Microstructural and Mechanical Properties of Porous 60NiTi Prepared by Conventional Press-and-sinter Method

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Abstract. An intermetallic nickel-titanium alloy, 60NiTi, comprised of approximately 60 wt.% Ni and 40 wt.% Ti, contains a broad combination of physical and mechanical properties such as high hardness, low elastic modulus, resistance to aqueous corrosion and good biocompatibility. These unique combinations make this alloy an attractive candidate for medical components such as implants and prosthesis, where biocompatible materials with high hardness and low stiffness are typically used. The conventional press-and-sinter method which represents the least complex, most flexible and economic powder metallurgy method was used to produce porous 60NiTi parts suitable for biomedical applications. The effect of sintering holding time on the microstructure and mechanical properties is investigated. The structure of the as sintered parts is quite porous which is beneficial based on the medical point of view. The ultimate compressive strength of the samples is higher than that of the compact human bone and can, therefore, meet the strength demand of implants for general bone replacement applications.

1 Introduction

An intermetallic nickel-titanium alloy, 60-NiTiNOL, composed of approximately 60 wt.% Ni and 40 wt.% Ti contains a broad combination of physical and mechanical properties such as high hardness, low elastic modulus, resistance to aqueous corrosion and good biocompatibility [1-5]. These unique combinations make this alloy an attractive candidate for medical components such as implants and prosthesis where hard and biocompatible materials with low stiffness are typically employed [4].

Implants for bone replacement in medicine should have a structure similar to the organic tissue to be replaced [4]. The ultimate compressive strength of the bone is less than 340 MPa [6], so the implants, which are going to be used for general bone replacement applications, are expected to show higher or at least 340 MPa strength.

The porous structure is beneficial for bone ingrowth and reduces the Young's modulus of the implant, which helps in mitigation of stress shielding phenomenon [4, 7, 8].

Powder metallurgical (PM) processing is an attractive way to produce porous 60NiTi objects of specific shape with adapted properties. In addition, powder metallurgy methods reduce the machining cost since they can provide near-net-shape components [9].

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Conventional press-and-sinter (P&S) represents the least complex, most flexible and economic powder metallurgy method available which also results in parts with good dimensional integrity [5, 10]. Due to these attractive reasons, this processing method is used to manufacture the parts in this research. The effect of sintering holding time on the microstructure and mechanical properties is investigated and the obtained results are compared with the prerequisites of bone replacement implants.

2 EXPERIMENTS

In the following section, the applied parameters to produce the samples by conventional press & sinter and the experiments done for obtaining the results are explained.

2.1 Materials

Table 1 lists the relevant information on the starting powders used in this study. The mean particle sizes for Ti and Ni powders are 27.2 μm and 12.57μm respectively and the morphologies of these powders are shown in Fig. 1. Ti powders are spherical while Ni powders have spiky, needle like texture, which is ideal for powder metallurgy applications.

Table 1. Particle size and impurity content of the starting powders

Powder	Particle size (μm)			O(wt.%)	C(wt.%)	N(wt.%)
	D_{10}	D_{50}	D_{90}			
Ti	11.74	27.2	49.04	0.111	0.004	0.047
Ni*	4.33	12.57	42.50	0.100	0.066	0.021

*Ni powders is produced by carbonyl gas process.

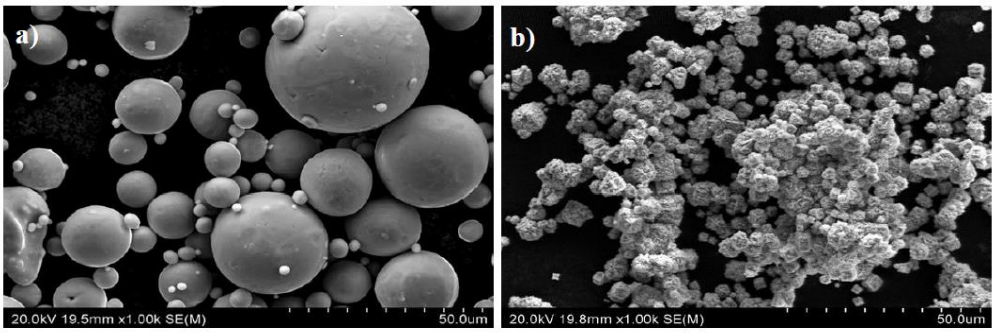

Figure 1. Morphologies of the starting powders (a) Ti (b) Ni

After characterizing the powders, a batch of powder mixture, i.e. Ni/Ti having a nominal composition of 60 wt.% Ni and 40 wt.% Ti, were gently mixed in a ball mill for 45min with a ball-to-powder weight ratio of 3:1.

2.2 Pressing and sintering

After mixing, powder mixtures were compacted into cylindrical discs (20 mm in diameter and 5 mm-thick) and compression testing cylinders (12 mm in diameter and 20 mm-thick) in a single-action steel die with 400 MPa pressure. Subsequently, the green compacts were sintered in a vacuum furnace at $3*10^{-3}$ Pa.

In the first stage, samples are heated till 700 °C by applying 10 °C/min heating rate. While in the second stage slow heating rate of 2 °C/min, from 700 °C till 900 °C was applied. Finally, in the last stage, 10 °C/min heating rate is used again to reach the 1050 °C. Samples were held at 1050 °C for

different holding times of 2 hours, 4 hours and 6 hours and finally furnace cooled with a slow cooling rate. Long term sintering was considered highly impractical in view of any industrial or practical applications for 60NiTi (wt.%), and therefore, in the current study, holding time was varied between 2 to 6 hours only.

2.3 Characterization methods and mechanical tests

Microstructures of the as-Sintered compacts were observed using a scanning electron microscope (Hitachi-su70) equipped with an Energy dispersive X-ray spectrometer (EDX). Scanning Electron Microscope (SEM) images were taken from the cross section of the samples in different magnifications. Standard metallographic procedures were used to prepare the specimen for microscopy, starting with rough grinding using a P220 (European scale) SiC paper and continuing with P360, P800 and P1200 at 300 rpm concluding with vibratory polishing with 3 µm colloidal silica. Finally, the grinded and polished samples were swab-etched with a room temperature aqueous solution of 1 vol.% HF and 10 vol.% HNO3 for 86 seconds [11]. X-ray Diffraction (XRD, Bruker D2 Phaser) was used to identify the generated phases after sintering.

2.4 Mechanical tests

The compressive properties of the 20-mm-thick samples compressed after 1050 °C sintering for different holding times were measured on an MTS 810 universal machine with a displacement rate of 0.01mm/s at room temperature. An alignment cage ensured the parallelism of all samples during testing. The ends of compression cylindrical samples (machined into 5-mm diameter and 7.5-mm height) were polished and smoothed using sand papers, and finally the ends were greased before compression tests.

3 Results and discussion

Results of the microstructural analysis, phase identification and mechanical tests are discussed in the following section.

3.1 Microstructural analysis and phase identification

Phase constituents were identified by using X-ray Diffraction (XRD, Bruker D2 Phaser). Based on the XRD results (Fig.2) austenitic B2 NiTi phase dominates with the presence of minor martensitic B19, intermetallic $NiTi_2$, Ni_3Ti and Ni_3Ti_2 (metastable phase) phases [12]. There is no evidence of Ni or Ti elements in XRD patterns. Pure Ni is carcinogenic and its release in body environment can be harmful [13]. Thus, from the medical standpoint, sintering process has been successful to vanish pure Ni.

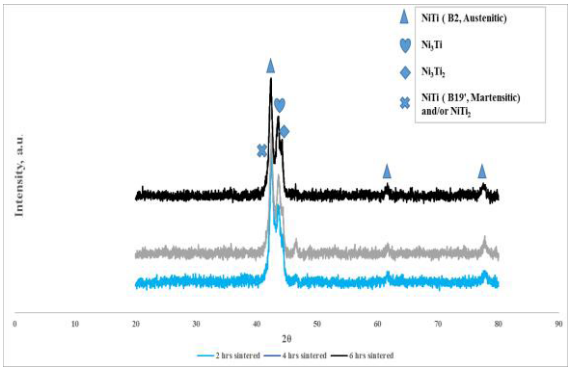

Figure 2. XRD patterns for the sintered 60-NiTi.

SEM images of samples compacted at 400 MPa and sintered at 1050°C for different holding times of 2 hours, 4 hours and 6 hours can be observed in Fig.3. As it can be seen from the SEM micrographs, samples are quite porous, and the majority of pores are interconnected. This is beneficial for bone ingrowth and in addition results in the decrease of stiffness. Decrease in stiffness helps prevention of stress-shielding phenomenon, which is so common in implants and often leads to implantation failure.

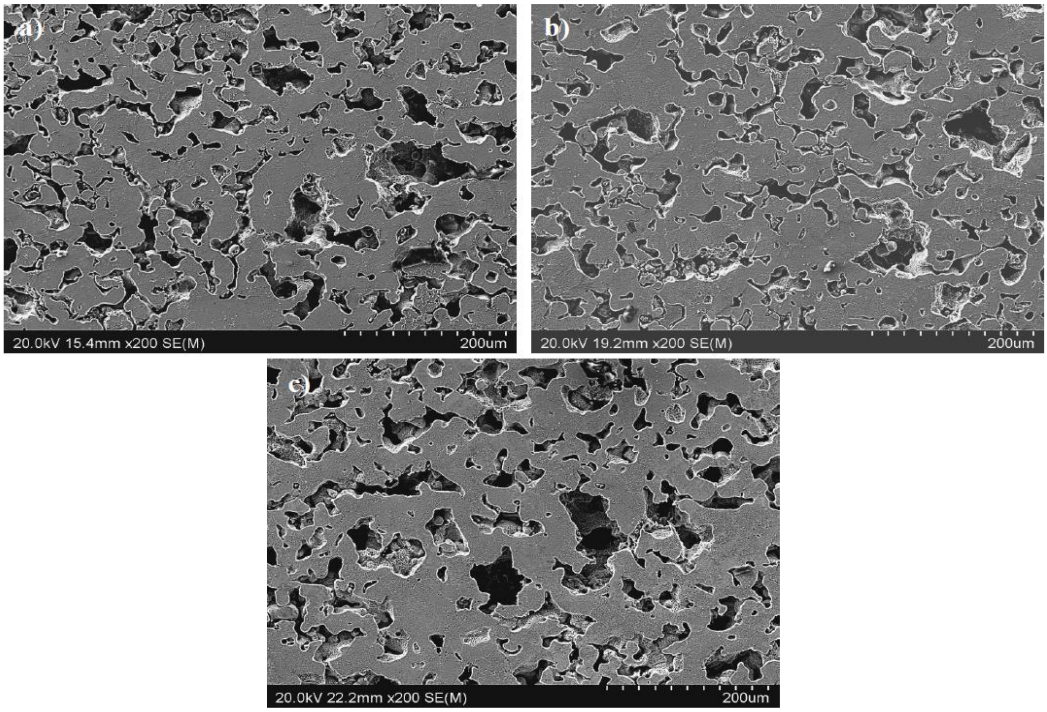

Figure 3. SEM images of 400 MPa compacted samples after sintering at 1050°C C and various holding times (a) 2 hours holding time (b) 4 hours holding time (c) 6 hours holding time

3.2 Mechanical tests

Fracture strength of the sintered samples were measured by applying compression tests. Results of the stress-strain fracture tests can be seen in Fig.4. As it can be observed, all the samples fracture in brittle manner. This can be attributed to the porous structure of the material and existence of sharp pores, which result in stress concentration and local deformation [8]. Furthermore, the increased instantaneous stiffness after linear deformation stage is larger than that of dense materials. Li et al. attributes this phenomenon to the decrease of porosity during compression test and the fact that there is stress concentration on the edge of pores [14].

In addition, the ultimate compressive strength (Fig.5) of the samples is higher than 340 MPa, which is higher than that of the compact human bone and as a result can meet the strength demand of bone implants [6]. The weakest portion in the material rules the strength of a material. In this regard, porosity, pore size and pore shape have significant influence on the strength of porous 60NiTi alloys [7, 8, 15].

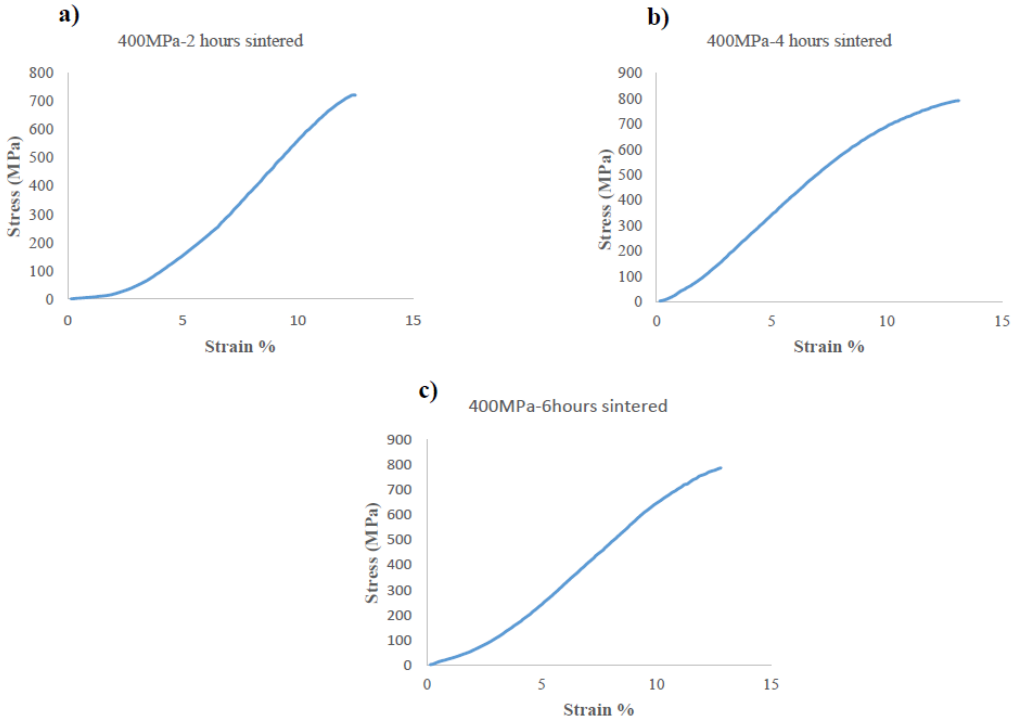

Figure 4. Fracture strength of 400 MPa compacted samples after sintering at 1050°C and various holding times (a) 2 hours holding time (b) 4 hours holding time (c) 6 hours holding time

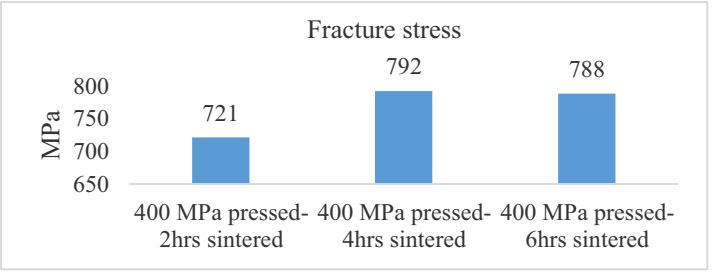

Figure 5. Ultimate fracture stress of the samples under compassion test.

In this stage, the porosity, due to the shrinkage of the pores, decreased with the increase of holding time. As a result, fracture strengths improvement is due to internal porosity reduction, which can result in decrease of the local stress concentrations [15]. However, fracture strength of 6 hours sintered sample is slightly less than the 4 hours sintered one. This means that the mechanical properties of the prepared porous 60NiTi alloy were mainly influenced by the size of the pores and their sharpness in the sample, but not the porosity. As it can be seen in Fig.3, 6 hours sintered samples have sharper pores compared to 4 hours sintered ones. Stress concentration emerges easily at the sharp edges of the pores, which results in the decrease in the strength of the porous materials [8].

4 Conclusions

In this study we synthesized porous 60NiTi alloys from Ni/Ti powder mixtures using a conventional press-and-sinter method. The effects of sintering holding time (2 hours, 4 hours and 6 hours) on mechanical strength of the sintered samples were investigated. Satisfactory results were obtained in all

the cases. Results show that pure carcinogenic Ni has been successfully vanished during sintering process. In addition, the structure of produced parts is quite porous which is good for bone ingrowth. The ultimate compressive strength of the samples is higher than that of the compact human bone, which is lower than 340 MPa. Therefore, the produced samples meet the strength demand of bone implants.

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