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THE OXIDATION REACTIONS OF HETEROGENEOUS
CARBON CATHODES USED IN THE ELECTROLYTIC
PRODUCTION OF ALUMINIUM

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A thesis submitted for the degree of Doctor of Philosophy at the School of
Engineering, University of Auckland, New Zealand

June 1997

This thesis is dedicated with love and gratitude to my parents
for their unceasing and unstinting support.

As a wise chap told my father "PhD stands for Please Help Dad."

ABSTRACT

A technique has been developed that allows the gasification reaction rates of representative samples of carbon-carbon composite materials to be examined. The technique involves heating the sample in a controlled and monitored environment; the product gases of the reaction are then analysed by a mass spectrometer, allowing their identification and quantification. The technique was used to characterise the oxidation reactions of cathode carbons. These materials are composites and so the oxidation reactions of their constituent raw materials were also examined. Surface area was determined for each sample, allowing specific rates of reaction to be determined, normalising surface area effects.

The anodes, cathodes and sidewalls of aluminium smelting cells are made of composite carbon materials comprising filler materials (such as coke, anthracite and graphite) and a binder (almost exclusively coal tar pitch). Whilst the oxidation of anode carbons has received extensive study the oxidation reactions of cathodes have been neglected largely because they have not been a cause of smelting cell failure. However, with the longer lives now being achieved from smelting cells the long term degradation reactions, such as oxidation, will have to be considered. Oxidation of cathodes in the area of the collector bar will increase resistance and affect the heat balance of the cell.

Gasification reactions of carbon materials are frequently characterised using techniques such as thermal gravimetric analysis (TGA). These techniques are accurate for examining such reactions when the sample is of small size and a single carbon type. To characterise composite carbons correlations have been made between the overall oxidation resistance (determined by weight loss) and the ignition temperature of one of the constituent materials (determined by TGA).

The results obtained using the new technique of product gas analysis (PGA) revealed an exponential dependence of oxidation rate on temperature for the carbons examined. At higher rates the limiting condition appeared to be mass transfer through the pores of the sample. Arrhenius plots of reaction rates allowed the activation energy of oxidation to be determined for each material. When the rate was controlled by the chemical reactivity of the material the activation energies determined agreed well with values obtained from the literature.

The two graphites examined had activation energies of 164 and 183 kJ.mol⁻¹, E_a of graphite has been measured in the range 175-281 kJ.mol⁻¹, the latter figure being for a highly pure graphite. For the two anthracites E_a was 113 and 118 kJ.mol⁻¹, literature values have it between 100 and 151 kJ.mol⁻¹. The pitches, used as binders of cathode carbons, had E_a equal to 112 and 123 kJ.mol⁻¹, values from the literature range from 121-165 kJ.mol⁻¹.

Activation energies were determined for the cathode materials, and were clearly influenced by the reactivity of the constituent materials. An amorphous cathode carbon, having nominally 30% graphite, had an activation energy of 121 kJ.mol⁻¹. A semigraphitic cathode material comprising 100% graphite in a pitch binder had an activation energy of 123 kJ.mol⁻¹. The similarity of these values to those for E_a of the pitch and anthracite indicates that the binder phase is having a strong influence on cathode reactivity. These values of E_a accord well with values determined for similar samples, reported in the literature ranging from 114 to 138 kJ.mol⁻¹. A semigraphitised cathode material had an activation energy of 176 kJ.mol⁻¹ in the same range as that of graphite. This sample oxidised significantly less rapidly at all temperatures.

The variation in reactivity of the constituent materials of cathode carbons accounts for the highly selective oxidation behaviour observed in these materials. Porosity development is rapid as binder matrix is preferentially oxidised, leading to an acceleration of oxidation rate with increasing burnoff. The rate begins to decelerate once all the binder matrix has been oxidised, the residue being less reactive than the starting material.

The structure of the materials was quantified using X-ray diffraction (XRD). A peak ratio method was employed, comparing the intensity of the d_{002} peaks of cathode carbons and a standard electrographite. Once effects of cathode porosity had been normalised an excellent correlation between increasing peak intensity ratio and increasing oxidation resistance was found.

ACKNOWLEDGMENTS

“Research is what I’m doing when I don’t know what I’m doing.”

Werner von Braun

This is my opportunity to thank all those people who helped me out when I didn’t know what I was doing and who put me straight when I thought I did.

First and foremost I wish to thank my supervisors Professor Barry Welch and Dr Margaret Hyland. They were each, in their own way, a godsend. Between them they allowed me the independence I needed to work hard and gave me the guidance I needed to work well.

SGL Carbon AG provided the backing necessary for a project of this nature and I would like to thank Dr Schwarz and Dr Hiltmann for the support of the last three years. The mercury porosimetry analysis used in this research was conducted by SGL Carbon and, without that, this jigsaw would be missing an important piece.

Dr Michael Hodgson and Mr David Stringer are workers of miracles that they make appear commonplace. They are attuned to computer mysteries at which the rest of us can only wonder!

The technicians of the University of Auckland are a special breed indeed with apparently unlimited reserves of patience. Gratitude must be extended to each of them but in particular I would like to thank Anthony Skilton for his guidance on the SEM and Steve Stover for all that metallographic know-how.

The Department of Chemical and Materials Engineering is a lively and active research environment thanks, in no small part, to the enthusiasm of the post-graduate students working there. So finally thanks to them and to everyone with whom I have come into contact throughout the course of this research, ideas are infectious.

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ABBREVIATIONS

XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive analysis of X-rays
λ	Wavelength
d	Spacing of crystal planes
θ	Angle
β	X-ray diffraction peak broadening
B	X-ray diffraction peak broadening due to finite crystallite size
b	X-ray diffraction peak broadening due to instrumental factors
\bar{L}	Average crystallite size
L_c	Crystallite stack height
L_a	Crystallite stack width
p	Proportion of disorientated graphite layers in a carbonaceous material
G	Degree of graphitisation of a carbonaceous material
P	Pressure
P_o	Saturated vapour pressure
V	Volume
L_m	Langmuir constant
V_{mono}	Amount of gas required to form a monolayer
A	Area
A_p	Projected area
TSA	Total surface area
ASA	Active surface area
C	$\exp[(\Delta H_A - \Delta H_L)/RT]$
ΔH_A	Heat of adsorption
ΔH_L	Heat of liquefaction
R	Gas Constant, $8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$
N_a	Avogadro's number, $6.02 \times 10^{23} \text{ mol}^{-1}$
r	Radius
γ	Surface tension

τ	Tortuosity
D	Diffusivity
r'	Rate
X	Burnoff, (mass of carbon reacted/original mass) x 100%
t	Time
R_i	Intrinsic reactivity
k_i	Intrinsic rate coefficient
$p(x)$	Partial pressure of gas species x
$n(x)$	Mole fraction of species x
m	Reaction order
ρ	Density
ϕ	Characteristic size
Ψ	Mass transfer coefficient
ARR	Air reactivity residue
ARD	Air reactivity dust
ARL	Air reactivity loss
I	Current
M_r	Molar mass
ϕ	Flow
V_m	Molar gas volume, 24.4651 l.mol ⁻¹
σ	Standard deviation
I_{ratio}	The ratio of intensity of a sample XRD peak to a standard XRD peak
Ea	Activation energy
μ	Linear absorption coefficient
μ/ρ	Mass absorption coefficient