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Densification, microstructure and properties of liquidphase sintered silicon carbide materials

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DENSIFICATION, MICROSTRUCTURE AND PROPERTIES OF LIQUID-PHASE SINTERED SILICON CARBIDE MATERIALS

Antionette Can

A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, 2004

DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____

(Signature of candidate)

_____ day of _____2004

ABSTRACT

The relationships between densification and microstructure, and between microstructure and mechanical and electrical properties of liquid phase sintered silicon carbide were studied in detail using hot pressing, gas pressure sintering and ultra–high pressure sintering techniques. Silicon carbide was sintered with 10 mass-% addition of the Y_2O_3-Al_2O_3 system, with various molar ratios.

Hot pressing was carried out at 1925^{o}C under 30 MPa, in argon, for half an hour. Materials were gas pressure sintered at 1925^{o}C, under a final gas pressure of 80 bars (8MPa), in argon, for an hour. Ultra-high pressure sintering was done at ca. 1550^{o}C, under 5.5 GPa pressure, for 15 minutes. The hot pressed and gas pressure sintered materials were subsequently heat treated at 1925^{o}C and 1975^{o}C. Most of the silicon carbide materials were sintered to a density around 99% of theoretical density.

The heat treatment of the hot pressed materials resulted in an increase in density not changing the porosity. The densities of the heat treated hot pressed materials corresponded to the density of the gas pressure sintered materials. This resulted from the difference in composition of grain boundary phases – yttrium silicates in the hot pressed materials and yttrium aluminates in the gas pressure sintered and heat treated materials.

The average silicon carbide grain size in the materials strongly depended on the densification method. In gas pressure sintered and heat treated materials the mean grain size was up to three times higher than that in the hot pressed materials. Grain growth appeared to be higher in the highest alumina-content materials. The heat treatment at 1975 °C resulted in more pronounced anisotropic grain growth.

The ratio of the silicon carbide polytypes of sintered materials and materials heat treated materials at 1925^{o}C, did not change significantly. In the materials heat treated at 1975^{o}C Rietveld analysis revealed a decrease in SiC-6H polytype and an increase in amount of 4H and 15R polytypes, compared to the materials heat treated at 1925^{o}C.This can be attributed to the increase in diffusion rates of aluminium into the SiC lattice at 1975^{o}C.

Segregation patterns were observed in the high yttria content materials, with Y_2O_3:Al_2O_3 molar ratios greater than or equal to two, after gas pressure sintering and heat treatments. This was suggested to be due to the poor wetting of the silicon carbide grains by the yttria-rich grain boundary phase.

On heat treatment, the Vickers hardness of hot pressed materials was found to be increased from 20 to 26 GPa and elastic modulus from 318 to 338 GPa. In addition, the log of the electrical conductivity of liquid phase sintered silicon carbide (measured at 330^{o}C) ranged from 10^{-8} to 10^{-3} with the changes in grain boundary phases observed after the heat treatments.

The grain boundary phase composition also influenced the strength of the materials, The highest strength, 657 $\pm$ 50 MPa, was measured for the hot pressed material containing the YAG phase.

Indentation fracture toughness was mostly influenced by the SiC grain growth during heat treatments. The most significant increase in fracture toughness, the largest being from 3.7 MPa.m$^{1/2}$ up to 5.6 MPa.m$^{1/2}$, was observed in the higher alumina content materials after heat treatment at 1975^{o}C. The increase in fracture toughness was attributed to the presence of a higher amount of platelet-like SiC grains within a broader grain size distribution. These elongated grains increased fracture toughness by increasing crack path deflection and crack bridging.

The electrical properties were evaluated by Impedance Spectroscopy measurements between room temperature and 330^{o}C. The LPS SiC materials can be classified into three groups with different electrical properties. This classification could be related to the grain boundary phases present in the materials. The materials with the lowest conductivity were all hot pressed materials, containing crystalline silicates and amorphous grain boundary phases. The materials with intermediate conductivity include gas pressure sintered materials and a hot pressed material, which contained crystalline aluminates ($Y_3Al_5O_{12}$, $YAlO_3$ and $Y_4Al_2O_9$) in their grain boundaries. The materials with the highest conductivity only contained the aluminates, $YAlO_3$ and $Y_4Al_2O_9$. A pseudo-percolation model of conduction was proposed, in which electrons move along a path which goes through the thinner intergranular layers, with largest nearest neighbour contact.

The temperature dependence of the log of the conductivity of hot pressed and gas pressure sintered materials showed that the conduction mechanism in these liquid-phase sintered silicon carbide materials was variable range hopping conduction of electrons between defect sites. The non-Arrhenius behaviour, together with the observed wide range of peak frequencies, led to the conclusion that the effect of silicon carbide itself was not observed in the impedance spectra. The $1/T^{0.25}$ log conductivity dependence showed that the Cole-Cole arcs are due to insulating grain boundary phases rather than semiconducting SiC.

In the Cole-Cole plots of the hot pressed and heat treated hot pressed materials only the effect of one phase could be observed. In the gas pressure sintered materials and the hot pressed material containing mainly YAG phase, the effects of two phases were seen in the frequency range measured.

Ultra-high pressure liquid-phase sintered silicon carbide materials showed ultra-fine SiC grains, which were highly inter-grown. Segregated grain boundary “core-rim” structures, consisting of an inner core of non-equilibrium yttria and outer rim of equilibrium yttrium silicate were observed in materials containing 4 mass-% to 15 mass-% sintering additives. The hardness of ultra-high pressure sintered 10 mass-% materials increased with alumina-content, from 20 GPa – 22 GPa, and increased with decrease in sintering additive, up to 23 GPa (for the 4 mass-% material).

To my parents, my sisters, my husband, Jarred;
and to Nathan “Nunu-Worm”, whom we will always dearly
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