Effects of the chemical composition of coal tar pitch on dimensional changes during graphitization

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Declaration

I, Lay Shoko (student number: 20427166), hereby declare that the work in this thesis with the title: **"Effects of the chemical composition of coal tar pitch on dimensional changes during graphitization"** is my own original work and has not previously been submitted to any other tertiary institution in whole or in part.

Signed at Potchefstroom on this day of ____ September 2013

Lay Shoko

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Abstract

Coal can be converted to different chemical products through processes such destructive distillation. The destructive distillation of coal yields coke as the main product with by-products such as coal tar pitch (CTP). CTP has a wide range of applications, especially in the carbon-processing industries. Typical applications include the manufacture of anodes used in many electrochemical processes, as well as Söderberg electrodes used in different ferroalloy processes. Söderberg electrodes are made from the thermal treatment of Söderberg electrode paste. The Söderberg electrode paste is a mixture of CTP (binding material) and coke/calcined anthracite (filler). Söderberg electrodes are characterised by a baking isotherm temperature. This temperature is located in the baking zone of the Söderberg electrode system. In the baking zone, the liquid paste is transformed into a solid carbonaceous material. Knowing the baking isotherm temperature is essential as it will ensure the safe, profitable and continuous operation of submerged arc furnaces. Thermomechanical analysis (TMA) was used in this study to determine the baking isotherm temperature of CTP samples. The baking isotherm temperature for all samples was found to lie between 450 and 475 °C irrespective of the initial chemical and physical composition of the CTP. TMA was also used to measure the dimensional changes that take place in the binding material (CTP) at temperatures above the baking isotherm. The dimensional changes of 12 CTP samples when heated from room temperature up to a maximum of 1300 °C were measured. The results indicated that all CTP samples shrank by approximately 14% in the first heating and cooling cycle. The second and third heating and cooling cycles gave a small change in dimensions of approximately 2% for all samples. The significant change in dimensions observed for all CTP samples during the first TMA thermal treatment cycle was attributed to the structural rearrangement that takes place within the carbonaceous material. The structural ordering of all CTP samples thermally treated was evaluated by X-ray diffractometry (XRD). XRD is widely used in the

determination of crystallinity/amorphousness of carbonaceous materials, interlayer distance (d-spacing), as well as the degree of ordering (DOG) in a given material. For comparison of structural ordering, XRD analysis was also performed on raw (as-received) CTPs, as well as CTPs thermally treated at 475 and 1300 °C. Prebaked electrode graphite was also analysed. From the XRD results, raw CTP was found to be amorphous with no significant ordering. The interlayer spacing (d_{002}) for all raw CTP samples averaged 3.70 Å, compared to 3.37 Å for prebaked electrode graphite. CTPs thermally treated at 1300 °C had a d-spacing of 3.51 Å. The DOG of raw samples was found to be negative which was indicative of the amorphousness of the raw CTP. The DOG increased with an increase in thermal treatment temperature, as was seen from the DOG of CTPs thermally treated at 1300 °C, which was calculated to be approximately -81% for all 12 samples. The calculated DOG for prebaked electrode graphite was 81%.

Prior to determining the baking isotherm temperature, as well as the changes in dimensions during thermal treatment, the chemical compositions of the 12 CTP samples were determined. In the chemical composition determination, fundamental properties such as softening point (SP), coking value (CV), toluene and quinoline insolubles (TI and QI, respectively) were evaluated. This was in addition to proximate and ultimate analysis. The information obtained from this diverse characterisation showed significant differences in the chemical composition of the 12 CTPs. By making use of multi-linear regression analysis (MLR), it was possible to predict or calculate less commonly determined characteristics (CV, TI and QI) from the more commonly obtained parameters (proximate and ultimate analysis parameters). It was found that MLR could be used successfully to calculate CV and TI, but less so for QI.

Additional chemical composition of CTP was determined by analytical techniques such as Fourier Transform Infra-Red spectroscopy (FT-IR) and Nuclear Magnetic Resonance spectroscopy (NMR). Results from the FT-IR analysis showed that the spectra for all 12 raw CTPs were similar, with differences only being in the FT-IR band intensities. The differences in FT-IR band intensities were supported by NMR analysis data, which gave quantitative information on the different structural parameters found in all CTPs. The structural composition of CTPs changed during thermal treatment, as was shown by the FT-IR analysis performed on raw CTPs samples, CTPs thermally treated at 475, 700, 1000 and 1300 °C, as well as prebaked electrode graphite.

Key words: Graphitization**,** Söderberg electrodes, thermochemical analysis, coal tar pitch, baking isotherm temperature, dimensional changes

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List of abbreviations

Abbreviation	Description
%	Percentage
% A	Percentage Absorbance
% T	Percentage Transmittance
°	Degrees
AAS	Atomic Absorption Spectrophotometer
ASTM	American Society for Testing Materials
ATR	Attenuated Total Reflectance
CP MAS	Cross Polarisation Magic Angle Spinning
CT	Coal Tar
CTP	Coal Tar Pitch
CV	Coking Value
DD	Dipolar Decoupling
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
FC	Fixed Carbon
FIR	Far Infrared
FTIR	Fourier Transform Infra-Red spectroscopy
GC	Gas Chromatography

GC-MS	Gas Chromatography-Mass Spectroscopy
HMB	Hexamethyl Benzene
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
IR	Infrared
kN	Kilo Newton
amu	Atomic mass unit
L	Litre
MAS	Magic Angle Spinning
MATLAB	Matrix Laboratory
MIR	Mid Infrared
MLR	Multi Linear Regression
N	Newton
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance Spectroscopy
PAHs	Poly Aromatic Hydrocarbons
ppm	Parts Per Million
QI	Quinoline Insolubles
SANS	South African National Standards
SP	Softening Point
TGA	Thermo Gravimetric Analysis
TI	Toluene Insoluble

TMA	Thermo Mechanical Analysis
XRD	X-Ray Diffraction spectroscopy

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