SiAlONs \((z=3)\) displayed more constant mechanical properties since their microstructure was less affected by the different nitrogen pressures.

### 6.2.2.2 Formation, densification and microstructure of O-SiAlONs

Figure 6.10 shows the effects of nitrogen pressures on the mass losses of O-SiAlONs during their sintering. O-SiAlONs were typically more sensitive to nitrogen pressures than \( \beta \)-SiAlONs. Indeed, when they were sintered under ambient conditions, O-SiAlONs decomposed readily and a thick and porous outer layer was formed whereas they displayed similar but significantly reduced behaviours when they were sintered under nitrogen overpressures \((\geq 0.4 \text{ MPa})\) as shown by the lower mass losses seen in Figure 6.10.
Figure 6.10: Influence of nitrogen pressure on the mass losses of O-SiAlONs with (a) $x=0.05$ and (b) $x=0.2$ during sintering with various amount of CaO.

Figure 6.11 shows the effects of nitrogen pressures on the densification of O-SiAlON ($x=0.05$) with various amounts of CaO. After sintering, the compositions achieved higher densities and lower open porosities with increasing CaO content. For a given composition, increasing pressures typically led to a slight change in bulk density and in open porosity, however these changes were small in comparison with the effect of the CaO additions. Table 6.2 presents the relative densities of these O-SiAlONs and their crystalline phase assemblage. On one hand, the formation of O-SiAlON was incomplete in absence of additives as shown by the presence of $\alpha$-$\text{Si}_3\text{N}_4$. On the other hand, all O-SiAlONs ($x=0.05$) sintered with additives had a similar crystalline phase assemblage (they were comprised of a major O-SiAlON phase and a minor $\beta$-$\text{Si}_3\text{N}_4$ phase) but the densities reached were typically too low to carry out relevant measurements of their mechanical properties.

Figure 6.11: Effects of nitrogen pressure on (a) the bulk density and (b) the open porosity of O-SiAlONs ($x=0.05$) with various amount of CaO.
Table 6.2: Crystalline phase composition and relative density of O-SiAlONs with x=0.05.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Nitrogen pressure (MPa)</th>
<th>O-SiAlON</th>
<th>β-Si$_3$N$_4$</th>
<th>α-Si$_3$N$_4$</th>
<th>Si</th>
<th>Relative density*</th>
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<tr>
<td>0 mol% CaO</td>
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<td>13</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td></td>
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<td>13</td>
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<td></td>
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<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>70.1%</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>86.4%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>80.7%</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>85.0%</td>
</tr>
<tr>
<td>4 mol% CaO</td>
<td>0.1</td>
<td>25</td>
<td>12</td>
<td>-</td>
<td>63</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>93</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>87.6%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>95</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>89.8%</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>93</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>96.2%</td>
</tr>
<tr>
<td>8 mol% CaO</td>
<td>0.1</td>
<td>24</td>
<td>16</td>
<td>-</td>
<td>60</td>
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</tr>
<tr>
<td></td>
<td>0.4</td>
<td>97</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>96.3%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>95.2%</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>89.5%</td>
</tr>
</tbody>
</table>

N/A: data not available, *the theoretical density used in the calculation was based on a material composed of a single phase SiAlON and a CaO crystalline intergranular phase.

Figure 6.12 shows the effects of nitrogen pressure on the densification of O-SiAlONs (x=0.2) with various amounts of CaO. In a similar way as in O-SiAlONs (x=0.05), the amount of CaO had a greater influence on the bulk density and the open porosity of O-SiAlONs (x=0.2) than the nitrogen pressures as shown in Figure 6.12. Table 6.3 presents the relative densities of these O-SiAlONs and their crystalline phase assemblage and, in contrast to O-SiAlONs (x=0.05), a large amount of Si remained unreacted in the samples containing high amounts of CaO (typically ≥ 4 mol%). These compositions with 8 mol% of CaO, which were not fully nitried after the nitridation stage, did not form a major phase of O-SiAlON. They were therefore not reported in Figure 6.10b and Figure 6.12. From an addition of 2 mol% of CaO, further increase in CaO led to a decrease in O-SiAlON phase and to an increase in the amount of remaining Si due to early pore closure during the nitridation stage which isolated Si from N$_2$ (see Chapter 4). Therefore only the samples sintered without additives or with a low amount of CaO led to a major O-SiAlON phase.
Figure 6.12: Effects of nitrogen pressure on (a) the bulk density and (b) the open porosity of O-SiAlONs (x=0.2) with various amount of CaO.

Table 6.3: Crystalline phase composition and relative density of O-SiAlONs with x=0.2.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Nitrogen pressure (MPa)</th>
<th>O-SiAlON</th>
<th>β-Si₃N₄</th>
<th>X-SiAlON*</th>
<th>Si</th>
<th>Mullite</th>
<th>Relative density**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mol% CaO</td>
<td>0.1</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>79.9%</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>94</td>
<td>2</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>79.7%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>89</td>
<td>6</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>85.8%</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>78.8%</td>
</tr>
<tr>
<td>1 mol% CaO</td>
<td>0.1</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>89.4%</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>97</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>95.4%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>95</td>
<td>3</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>91.1%</td>
</tr>
<tr>
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<td>1.0</td>
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<td>3</td>
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<td>-</td>
<td>-</td>
<td>89.6%</td>
</tr>
<tr>
<td>2 mol% CaO</td>
<td>0.1</td>
<td>55</td>
<td>12</td>
<td>3</td>
<td>30</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td>0.4</td>
<td>79</td>
<td>21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>91.3%</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>90</td>
<td>3</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>85.9%</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>90</td>
<td>-</td>
<td>1</td>
<td>9</td>
<td>-</td>
<td>95.8%</td>
</tr>
<tr>
<td>4 mol% CaO</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
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<td>-</td>
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<td></td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>8 mol% CaO</td>
<td>0.1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>31</td>
<td>7</td>
<td>-</td>
<td>43</td>
<td>19</td>
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</tr>
<tr>
<td></td>
<td>0.7</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>73</td>
<td>-</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: data not available, *the amount of these phases was roughly estimated as a lack of data in the XRD database did not allow to take them into account in the semi-quantitative analysis, **the theoretical density used in the calculation was based on a material composed of a single phase SiAlON and a CaO crystalline intergranular phase.

O-SiAlONs did not show simultaneously high relative densities and similar phase compositions, it was therefore not relevant to investigate the effects of nitrogen pressure on their mechanical properties and microstructural changes. However it can be noted that when sintered at 1600°C for 4 h, the changes in nitrogen pressures had an influence on the composition, thickness and porosity of the surface of the samples. ESEM micrographs of the outer layer of O-SiAlONs (x=0.2) sintered under various nitrogen...
pressures are shown in Figure 6.13. Under ambient conditions, a thick (~275 µm) and porous layer was formed at the surface of the sample. XRD analysis showed that this layer was composed of a major phase of β-SiAlON and a minor phase of O-SiAlON while the core of the pellet was essentially composed of O-SiAlON (Table 6.3). Under 0.4 MPa the outer layer was thinner (~85 µm), and under 0.7 MPa or higher nitrogen overpressures, this layer was not observable as shown in Figure 6.13 (c and d) and XRD analysis revealed that the surface was indeed essentially O-SiAlON.

![Figure 6.13: ESEM micrographs of O-SiAlONs (x=0.2) sintered with 1 mol% CaO under (a) 0.1 MPa, (b) 0.4 MPa, (c) 0.7 MPa and (d) 1.0 MPa.](image)

The thick porous layer of mainly β-SiAlON which was formed at the surface of the O-SiAlONs (Figure 6.13) and the high mass losses measured in these conditions (see Figure 6.10) both indicate that O-SiAlONs were undergoing severe decomposition under ambient conditions, however all these effects were greatly reduced under higher nitrogen pressures.

### 6.2.3 Conclusions

The post nitridation sintering at 1600°C for 4 h of the SiAlONs nitrided in Chapter 4 has led to the following conclusions:

- The β-SiAlON compositions were comprised of a β-SiAlON phase and of an intergranular phase containing the DyAG additive. Most of the samples achieved relative densities in excess of 90% and similar phase composition, it was therefore possible to measure and compare their mechanical properties and microstructure.
• In β-SiAlONs (z=1), increasing nitrogen pressures led to a decrease in grain size. Such effect was not observed in β-SiAlONs (z=3) (which contained less Si in their starting composition) probably because even under high nitrogen pressures the overall number of seed crystals remained small enough so that the grains did not impede on each other growth.

• The grains in β-SiAlON (z=3) were twice as large as the grains in β-SiAlONs (z=1) and while β-SiAlON (z=1) grains were mainly equiaxed, β-SiAlONs (z=3) were composed of a mixture of elongated and equiaxed grains. These elongated grains did not however have a positive effect on the fracture toughness, suggesting that the intergranular phase and the grain/grain boundary bonding strength was too strong to offer a preferential path to the crack propagation.

• The O-SiAlON compositions were comprised of a major O-SiAlON phase and a minor β-Si$_{3}$N$_{4}$ phase with the exception of compositions targeted to $x=0.05$ without additive and of compositions targeted to $x=0.2$ with large amount of additives. In addition to these differences, there was a great disparity in the relative densities achieved. This was due to the strong dependence of O-SiAlONs on nitrogen overpressures which significantly limited their decomposition.

• Nitrogen pressures had a major influence on the microstructure of the outer layer of O-SiAlONs. They reduced the thickness, the porosity and the compositional change of this layer as well as the mass losses during the sintering.

6.3 Effects of nitrogen pressure on the overall firing process:

different nitrogen pressures during nitriding and sintering

The previous section, where the sintering was carried out at the same pressures as the nitridation, has shown that nitrogen pressures had an influence on the grain growth and on the mechanical properties of β-SiAlONs prepared by silicothermal reduction, however it was not possible to observe such behaviour for O-SiAlONs. The following experiments were aimed at obtaining O-SiAlON materials on which mechanical and microstructural analyses would be relevant, and targeted at isolating the effects of nitrogen pressures during each stage of the firing (i.e. during nitridation and sintering). In order to achieve this, SiAlONs have been nitrided and sintered under different combinations of nitrogen pressures. In one case the SiAlONs have been nitrided under different nitrogen pressures and then sintered under 0.7 MPa of N$_2$ and on the other hand they have been nitrided under 0.7 MPa before being sintered under different nitrogen pressures.
6.3.1 Experimental procedure

The nitriding schedule used in the previous section was mainly designed to observe SiAlONs when they were fired under ambient conditions. In view to observe the effects of nitrogen pressures on the significantly shorter nitriding schedule, the present experiment was realised based on the nitriding schedule described in Chapter 5 (see Figure 5.2). A 4-h hold was added to this schedule to form dense β-SiAlONs ($z=1$) and O-SiAlONs ($x=0.05$) with respectively 2 mol% of DyAG and YAG. In order to reproduce industrial conditions, nitridation and sintering were conducted as a single firing schedule as shown in Figure 6.14. The nitrogen pressures were adjusted during the $5^\circ C.min^{-1}$ ramp between the 1-h hold at 1400$^\circ C$ and the 4-h hold at 1600$^\circ C$ to match the experiment’s requirements described in Table 6.4.

![Heating schedule and nitrogen pressure profile](image)

Figure 6.14: Heating schedule and nitrogen pressure profile. Bold parameters were adjusted according to Table 6.4.

The degrees of nitridation reported in the following experiment, which were measured by mass change (see Section 3.3.3.1), were inclusive of any mass loss suffered by the material during its sintering at 1600$^\circ C$. The degrees of nitridation were therefore expected to be lower after sintering than after nitridation. They were however projected to be higher under 0.7 MPa in both β and O-SiAlONs than under lower pressures where the mass losses were likely to be greater (see Section 5.3.1). As a consequence, 0.7 MPa was used as the reference setting in the following experiments as shown in Table 6.4. Lower degrees of nitridation should indicate either lower amounts of Si nitrided or higher mass losses (as expected when the SiAlONs were fired under lower nitrogen pressures). The phase composition was determined by XRD analysis, Vickers hardness was carried out to evaluate mechanical properties and ESEM was used to observe the microstructure.
Table 6.4: Summary of the combinations of nitrogen pressure.

<table>
<thead>
<tr>
<th>Code</th>
<th>Nitrogen pressures (MPa) during:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitridation</td>
</tr>
<tr>
<td>N1S7</td>
<td>0.1</td>
</tr>
<tr>
<td>N4S7</td>
<td>0.4</td>
</tr>
<tr>
<td>N7S7</td>
<td>0.7</td>
</tr>
<tr>
<td>N7S1</td>
<td>0.7</td>
</tr>
<tr>
<td>N7S4</td>
<td>0.7</td>
</tr>
<tr>
<td>N7S7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

6.3.2 Results and discussions

In Section 6.2, nitrogen pressures were kept identical throughout the whole firing schedule. It was therefore not possible to differentiate at which stage of the firing schedule nitrogen pressure had an effect on the microstructure and grain growth of β and O-SiAlONs. This experiment allows to study the effects that nitrogen pressure has on both stages.

6.3.2.1 Effects of nitrogen pressure on the grain growth of β-SiAlONs

According to Section 6.2.2.1, the effects of nitrogen pressure were more significant in β-SiAlONs (z=1) than in β-SiAlON (z=3) which had a lower Si content. In addition, β-SiAlONs (z=1) exhibited greater hardness and fracture toughness than the β-SiAlONs (z=3) hence only β-SiAlONs (z=1) with 2 mol% of DyAG were used in this experiment.

Figure 6.15 presents the influence of nitrogen pressure on the degree of nitridation of β-SiAlONs (z=1) after nitridation and sintering under the combinations of pressures described in Table 6.4. The influence of nitrogen pressures on the degree of nitridation was typically limited with the exception of the SiAlONs nitrided under 0.1 MPa (N1S7) where full conversion was not achieved (~63%) as shown in Figure 6.15a. The degree of nitridation of β-SiAlONs nitrided under 0.1 MPa (Figure 6.15a) was higher after sintering (under 0.7 MPa) than after the nitridation stage confirming that Si was not fully nitrided after 1 h at 1400°C (end of the nitridation stage). In contrast, the degree of nitridation of β-SiAlONs nitrided under overpressures (0.4 MPa and 0.7 MPa, Figure 6.15) was slightly higher at the end of the nitridation than after sintering suggesting that small mass losses occurred during the latter stage. The highest degrees of nitridation were obtained after nitridation under 0.7 MPa and the following sintering under different nitrogen pressures led to slightly smaller degrees of nitridation (Figure 6.15b). Although this difference was small after 4 h at 1600°C, the degree of nitridation decreased with increasing nitrogen pressures indicating that higher nitrogen pressures limited the mass...
losses (Section 6.4 describes the decomposition of β and O-SiAlONs under different nitrogen pressures and different holding times). The nitrogen pressure of 0.7 MPa led to both the highest degrees of nitridation after nitridation and the lowest mass losses during sintering.

Figure 6.15: Influence of nitrogen pressure on the degree of nitridation of β-SiAlONs (z=1) (a) sintered under 0.7 MPa, and (b) nitrided under 0.7 MPa.

Figure 6.16 displays the bulk density and open porosity of β-SiAlONs nitrided and sintered under the combination of nitrogen pressures described in Table 6.4. The bulk density increased and the open porosity decreased with higher pressures during the nitridation as shown in Figure 6.16a. This was consistent with the increase of the degree of nitridation seen in Figure 6.15a. Upon conversion of Si to Si$_3$N$_4$, the bulk density increased (Si$_3$N$_4$ has a higher density than Si) and the open porosity decreased since the volume increase associated with the nitridation reaction was accommodated within the pore structure. Figure 6.16b shows a slight increase in bulk density along with a slight decrease in open porosity in β-SiAlONs sintered under increasing nitrogen pressures which confirms that higher nitrogen pressures reduced mass losses during sintering.

Figure 6.16: Influence of nitrogen pressure on the bulk density and open porosity of β-SiAlONs (z=1) (a) sintered under 0.7 MPa, and (b) nitrided under 0.7 MPa.
Effects of N\textsubscript{2} pressure on the microstructure and decomposition of β and O-SiAlONs

Figure 6.17: ESEM micrographs of β-SiAlON (z=1) sintered under 0.7 MPa after nitridation under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.

Figure 6.17 shows ESEM micrographs of the core of the pellets following the sintering at 1600°C, and the closed porosity was clearly higher in the β-SiAlONs nitrided under ambient conditions than under nitrogen overpressures. The low degree of nitridation achieved after nitridation under 0.1 MPa then sintering under 0.7 MPa (N1S7) and the absence of Si in these pellets indicates that part of the Si had been lost by volatilisation before it could be nitrided. This led to lower bulk density and higher porosity since the pores could not be filled with Si\textsubscript{3}N\textsubscript{4}. Nitrogen overpressures were therefore essential during the nitriding step to both nitride and densify β-SiAlONs. When β-SiAlONs were nitrided under 0.7 MPa but sintered under various pressures (Figure 6.16b), the porosity in the core of the pellets was similar to Figure 6.17c in any configuration as shown in Appendix I. This shows that when the nitridation was complete after the nitriding step (which was the case under nitrogen pressures of 0.7 MPa, see Figure 6.15b), the nitrogen pressures during the sintering were essentially useful to limit the decomposition of SiAlONs as shown by the ESEM micrographs of the surface of β-SiAlONs (z=1) nitrided under 0.7 MPa and sintered under various nitrogen pressures in Figure 6.18.

Figure 6.18: ESEM micrographs of β-SiAlON (z=1) nitrided under 0.7 MPa and sintered under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.
The crystalline phase assemblage was not significantly affected by the different nitrogen pressures employed during the nitridation and the sintering. The pellets were all comprised of a single crystalline phase of $\beta$-SiAlON. ESEM micrographs (Figure 6.18) of the $\beta$-SiAlONs sintered under various nitrogen pressures show that a surface layer was formed in all $\beta$-SiAlONs. The thickness of this layer decreased, from around 300 $\mu$m to 50 $\mu$m, with increasing nitrogen pressures. XRD semi-quantitative analysis of this layer indicated that it was comprised of $\beta$-SiAlON and Dy-$\alpha$-SiAlON in proportions varying between 60% and 40% in mass. EDS analysis showed that the brightest areas in the outer layers in Figure 6.18 corresponded to Dy-$\alpha$-SiAlON, while the grey areas corresponded to $\beta$-SiAlON. This and the higher open porosity and lower bulk density observed in Figure 6.16b lead to conclude that $\beta$-SiAlONs decomposition into Dy-$\alpha$-SiAlON was accompanied by a mass loss (see Figure 6.15b). This decomposition which was reduced by nitrogen overpressures could be described by the following reaction:

$\text{(6.5) } 567\beta\text{-SiAlON}_2 + 81\text{Dy_2O}_3 + 135\text{Al}_2\text{O}_3 \rightarrow 234\text{Dy}_{9/11}\text{Si}_{219/26}\text{Al}_{93/26}\text{O}_{3/2} \text{N}_{29/2} + 864\text{SiO(g)} + 288\text{N}_2(g)$

While nitrogen pressure had a great influence on the porosity during the nitridation as shown in Figure 6.17, they also had an influence on the microstructure of $\beta$-SiAlONs. Besides the pores which appear black on Figure 6.17, the dark grey areas represent clusters of large grains while the light grey areas are clusters of smaller grains. The different shades of grey were due to the concentration of intergranular phase which contains Dy, a heavy element that appears much brighter than Si, Al, O or N in the ESEM. There was less intergranular phase in the clusters of the larger grains and therefore they appeared darker than the clusters of smaller grains.

![ESEM micrographs of $\beta$-SiAlON (z=1) sintered under 0.7 MPa after nitridation under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.](image)

Figure 6.19: ESEM micrographs of $\beta$-SiAlON (z=1) sintered under 0.7 MPa after nitridation under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.

Figure 6.19 shows the ESEM micrographs of $\beta$-SiAlON (z=1) sintered under 0.7 MPa. At the end of the sintering under 0.7 MPa, the relative amount of larger grains was greater in the $\beta$-SiAlONs that had
been nitrided under 0.1 MPa (Figure 6.17), and the average size of the smaller grains was also larger for samples that had been nitrided under lower nitrogen pressures as shown in Figure 6.19. In contrast, the ESEM micrographs of β-SiAlONs (z=1) nitrided under 0.7 MPa (Figure 6.20) show that when β-SiAlONs were nitrided under 0.7 MPa and sintered under various nitrogen pressures, the relative amount of large grains did not significantly change and the size of the smaller grains remained similar. This indicates that nitrogen pressure had an effect on the grain growth during the nitridation, but did not have an influence on the grain size during a sintering occurring after a nitridation under 0.7 MPa. Nitrogen pressure probably led to the formation of a greater number of Si$_3$N$_4$ seed crystals during the nitridation which in turn led to the finer microstructure in the final SiAlON material. Under higher nitrogen pressures, the nitridation was complete after the nitriding step, explaining why the nitrogen pressure during the sintering did not have an influence on the grain growth. Nitrogen pressures during the sintering would be expected to have an effect on the grain growth only if the nitridation reaction was not complete after the nitriding step. This configuration was not investigated because the material would suffer significant mass losses during the short nitriding schedule used (see Chapter 5), and because the goal of the nitriding stage is to reach full nitridation.

Figure 6.20: ESEM micrographs of β-SiAlON (z=1) nitrided under 0.7 MPa then sintered under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.

Vickers hardness measurements were carried out on all the samples with the exception of the excessively porous pellets nitrided under ambient conditions (N1S7). All the pellets that had a bulk density in excess of 3.0 g.cm$^{-3}$ achieved similar Vickers hardness of around 13 GPa. The pellets sintered under ambient conditions had a slightly lower bulk density and displayed a lower hardness of 11.8 GPa. The relation between hardness and grain size that was observed in Section 6.2.2.1 was not confirmed here. The difference between the β-SiAlONs nitrided under overpressures was not significant to draw any conclusion, and the pellets nitrided under ambient conditions were too porous to rule out the effect of the porosity on the hardness. However the samples achieved hardness of the
same magnitude as that measured in Section 6.2.2.1 in samples with similar amounts of additive showing that the short nitriding schedule did not have a negative influence on the mechanical properties. The hardness was however below the value of 15 GPa typically reported for dense β-SiAlONs [110, 116]. Section 6.4 investigates the possibility of obtaining β-SiAlONs produced by silicothermal reduction routes with the short nitriding schedule with hardness comparable to that reported in literature by modifying the holding time and temperature of the sintering stage.

6.3.2.2 Effects of nitrogen pressure on the grain growth of O-SiAlONs

CaO was used in Chapter 4 in order to alter the porosity of O-SiAlONs during the nitridation, however according to Chapter 3, YAG was the most effective additive to produce O-SiAlONs with low mass losses and high relative densities. Therefore in this section, O-SiAlONs (x=0.05) with 2 mol% of YAG were fired according to the schedule described in Figure 6.14 under the combinations of nitrogen pressures shown in Table 6.4.

Figure 6.21 and Figure 6.22 show the degree of nitridation, the bulk density and the open porosity of O-SiAlONs (0.05) fired under the different combinations of nitrogen pressures described in Table 6.4. Nitrogen pressure had a major influence on the nitridation and sintering of O-SiAlONs as seen in Figure 6.21 and Figure 6.22. In addition to being essentially fully nitrided after nitridation (i.e. after 1 h at 1400°C) under overpressures (Figure 6.21a), O-SiAlONs achieved similar bulk density and open porosity (Figure 6.21b) after sintering under 0.7 MPa (N4S7 and N7S7) indicating that the nitrogen pressures had a similar effect on these two materials once Si was nitrided. The O-SiAlONs nitrided under ambient conditions (N1S7) however displayed negative degrees of nitridation indicating that mass losses, which were greater than the mass gain due to nitrogen pick-up, occurred during the nitridation (Figure 6.21a). They also already had a completely different phase composition after nitridation (they still had a large amount of Si after 1 h at 1400°C as shown in Figure 5.13) that it was not possible to characterise the sintered samples due to their extreme decomposition above 1400°C.
Effects of $N_2$ pressure on the microstructure and decomposition of $\beta$ and O-SiAlONs

Figure 6.21: Influence of nitrogen pressure on (a) the degree of nitridation and (b) the bulk density and the open porosity (dotted line) of O-SiAlONs ($x=0.05$) sintered under 0.7 MPa.

Independently of the combination of pressures employed, the degrees of nitridation after sintering were systematically lower than those measured after the nitridation stage, i.e. after 1 h at 1400°C (Figure 6.21a and Figure 6.22a). This indicates that O-SiAlONs lost mass during the sintering stage. Figure 6.22 shows that bulk density and degree of nitridation increased, and the open porosity decreased, with increasing pressures during the sintering. This concurs with the observations made on $\beta$-SiAlONs that showed that nitrogen overpressure limited the mass losses and the subsequent formation of open pores. This decomposition of O-SiAlONs was typically much greater than that of $\beta$-SiAlONs (see Figure 6.15b), however higher nitrogen overpressures similarly reduced it.

Figure 6.22: Influence of nitrogen pressure on (a) the degree of nitridation and (b) the bulk density and the open porosity (dotted line) of O-SiAlONs ($x=0.05$) nitrided under 0.7 MPa.

In summary, the effects of nitrogen pressure were different depending on which stage of the firing schedule they were used at. Overpressures enhanced the nitridation of Si and prevented it from
reacting with SiO$_2$ and being lost by volatilisation during the nitridation stage (see Chapter 5) whereas they solely reduced the decomposition of O-SiAlON during the sintering.

Figure 6.23 shows the influence of nitrogen pressures on the crystalline phase assemblage of O-SiAlONs ($x$=0.05). Apart from the O-SiAlONs that were nitrided under 0.1 MPa and for which no characterisation was feasible due to the fact that they decomposed and destroyed the crucible during the subsequent sintering, the other samples were all composed of a major phase of O-SiAlON and a minor phase of $\beta$-SiAlON as shown in Figure 6.23. ESEM micrographs of O-SiAlONs ($x$=0.05) nitrided under 0.7 MPa and sintered under various nitrogen pressures are presented in Figure 6.24. They show that all the samples had a porous outer layer and that its thickness decreased with increasing nitrogen pressures. XRD analysis indicated that this layer was essentially composed of $\beta$-SiAlON (the peaks position typically matched those of $\beta$-Si$_3$N$_4$ however, since no internal calibration was used here, and since $\beta$-Si$_3$N$_4$ can be considered as a $\beta$-SiAlON with $z$=0, this phase will simply be called $\beta$-SiAlON). The combined decrease of open porosity and mass loss (Figure 6.22) was consistent with the decrease of the thickness of the outer layer with higher nitrogen pressures. This suggests that O-SiAlONs decomposed into $\beta$-SiAlON at the interface with the atmosphere and that this decomposition was accompanied by a mass loss by volatilisation. This confirms that the decomposition reaction of O-SiAlONs could be written as described previously in reaction (3.23):

$$6\text{Si}_{1.95}\text{Al}_{0.05}\text{O}_{1.05}\text{N}_{1.95} \rightarrow \text{Si}_{5.7}\text{Al}_{0.3}\text{O}_{0.3}\text{N}_{7.7} + 6\text{SiO(g)} + 2\text{N}_2(\text{g})$$

Figure 6.23: Influence of nitrogen pressure on the crystalline phase assemblage of O-SiAlONs (a) sintered under 0.7 MPa, and (b) nitrided under 0.7 MPa.
Effects of \( \text{N}_2 \) pressure on the microstructure and decomposition of \( \beta \) and O-SiAlONs

The thickness of the outer layer (Figure 6.24) varied between approximately 75 \( \mu \)m under 0.7 MPa and 350 \( \mu \)m under 0.1 MPa which represented therefore between 1.4\% and 6.5\% of the total cross section area (the pellets had a 10.5 mm diameter after sintering). XRD semi-quantitative analysis gave relative amounts of \( \beta \)-SiAlON around 10\% in mass (Figure 6.23b) which was higher than what was expected if \( \beta \)-SiAlON was only formed in the outer layer thus suggesting that \( \beta \)-SiAlON was not only located at the surface of the pellet but also in the core of the pellets.

![Figure 6.24: ESEM micrographs of O-SiAlON (x=0.05) with 2 mol\% of YAG nitried under 0.7 MPa and sintered under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.](image)

Figure 6.25 shows the ESEM micrographs of different areas of an O-SiAlON (x=0.05) nitried under 0.4 MPa and sintered under 0.7 MPa. The microstructure of the outer layer (Figure 6.25a) was composed of a great amount of pores and intergranular phase and of large equiaxed \( \beta \)-SiAlON grains while the core of the pellets (Figure 6.25c) was mainly composed of fine needle-like O-SiAlON grains. None of the large \( \beta \)-SiAlON grains were found in the core of the sample, however small hexagonal grains can be observed among the needle-like O-SiAlON structure suggesting that the formation of the \( \beta \)-SiAlON phase had two origins. The large \( \beta \)-SiAlON grains of the outer layer were formed from the decomposition of O-SiAlON while the smaller \( \beta \)-SiAlONs grains in the core of the samples were probably formed from a local compositional shift (i.e. an area poor in SiO).
Figure 6.25: ESEM micrographs of O-SiAlON (x=0.05) with 2 mol% of YAG nitrided under 0.4 MPa and sintered under 0.7 MPa.

Figure 6.26 shows the ESEM micrographs of O-SiAlONs (x=0.05) nitrided under 0.7 MPa and sintered under various nitrogen pressures. There were no differences in the microstructure of the core of these O-SiAlONs nitrided under 0.7 MPa and sintered under various pressures. Moreover, the grain size was clearly smaller than in the O-SiAlONs nitrided under 0.4 MPa (Figure 6.25c). These observations were similar to the ones made for β-SiAlONs, which confirms the influence of nitrogen pressure on the grain growth during the nitridation as detailed in Section 6.2.2.1.

Figure 6.26: ESEM micrographs of O-SiAlON (x=0.05) with 2 mol% of YAG nitrided under 0.7 MPa and then sintered under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.

Similarly as for β-SiAlONs, there was no significant difference in hardness between all the O-SiAlONs prepared in this experiment with the exception of the ones nitrided under ambient conditions which destroyed the crucible. It seems that the grain size had no effect on the hardness since the significantly larger grains observed in O-SiAlONs nitrided under 0.4 MPa (N4S7) did not lead to significantly different hardness. All of the O-SiAlONs measured displayed hardness around 12.7 GPa. This was actually lower than the values typically encountered in literature [8] showing that O-SiAlONs produced by silicothermal reduction route with a short firing schedule did not achieve similar mechanical properties to O-SiAlONs produced in a traditional way. Longer sintering schedules are investigated in Section 6.4 to improve these properties.
6.3.3 Conclusions

The production of SiAlONs by silicothermal reduction route under various combinations of nitrogen pressures during nitridation and sintering has led to the following conclusions:

• Nitrogen overpressures were essential during nitridation to form dense SiAlONs under the short nitriding schedule. They led to higher degrees of nitridation which in turn helped to fill the pores upon the volume expansion associated with the nitridation reaction.

• Nitrogen pressures significantly reduced the decomposition of β and O-SiAlONs during the sintering stage. The materials formed were more homogeneous as the outer porous layer issued from this decomposition was reduced from around 300 µm to 50 µm. β-SiAlON decomposed into Dy-α-SiAlON and O-SiAlON decomposed into β-SiAlON. These two reactions were accompanied by a mass loss which was identified as SiO gas.

• The overall grain growth was clearly altered by nitrogen pressures during the nitridation. A greater number of Si$_3$N$_4$ seed crystals was probably formed under higher nitrogen pressures during nitridation, which led to the formation of a finer microstructure as the grains impeded on each other’s growth.

• It was not confirmed that the change in grain size had any effect on the hardness of the samples. Such changes in hardness observed in Section 6.2 may therefore have been due to differences in closed porosity which is difficult to evaluate with accuracy especially in SiAlON (see Sections 3.3.3.3 and 6.2.2.1).

• β and O-SiAlONs prepared with the short heating schedule achieved hardness comparable to the ones prepared under the longer schedule showing that it is possible to use nitrogen pressures to shorten the overall heating schedule without altering mechanical properties.

6.4 Nitrogen pressure and decomposition of SiAlONs

A combination of silicothermal reduction route and low nitrogen gas overpressure led to the full formation of low cost β and O-SiAlONs in significantly shorter times than with pressureless methods (see Chapter 5). However, the products obtained were not fully dense since no dwelling time was employed once the final temperature had been reached. In the previous sections (Chapter 6), the SiAlONs were sintered for 4 h at 1600°C under various nitrogen pressures. The materials that achieved the lowest mass losses and highest bulk densities were the ones that had been fired under nitrogen overpressures throughout the whole schedule. These samples led to the highest hardness amongst those prepared in this work, however they did not reach the typical values encountered in the literature. Therefore the possibility of producing SiAlONs dense enough to be used for refractory applications
has been investigated. The densification involves the use of dwelling times at the sintering temperatures, however depending on the size of the product, these dwelling times may vary: in research conditions, the products studied are of a rather modest size (ø12 mm x 5 mm) therefore the time required to sinter a product useable as a refractory is likely to be shorter than that needed to densify a product a few millimetres thick. With a view to transfer this technology to the industry, long dwelling times (up to 16 h) have been used. Such times at the sintering temperatures are expected to have effects other than only pore elimination. SiAlONs are known to be susceptible to decompose at high temperature, and since β and O-SiAlONs have different stability regions, they were expected to have different behaviours, for instance O-SiAlONs were likely to show greater decomposition whereas β-SiAlONs are more stable at sintering temperatures.

6.4.1 Experimental procedure
In Chapter 5, β and O-SiAlONs were nitrided under 0.7 MPa with a 5°C.min⁻¹ ramp up to 1400°C, followed by a 1-h hold at this temperature. The SiAlONs were consecutively heated up to 1500°C, 1600°C or 1700°C at 5°C.min⁻¹ and were cooled down upon reaching the final temperature (see Section 5.2). In order to obtain materials with higher density, β and O-SiAlONs have been held at these three temperatures for 2, 4, 8 and 16 h. After each hold the samples were cooled at 10°C.min⁻¹ down to 1000°C, and the rest of the cooling down was done at the natural rate of the furnace. In addition the experiment was conducted at 1600°C under a higher nitrogen pressure of 1.0 MPa.

The raw material preparation and the characterisation of the sintered products were identical to those described in Sections 3.3.1, 3.3.3 and 6.2.1.2. In contrast to Chapter 3, the materials were fired under a single schedule. The mass losses during the sintering were therefore calculated considering that the samples were fully nitrided (see Figure 5.3) upon reaching their sintering temperature (i.e. the temperature at which they were held).

6.4.2 Results and discussions
The purpose of this experiment was to produce SiAlONs with sufficient density to be used as refractory materials. This implied using long dwelling times at the sintering temperatures which could adversely lead to advanced decomposition. The effect of dwelling time on the decomposition of SiAlONs sintered under nitrogen overpressure was investigated and the mechanical properties were characterised to determine if SiAlONs produced by silicothermal reduction under a short nitriding schedule achieved similar properties as SiAlONs produced by pressureless method.
6.4.2.1 Effects of dwelling time on the densification of β and O-SiAlONs

The evolution of the densification of β and O-SiAlONs is shown in Figure 6.27. The sintering temperature of 1500°C was clearly not sufficient to densify the β-SiAlONs since, after 16 h, the bulk density was only of 2.92 g.cm⁻³ (approximately 90% of the theoretical density). However β-SiAlONs achieved relative density in excess of 95% after a 4-h hold at 1600°C as seen in Figure 6.27a. Longer holds or higher temperatures led to higher bulk densities (up to 97% of the theoretical density) but it was not possible to obtain fully dense materials. On the other hand, the open porosity was low, around 1.5%, and they displayed a final shrinkage of only 8% (see Appendix J). XRD analysis showed that these SiAlONs were comprised of a major β-SiAlON phase and traces of Dy-α-SiAlON.

Figure 6.27: Effect of sintering time and temperature on the bulk density (solid lines) and open porosity (dashed lines) of (a) β-SiAlONs and (b) O-SiAlONs.

A hold of 2 h at 1500°C was sufficient to obtain O-SiAlONs with bulk density in excess of 2.71 g.cm⁻³ (approximately 95% of the theoretical density) and open porosity around 2%. While it is generally expected that higher temperatures and longer dwelling times should favour densification, this was not the case in O-SiAlONs. Indeed their bulk density did not increase with holds longer than 4 h (at 1500°C or 1600°C) while their open porosity did increase (Figure 6.27b). For these reasons, it was not possible to densify O-SiAlONs at 1700°C. The samples were typically comprised of a major O-SiAlON phase and a minor β-Si₃N₄ phase.

6.4.2.2 Effects of dwelling time on the decomposition of β and O-SiAlONs

Section 6.3.2 showed that both β and O-SiAlONs decomposed at 1600°C and developed a surface layer which was reduced under higher nitrogen pressures (see Figure 6.18 and Figure 6.24). Figure 6.27 showed that while the densification of β-SiAlONs was improved with increasing the dwelling time at high temperatures, this was not achievable in O-SiAlONs. This suggests that the decomposition...
undergone by β-SiAlONs was not so critical as to hinder their densification at high temperature, and that it was not the case for O-SiAlONs.

**Decomposition of β-SiAlONs**

Figure 6.28 shows the effects of sintering time and temperature on the mass losses and the thickness of the surface layer of β-SiAlONs. The mass losses and the thickness of the surface layer increased when β-SiAlONs were sintered at higher temperatures or for a longer time at the same temperature. Moreover the beneficial effect of nitrogen overpressures on the decomposition observed after 4 h at 1600°C in Figure 6.18 was confirmed as the β-SiAlONs sintered under 1.0 MPa systematically had lower mass losses than the ones sintered under 0.7 MPa (Figure 6.28). In any case, the mass losses were typically small in β-SiAlON as they did not exceed 2% even after 16 h at 1700°C. The evolution of the mass losses as a function of the dwelling time was not linear (Figure 6.28a): in all the sintering temperature/sintering pressure configurations, the mass losses were great in the first 2 hours of the hold, after which they increased only slightly. The evolution of the thickness of the surface layer (Figure 6.28b) was consistent with that of the mass loss confirming that the decomposition was essentially a surface phenomenon. Figure 6.29 shows the ESEM micrographs of the surface layer of β-SiAlONs. This surface layer had a low porosity indicating that the decomposition of β-SiAlON led to the formation of a coherent Dy-α-SiAlON layer. This explains why the mass losses were significant in the first hours of each hold, when the Dy-α-SiAlON layer was formed, and why the decomposition was limited after longer holds. By analogy to oxidation behaviours [117], this could be characterised as a passive decomposition.

![Figure 6.28: Effect of sintering time and temperature on (a) the mass losses and (b) the thickness of the surface layer of β-SiAlONs sintered under nitrogen overpressure.](image-url)
Effects of N\textsubscript{2} pressure on the microstructure and decomposition of β and O-SiAlONs

Figure 6.29: ESEM micrographs of the surface layer of β-SiAlONs sintered under 0.7 MPa for (a) 0, (b) 2, (c) 4, (d) 8 and (e) 16 h at 1600°C.

Decomposition of O-SiAlONs

Figure 6.30 shows the effect of sintering time and temperature on the mass losses and the thickness of the surface layer of O-SiAlONs. Although lower sintering temperatures and higher nitrogen overpressures reduced the mass losses (Figure 6.30a) as with β-SiAlONs, the mass losses increased linearly with the dwelling time for all conditions. The thickness of the surface layer followed the same trend as the mass losses as shown in Figure 6.30b. The major difference with β-SiAlON lies in the porosity of this layer, which was very porous in O-SiAlONs as seen in the ESEM micrographs of their surface (Figure 6.31). This suggests that the decomposition of O-SiAlON did not lead to the formation of a coherent layer.

Higher nitrogen pressures had a significant effect of reducing the rate of decomposition, leading to smaller mass losses and thinner surface layers (see Figure 6.13, Figure 6.24 and Figure 6.30). The decomposition of O-SiAlON into β-SiAlON was accompanied with the formation of SiO gas according to reaction (3.23). Higher nitrogen pressures led to an increase of the partial pressure of SiO at the surface of the sample. This higher partial pressure of SiO was therefore closer to the equilibrium pressure of reaction (3.23), hence reducing the reaction rate. Since the formation of β-SiAlON did not lead to a coherent layer with low porosity, but to a highly porous layer, SiO was always able to diffuse
out of the sample through the open porosity. The decomposition reaction was probably mainly controlled by the partial pressure of SiO at the surface of the samples and by the diffusion of SiO out of the samples. Unlike the β-SiAlON decomposition which was described by analogy to passive oxidation, in this case the behaviour would be better characterised as active decomposition. However, oxidation behaviours controlled by diffusion typically follow a parabolic law [118] and the trend observed in the decomposition of O-SiAlONs appeared to be linear. This may be due to the fact that the dwelling times employed in these experiments only extended up to 16 h, which is longer than typically employed in sintering, but is short compared to the time typically used for oxidation studies [119]. Therefore further experiments at extended times would be necessary to establish whether or not this linearity is a true phenomenon. Increasing nitrogen pressures were a way to limit this decomposition, however the pressures employed in this work (1.0 MPa at 1600°C and 0.7 MPa at 1500°C) were not sufficient to maintain a partial pressure of SiO high enough to fully stop the decomposition.

Figure 6.30: Effect of sintering time and temperature on (a) the mass losses and (b) the thickness of the surface layer of O-SiAlONs sintered under nitrogen overpressure.
Effects of N$_2$ pressure on the microstructure and decomposition of β and O-SiAlONs

**Figure 6.31:** ESEM micrographs of the surface layer of O-SiAlONs sintered under 0.7 MPa for (a) 0, (b) 2, (c) 4, (d) 8 and (e) 16 h at 1600°C.

In an industrial context, it would not be necessary to fully stop the decomposition to produce a satisfactory material. Indeed, in that case, the goal would be to densify the O-SiAlONs before significant decomposition occurs. For instance, after 4 h at 1500°C or 1600°C, the mass losses and the surface layer were small (respectively below 2.5% and 70 µm, Figure 6.30) while the bulk density had already reached its maximum (see Figure 6.27b).

6.4.2.3 Effects of the dwelling time on the mechanical properties of β and O-SiAlONs

Only the most dense materials according to Figure 6.27 were considered for Vickers hardness characterisation, which typically corresponded to SiAlONs sintered for a minimum of 4 h at the sintering temperatures. Figure 6.32 displays the influence of the sintering time and temperature on the Vickers hardness of β and O-SiAlONs.

β-SiAlONs, for which the mass losses were always below 2%, reached their maximum hardness after 8 h at a sintering temperature equal or above 1600°C and their hardness did not increase after longer hold. While the closed porosity is difficult to evaluate with accuracy, comparison of the Vickers hardness is a good way to estimate how much of the closed porosity had actually been eliminated during the densification. Figure 6.32a shows that the Vickers hardness of β-SiAlONs sintered at
1600°C continued to increase until at least 8 h at this temperature, with a significant increase in hardness observed between the 4-h and the 8-h hold. The β-SiAlONs were densified much faster under 1700°C (see Figure 6.27a) and they reached a hardness of 14.7 GPa after the 4-h hold. The Vickers hardness obtained in this work sets these β-SiAlONs well within the 14-17 GPa range typically encountered for β-SiAlONs [3, 15, 116, 120-123] where the hardest materials were typically achieved with the more expensive Si₃N₄ as starting powder.

![Figure 6.32: Effect of sintering time and temperature on the Vickers hardness of (a) β-SiAlONs and (b) O-SiAlONs.](image)

In contrast with β-SiAlONs, the hardness in O-SiAlONs typically did not increase with dwelling time (Figure 6.32b) with the exception of the increase between the 4-h and the 8-h hold at 1500°C which shows that the O-SiAlONs were not yet dense after the shorter hold at this lower temperature. The maximum hardness of 13 GPa was reached after 4 h at 1600°C, or 8 h at 1500°C under 0.7 MPa. Longer dwelling times only led to O-SiAlONs with greater decomposition (see Figure 6.30) but did not lead to products with higher relative density. The Vickers hardness obtained also sets these O-SiAlONs well within the 12-15 GPa range typically encountered for O-SiAlONs [3, 124, 125] although a few harder O-SiAlONs have already been produced (up to 17 GPa) [42].

While beneficial to reduce the decomposition during the sintering, the increase of nitrogen overpressure from 0.7 MPa to 1.0 MPa systematically led to a decrease in hardness (Figure 6.32) for both β and O-SiAlONs. This indicates that it was more difficult to densify SiAlONs fired under 1.0 MPa than under 0.7 MPa. The higher nitrogen pressure at the time of the pore closure led to closed pores containing a higher nitrogen pressure which in turn hindered the densification as the pore elimination then depends on the diffusion of the entrapped gas out of the pellet [89, 95]. The difference between the hardness of the SiAlONs fired under 0.7 MPa and 1.0 MPa was however reduced (Figure
with increasing the dwelling time confirming that the SiAlONs fired under 1.0 MPa only required extra time to densify.

6.4.3 Conclusions

The production of $\beta$ and O-SiAlONs by silicothermal reduction under long dwelling times and low nitrogen overpressures has led to the following conclusions:

- A minimum temperature of 1600°C was required to densify $\beta$-SiAlONs ($z=1$) with 2 mol% of YAG. These $\beta$-SiAlONs reached relative density in excess of 96% after 8 h at their sintering temperature (either 1600°C or 1700°C), which also corresponded to the conditions under which the highest Vickers hardness of 15 GPa was obtained.
- Under nitrogen pressures of 0.7 MPa or higher, the mass losses were always less than 2%. While these mass losses increased significantly in the first hours of each hold, they did not continue to do so with longer holds. The decomposition of $\beta$-SiAlON was a surface phenomenon, and the formation of Dy-$\alpha$-SiAlON created a coherent outer layer with a low porosity which hindered further decomposition.
- It was possible to densify O-SiAlONs ($x=0.05$) at lower temperatures than $\beta$-SiAlONs. Indeed a temperature of 1500°C was sufficient to obtain O-SiAlONs with relative density in excess of 95%, however the highest temperature of 1700°C did not have a beneficial effect on the densification as the decomposition of O-SiAlON became the overwhelming reaction. The highest Vickers hardness of 13 GPa was reached after either 4 h at 1600°C or 8 h at 1500°C.
- At the sintering temperature, O-SiAlONs decomposed into $\beta$-SiAlON and SiO gas. The mass losses and the thickness of the surface layer both increased linearly with the dwelling time at a given temperature. In contrast to $\beta$-SiAlONs, the mass losses did not stop increasing and the surface layer was significantly more porous than the one formed in $\beta$-SiAlONs.
- Each SiAlON phase had a different behaviour regarding the decomposition during sintering. $\beta$-SiAlONs underwent a passive decomposition hence longer dwelling times, if required to densify the products, did not deteriorate the mechanical properties of the material. However O-SiAlONs underwent an active decomposition, and the dwelling time and nitrogen pressure must be carefully selected to obtain a dense material with limited decomposition.
- Higher nitrogen pressures reduced the decomposition probably by leading to an increase of the partial pressure of SiO in the surface layer.
- Higher nitrogen pressures typically led to samples with lower Vickers hardness indicating a higher closed porosity probably due to the extra time required for the entrapped gas to diffuse
out of the samples. After 16 h, the difference in hardness between SiAlONs fired under 0.7 MPa and 1.0 MPa was no longer significant, confirming that only longer dwelling times were required to densify SiAlONs under higher pressures.

6.5 Summary

This experiment has shown that the effects of nitrogen pressure were different depending on which stage of the firing schedule they were used at. Overpressures were crucial during the nitriding stage since they enhanced the nitridation of Si and prevented Si from reacting with SiO₂. Samples that were fully nitrided (through the use of overpressure) after the nitridation stage could subsequently be sintered successfully under any nitrogen pressure without exhibiting any creep behaviour. For these samples (nitrided correctly), increasing the pressure during the second the sintering stage, was beneficial for reducing the decomposition and therefore the formation of open porosity. Without overpressure, the samples suffered great mass losses during the nitridation, and therefore, during the sintering these materials could not achieve high densities even when higher overpressures were employed in this second stage. Nitrogen pressure also modified the microstructure and had an impact on the mechanical properties. The grain size was reduced with increasing pressures, however the changes in mechanical properties were most likely due to changes in the closed porosity rather than the differences in microstructure.

β and O-SiAlONs were prepared by silicothermal reduction with 2 mol% of additives. After nitridation schedules as short as 1 h at 1400°C and sintering for 4 h at 1600°C under nitrogen overpressures, these materials already achieved densities typically above 96% of the theoretical density and hardness around 13 GPa. These characteristics were lower than that typically reported in literature for β and O-SiAlONs however longer sintering times (of 8 h at 1600°C) improved the hardness of β-SiAlONs up to 15 GPa. The behaviour of O-SiAlONs was different as longer times at the sintering temperatures led to greater decomposition which in turn lowered the hardness. The maximum hardness of 13 GPa for O-SiAlONs was therefore obtained after 4 h at 1600°C or 8 h at 1500°C under 0.7 MPa.

While higher nitrogen pressures were clearly limiting the decomposition of both β and O-SiAlONs, these two SiAlON phases had distinct behaviours at high temperatures. The decomposition of β-SiAlONs led to the formation of a low porosity Dy-α-SiAlON surface layer. This coherent layer did not grow beyond 80 μm, even after 16 h at 1700°C under 0.7 MPa of nitrogen, and the mass losses associated with this decomposition did not exceed 2%. This shows that β-SiAlONs products of any size could potentially be produced and densified by silicothermal reduction. The case of O-SiAlONs
was more complex since the decomposition of O-SiAlON into β-SiAlON formed a very porous surface layer whose thickness increased linearly with time. It was possible to form dense O-SiAlONs, however the sintering schedule (i.e. sintering temperature, dwelling time and nitrogen pressure) needed to be carefully selected, knowing that longer dwelling times and higher temperatures may not always lead to more dense materials.

Finally, nitrogen pressures which were of utmost importance in the formation of SiAlONs prepared by silicothermal reduction with a short nitriding schedule (see Chapter 5), may lead to residual pressure in the closed porosity and hinder the densification at higher temperature. It would therefore be necessary to determine the minimum nitrogen pressure during the nitridation that would lead to full conversion of Si to Si₃N₄ such that the residual pressure in the pores is reduced to a minimum. Once most of the porosity has been closed, the nitrogen pressure could be increased to further reduce the decomposition.
CHAPTER 7
OVERALL SUMMARY

Due to the remarkable set of properties that SiAlONs display, they can be used for a wide range of applications. The cost of production for these materials is high and a reduction in costs is therefore a significant driver for research in these materials. One way to do so is to reduce the cost of the raw material. It has been shown that replacing the starting Si$_3$N$_4$ powder by Si leads to greater porosity and a degradation of the mechanical properties, therefore this option cannot be selected for those applications where mechanical properties are of utmost importance. However it can be considered as a viable alternative for applications that are less demanding structurally, and particularly where other properties are paramount (thermal, chemical). Refractory applications are a good example of this, and materials proposed for these kinds of applications are the primary focus of the current research. Using Si as the starting powder (this process is called reaction bonding) is a good alternative to reduce the costs of production while manufacturing a material that still meets the requirements for such applications. In addition to the substitution of Si, halloysite clay can also be employed instead of Al$_2$O$_3$ (and partially Si) in the starting powder (this process is called silicothermal reduction route) to facilitate forming by pressing, slip casting and extrusion. These two methods - reaction bonding and silicothermal reduction - both require Si to react with N$_2$ to form Si$_3$N$_4$ in situ, which can then react with the rest of the powder to form SiAlONs. These two processing routes were compared, in both the initial nitridation stage and the subsequent higher temperature sintering stage. While there was a slight difference in the reaction path during the nitriding stage, there was no significant difference in terms of phase composition and density after the sintering. Consequently, it was concluded that if an alternative route can be used to produce SiAlONs, it is of greater interest to employ the silicothermal reduction route in industrial production as this method allows to benefit from the properties of the halloysite clay during forming.
Most often the starting powder is nitrided (and the SiAlON is formed) prior to the product being pressed into shape. While this method has the advantage of leading to higher degrees of nitridation, it nullifies the beneficial effects of using halloysite and makes the firing of SiAlON a two-step process. As a result, it is of interest to press the starting mixture into shape before the nitridation, thus facilitating the forming and simplifying the production process since only one firing schedule is required. However the feasibility of this second method depends on the ability of N₂ to penetrate the sample and react with the free Si. Powder beds are typically used to prevent decomposition during the pressureless sintering of SiAlONs as they modify the local environment. Under gas pressure, when they were fired without powder bed, SiAlONs showed a higher conversion of Si to Si₃N₄ during the nitridation and lower mass losses during the sintering than when they were fired with powder bed. Nitridation was dependent on the ability of N₂ to penetrate the sample, and powder beds seemed to provide a more difficult access to Si. Low gas pressures (up to 1.0 MPa) can therefore act as a substitute to powder beds which would simplify the production process. The notion of restricted access to Si was confirmed as lower degrees of nitridation were achieved in samples with an open porosity below a certain threshold. It is therefore important for industry to adjust the open porosity of the samples to the thickness of the product and the penetration strength of the gas. This open porosity can be controlled by both the initial compaction of the product and the type of additive.

Under pressureless sintering, since the period of time required to nitride Si is lengthy, long dwelling times and slow heating rates are generally employed. In addition to the obvious limitation this creates in terms of industrial production, the long holding times also lead to mass losses during the nitridation of SiAlON at temperatures close to the melting point of Si. Gas pressure sintering allowed a 90% reduction of the dwelling time from approximately 10h to 1h thus limiting the mass losses, and resulting in high degrees of nitridation (approximately 95%).

In summary, gas pressure sintering with nitrogen pressure less than 1.0 MPa allowed the production of β and O-SiAlONs by silicothermal reduction without powder bed, and the use of firing schedules as short as the ones employed for traditional liquid phase sintering (processing route using Si₃N₄ as the starting powder). These SiAlONs showed the same Vickers hardness as materials prepared by pressureless sintering, but was slightly lower than that achieved by traditional liquid phase sintering. The potential benefits in terms of costs and ease of production make the gas pressure sintering of SiAlONs prepared by silicothermal reduction attractive for refractory applications.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE WORK

8.1 Conclusions

With a view to reducing the cost of production of SiAlONs for their use as refractory materials, the preparation of SiAlONs by alternative routes such as reaction bonding and silicothermal reduction routes in combination with the use of N₂ pressures during both nitriding and sintering stages has led to the following conclusions:

- The long dwelling times at temperatures between 1250°C and 1400°C typically used for the nitridation of SiAlONs under pressureless methods led, even under N₂ pressure, to constant mass loss which was due to the loss of Si from the samples. The degree of nitridation and the composition of SiAlONs with low levels of substitution were consequently less affected by this loss of Si than the SiAlONs with higher levels of substitution.
- The final crystalline phase assemblage and the density of SiAlONs prepared by reaction bonding and silicothermal reduction were similar after sintering under various conditions and with different types of additives for both β and O-SiAlONs.
- While powder beds are used to reduce the decomposition of SiAlONs during pressureless sintering, they should not be used in a one-step process (i.e. with nitriding and sintering carried out consecutively during the same schedule) to produce SiAlONs by reaction bonding or silicothermal reduction as they hinder the nitridation reaction by restricting access to Si. N₂ pressures enhanced the nitridation and prevented decomposition at higher temperature, which therefore allowed the use of a one-step firing schedule and eliminated the need for powder bed.
Conclusions and recommendations for future work

Although early pore closure is attractive since it may lead to a reduction of the time and temperature of sintering, it may be an impediment to the nitridation as it restricts access to Si. For β and O-SiAlONs prepared by silicothermal reduction, a minimum open porosity of 10% was required to obtain full nitridation when gas pressures were employed.

Both β and O-SiAlONs prepared by the silicothermal reduction route reached full nitridation after 1 h at 1400°C under 0.7 MPa of N₂ whereas it was not possible to achieve such high degrees of nitridation when they were nitrided without overpressure due to Si evaporating (through its reacting with SiO₂) and/or melting out of the samples.

Higher N₂ pressures during the nitridation led to SiAlONs with a finer microstructure after sintering due to the higher amount of seed crystals formed during the first stage. However this difference did not affect the Vickers hardness of the samples which was more affected by the porosity than the microstructure.

A minimum temperature of 1600°C was required to densify β-SiAlONs with DyAG additions. The decomposition of β-SiAlON was a surface phenomenon, and the formation of Dy-α-SiAlON created a coherent outer layer with a low porosity which hindered further decomposition.

A temperature of 1500°C was sufficient to obtain O-SiAlONs with high density. Higher temperatures did not necessarily have a beneficial effect on the densification as O-SiAlONs decomposed into β-SiAlON and SiO gas at the sintering temperature. At a given temperature, the mass lost from the pellets and the thickness of the resultant porous surface layer both increased linearly with the dwelling time. Higher N₂ overpressures of 1.0 MPa reduced the decomposition but could not completely prevent it.

The Vickers hardness of the β and O-SiAlONs prepared by silicothermal reduction under gas pressure sintering were approximately 15 GPa and 13 GPa respectively which showed that it was possible to shorten the nitridation stage without having a negative influence on this mechanical property in comparison with that reported in literature.

8.2 Recommendations for future work

In light of the work realised in this thesis, the author would recommend further investigation in the following areas:

- Determination of the minimum N₂ pressure required to fully nitride SiAlON under the short nitriding schedule described in Chapter 5 and of the influence of the size and the green density of the product on the nitridation stage.
The work on the decomposition of O-SiAlON at high temperatures (typically above 1500°C) suggested the existence of a linear relationship between the progression of the decomposition reaction and the dwelling time. This relationship should be further investigated through the use of a wider range of pressures, temperatures and dwelling times. Determination of the exact relationship between decomposition and time could be used as an important predictive tool for the design of heating schedules particularly for larger or complex shape samples as would be experienced in industry.

The possibility of producing a layered refractory product of β/O-SiAlON should be investigated. The core of the product would be O-SiAlON, and the surface layer would be comprised of β-SiAlON. This would allow to benefit from the lower sintering temperature of the O-SiAlONs and the layer of β-SiAlON would provide both a harder material and would help reduce the decomposition of the underlying O-SiAlON.
Appendix A: Calculation of the degree of nitridation in SiAlONs

As explained in Section 3.3.3.1, the degree of nitridation represents the amount of N\textsubscript{2} that has actually entered the structure in comparison with that required theoretically to convert the starting mixture to SiAlON. The following section describes the calculation of the degree of nitridation in SiAlONs prepared by silicothermal reduction.

In this work, additives are generally added to the SiAlON mixture. They may help the nitridation by reacting with other species composing the SiAlON mixture, or even form an intermediate phase with N\textsubscript{2} but in overall they are considered neutral and will not lead to a permanent mass change. The first step consists of calculating the mass of pure SiAlON (i.e. without additive) in the sample which is the initial mass of the sample minus the mass of additive.

\begin{equation}
    m_{\text{pure SiAlON}} = m_{\text{sample initial}} - m_{\text{additive}}
\end{equation}

The second step is the calculation of the amount of water contained in the SiAlON mixture. According to equations (3.3), (3.4), (3.7) or (3.8) and depending on the targeted SiAlON phase, a powder mixture for the formation of SiAlON by silicothermal reduction is composed of a moles of halloysite, b moles of Si (Sicomill, grade 4D) and c moles of AlN (Tokuyama, grade E) or SiO\textsubscript{2} (required to form β or O-SiAlON respectively). One mole of halloysite clay (NZCC, ultrafine-H) of formula (Al\textsubscript{2}O\textsubscript{3}. 2.4SiO\textsubscript{2}. 2.2H\textsubscript{2}O) has 2.2 moles of H\textsubscript{2}O and therefore a pellet of pure SiAlON contains a percentage of water in mass of:

\begin{equation}
    \text{mass\%}_\text{H}_2\text{O} = \frac{2.2a\times M_{\text{H}_2\text{O}}}{a\times M_{\text{halloysite}} + b\times M_{\text{Si(Sicomill)}} + c\times M_{\text{AlN(Tokuyama or SiO}_2)}
\end{equation}

The mass of the sample without water is therefore:

\begin{equation}
    m_{\text{sample initial without H}_2\text{O}} = m_{\text{sample initial}} - \text{mass\%}_\text{H}_2\text{O} \times m_{\text{pure SiAlON}}
\end{equation}
The third step is the calculation of the mass change due exclusively to the nitridation reaction. It corresponds to the amount of $N_2$ that entered the sample:

\[(A.4) \quad m_{N_2 \text{ that entered the sample}} = m_{\text{sample final}} - m_{\text{sample initial without } H_2O}\]

The oxygen content is given in mass percentage of oxygen by the supplier, hence the mass percentage of Si in the silicon powder (Sicomill, grade 4D) is:

\[(A.5) \quad \text{mass\%Si in } Si_{\text{Sicomill}} = 1 - \frac{\text{mass\%O} \times M_{SiO_2}}{2 \times M_O}\]

The mass of Si that should theoretically react is therefore:

\[(A.6) \quad m_{Si} = \frac{b \times M_{Si_{\text{Sicomill}}} \times \text{mass\%Si in } Si_{\text{Sicomill}}}{a \times M_{\text{halloysite}} + b \times M_{Si_{\text{Sicomill}}} + c \times M_{\text{AlN, Tokuyama or SiO}_2}} \times m_{\text{pure SiAlON}}\]

The actual mass gain is to be compared to the theoretical mass gain if the nitridation reaction was fully completed. The mass of $N_2$ expected to enter the structure is related to the mass of Si present in the sample according to equation (2.1):

\[(A.7) \quad m_{N_2 \text{ that can theoretically enter the sample}} = \frac{2}{3} \times \frac{M_{N_2}}{M_{Si}} \times m_{Si}\]

Finally the degree of nitridation is the ratio of the mass of $N_2$ that entered the sample by the mass of $N_2$ than can theoretically enter the sample:

\[(A.8) \quad \text{Degree of nitridation} = \frac{m_{N_2 \text{ that entered the sample}}}{m_{N_2 \text{ that can theoretically enter the sample}}}\]

The calculation of the degree of nitridation in SiAlONs prepared by reaction bonding is similar to the calculation above with the exception of halloysite being replaced by $Al_2O_3$. In this case it is considered that water is not present in the starting mixture.
Appendix B: Distribution of Ca, Y and Zr elements in SiAlONs nitrided at 1350°C

Figure B.1: ESEM micrographs of O-SiAlON (O3.2) nitrided at 1350°C with 2 mol% of (a) CaO, (b) YAG and (c) ZrO₂ and EDS mapping of (a1) Ca, (b1) Y and (c1) Zr.
Appendix C: XRD analysis, the JCPDS file numbers

8H-AlN polytype: 48-1620
15R-AlN polytype: 42-0160
α-Si$_3$N$_4$: 41-0360
Al$_2$O$_3$: 46-1212
AlN: 25-1133
AlN (cubic): 80-0010
β-Si$_3$N$_4$: 33-1160
β-SiAlON (z=1): 48-1615
β-SiAlON (z=4): 76-0598
Mullite: 15-0776
O-SiAlON (x=0.2): 40-0672
Si: 27-1402
Si$_2$ON$_2$: 47-1627
SiO$_2$ (α-quartz): 46-1045
SiO$_2$ (β-quartz): 47-1144
X-SiAlON: 48-0637
Y$_2$O$_3$: 41-1105
YAG: 33-0040
Appendix D: Complementary results from the experimental design

Figure C.1: Influence of design parameters on the relative density of β-SiAlONs (z=1 and z=4) and O-SiAlONs (x=0.05 and x=0.2) prepared by reaction bonding (green) and silicothermal reduction route (black).
Appendix E: Stepwise nitridation of Si in pure Si powder and in SiAlON powder

Stepwise nitridation of Si powder

Figure D.1: Evolution of the nitridation in a Si powder nitrided under flowing nitrogen.

Stepwise nitridation of β-SiAlON powder

Figure D.2: Evolution of the nitridation of Si in a β-SiAlON powder under flowing nitrogen.
Appendix F: Effect of nitrogen pressures on the densification during the nitridation

Table E.1: Comparison of expected porosity and measured open porosity of β-SiAlON under 0.1 and 0.7 MPa.

<table>
<thead>
<tr>
<th>Degree of nitridation</th>
<th>Calculated porosity</th>
<th>Measured open porosity under 0.1 MPa of N₂</th>
<th>Measured open porosity under 0.7 MPa of N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>32.0%</td>
<td>32.0%</td>
<td>32.0%</td>
</tr>
<tr>
<td>14.0%</td>
<td>30.5%</td>
<td>-</td>
<td>30.1%</td>
</tr>
<tr>
<td>14.4%</td>
<td>30.5%</td>
<td>31.4%</td>
<td>-</td>
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<tr>
<td>27.0%</td>
<td>29.2%</td>
<td>29.4%</td>
<td>-</td>
</tr>
<tr>
<td>43.0%</td>
<td>27.5%</td>
<td>30.6%</td>
<td>-</td>
</tr>
<tr>
<td>50.5%</td>
<td>26.7%</td>
<td>-</td>
<td>24.6%</td>
</tr>
<tr>
<td>52.9%</td>
<td>26.4%</td>
<td>31.8%</td>
<td>-</td>
</tr>
<tr>
<td>93.3%</td>
<td>22.2%</td>
<td>-</td>
<td>20.3%</td>
</tr>
<tr>
<td>96.0%</td>
<td>21.9%</td>
<td>-</td>
<td>20.9%</td>
</tr>
</tbody>
</table>

The expected porosity is calculated as if the 22% volume expansion due to conversion of Si to Si₃N₄ was entirely accommodated within the pore structure and was the only factor influencing the porosity (i.e. no extra densification due to grain rearrangement or no mass losses). 32% open porosity has been used as the starting open porosity before nitridation according to the values measured for β-SiAlONs pellets before nitridation.
Appendix G: Evolution of the crystalline phase compositions of β and O-SiAlONs nitrided under a straight ramp of 5°C.min⁻¹

Figure F.1: Crystalline phase composition of β-SiAlON (z=1) nitrided under 0.7 MPa of nitrogen.

Figure F.2: Crystalline phase composition of β-SiAlON (z=1) nitrided under 0.1 MPa of nitrogen.
Figure F.3: Crystalline phase composition of O-SiAlON nitrided under 0.7 MPa of nitrogen.

Figure F.4: Crystalline phase composition of O-SiAlON nitrided under 0.1 MPa of nitrogen.
Appendix H: Crystalline phase composition of $\beta$-SiAlON ($z=3$) after nitridation

Figure G.1: Crystalline phase composition of $\beta$-SiAlON with $z=3$ nitrided under 1.0 MPa of nitrogen with different amounts of DyAG.
Appendix I: Microstructure of $\beta$-SiAlONs fired under different $N_2$ pressures

Figure H.1: ESEM micrographs of $\beta$-SiAlONs ($z=1$) sintered with 1 mol% DyAG under (a) 0.1 MPa, (b) 0.4 MPa, (c) 0.7 MPa and (d) 1.0 MPa.
Figure H.2: ESEM micrographs of β-SiAlONs (z=3) sintered with 1 mol% DyAG under (a) 0.1 MPa, (b) 0.4 MPa, (c) 0.7 MPa and (d) 1.0 MPa.

Figure H.3: ESEM micrographs of β-SiAlON (z=1) nitrided under 0.7 MPa then sintered under (a) 0.1 MPa, (b) 0.4 MPa and (c) 0.7 MPa.
Appendix J: Shrinkage in $\beta$ and O-SiAlONs prepared by silicothermal reduction

Figure I.1: Effect of sintering time and temperature on the shrinkage of (a) $\beta$ and (b) O-SiAlONs.
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