

7. SUMMARY AND CONCLUSIONS

7.1 Relationships between Densification, Microstructure and Properties

Silicon carbide was liquid-phase sintered using the Y_2O_3 - Al_2O_3 sintering additive system. Most systems studied contained 10 mass-% sintering additives. The Y_2O_3 : Al_2O_3 molar ratio was varied, with four main compositions being studied, namely $1Y_2O_3:4Al_2O_3$, $3Y_2O_3:5Al_2O_3$, $1Y_2O_3:1Al_2O_3$ and $4Y_2O_3:2Al_2O_3$. These different compositions were hot pressed, gas pressure sintered and ultra –high pressure sintered. Hot pressing was done at $1925^{\circ}C$, under 30 MPa, in argon, for half an hour. Gas pressure sintering was carried out at $1925^{\circ}C$, under a final gas pressure of 80 bars in argon atmosphere for 1 hour. Ultra-high pressure sintering was done at ca. $1550^{\circ}C$, under 5.5 GPa pressure, in vacuum, for 20 minutes. The hot pressed and gas pressure sintered materials were additionally heat treated at $1925^{\circ}C$ for three different holding times (1.5 hours, 5 hours and 8hours) and at a higher temperature, $1975^{\circ}C$, for 5 hours.

Because of the non-equilibrium sintering conditions in ultra-high pressure sintering, these materials were dealt with separately and not directly compared with the results of the hot pressed and gas pressure sintered materials.

The following conclusions were made:

- 1) Densification kinetics measured during hot pressing showed that the densification of the higher Y_2O_3 -content compositions was slower at lower temperatures. This was related to the melting points of the different compositions in the Y_2O_3 - Al_2O_3 - SiO_2 system. These reduced densification

rates in higher Y_2O_3 -content materials, was also observed during gas pressure sintering. The uniaxial pressure in hot pressing was able to fully densify the high Y_2O_3 -content materials, whereas these materials could not be fully densified (more than 99%) during gas pressure sintering. She *et al.*⁽¹⁴⁹⁾ observed similar decrease in densification during pressureless sintering with an increase in Y_2O_3 in their Y_2O_3 - Al_2O_3 sintering additives. They attributed it to the increased eutectic temperature with the higher Y_2O_3 -content, which results in less liquid formation during densification.

2) Higher Y_2O_3 -content in the material, also resulted in segregated patterns being observed in the gas pressure sintered and post-sintering heat treated materials, which implies that the more yttria-rich phases with an Y_2O_3 : Al_2O_3 molar ratio higher than 2, does not wet the silicon carbide.

3) Gas pressure sintering and post-sintering heat treatments of hot pressed materials, resulted in an increase in density, elastic modulus, hardness and electrical dc conductivity, when compared to the hot pressed materials. This was due to the observed change in grain boundary phases from crystalline and amorphous silicate phases in hot pressed materials to yttrium-aluminates in gas pressure sintered and post-sinter heat treated materials. Rietveld quantitative phase analysis calculations confirmed these changes in grain boundary phase composition. The change from silicates to aluminates, confirmed the evaporation of SiO in gas pressure sintered and heat treated materials. The presence of traces of Si in the GPS and heat treated materials and a shift in the Y_2O_3 : Al_2O_3 ratio also indicated some decomposition of Al_2O_3 in these materials.

4) Post-sintering heat treatments also resulted in an increase in silicon carbide grain size. Heat treatments at 1925°C , resulted in grain growth, and after an 8 hour heat treatment a wide distribution of grain sizes with large platelet-like grains was observed. The heat treatments at 1925°C did not result in a significant change in SiC polytype content.

Diffusion of Al into the SiC is suggested to stabilise 4H and 15 R polytypes⁽⁴⁾ and to promote anisotropic grain growth. Since both of these microstructural changes were not observed to be significant at 1925°C, it was suggested that diffusion of Al into the SiC during heat treatments at 1925°C is not significant, although TEM studies are needed to confirm this.

Post-sintering heat treatment at a higher temperature, 1975°C, was needed to increase the diffusion of Al into the SiC lattice. Evidence of increased Al diffusion into the lattice was given by the significant increase in the SiC-4H and 15R polytype content, and the appearance of broader SiC grain size distributions, with an increased amount of platelet-like SiC grains. Observations in the literature support presented arguments, namely that higher temperature (higher than 1925°C) is needed for increased Al diffusion into the SiC lattice and consequent microstructural changes^(41,111).

5) In the literature most work had been focussed on showing the importance of the β to α SiC phase transformation for the increased formation of platelet-shaped large SiC grains. Kim *et al.*⁽¹³⁾ showed that it was possible to achieve this using only α -SiC, if the silicon carbide grains in the starting powder was below a critical grain size. The present results are in agreement with Kim *et al.*'s work. To create platelet-like grains sufficient grain growth has to occur. In the case of Kim *et al.*'s work, the anisotropic grain growth was accelerated by reducing the SiC grain size. In the present work this was achieved by increasing the temperature.

6) Fracture toughness of the materials appeared to not be as sensitive to grain boundary phase changes as hardness was, since fracture toughness of the HP and GPS materials were similar. The fracture toughness was also not as sensitive to the increase in grain size, as it was to increase in fraction of higher aspect ratio silicon carbide grains. Studies of the crack path in selected materials, showed an increase in crack

deflection and crack bridging in the heat treated materials. The HT3GP1Y4Al material had increased grain size and some platelet formation, compared to the un-heat treated materials GP3Y5Al and GP1Y4Al, which gave rise to an increase in fracture toughness, from 3.5 MPa.m^{1/2} in the gas pressure sintered to 4.7 MPa.m^{1/2} in the HT3GP1Y4Al material. However, the most significant increase in fracture toughness was observed for materials intensively forming platelet-like grains during heat treatment. Increase in fracture toughness observed from 3.7 MPa.m^{1/2} in the HP3Y5Al material to 5.6 MPa.m^{1/2} in the HT5HP3Y5Al. All the other sintered materials, also showed a more significant increase in fracture toughness after heat treatment at 1975°C in comparison to the heat treatment at 1925°C.

7) Although the fracture toughness appeared to be only dependent on the silicon carbide grain size distribution and not the grain boundary chemistry, there is a relationship between fracture toughness and grain boundary chemistry after heat treatment. This is caused by the fact that the grain growth of the heat treated materials appear to be dependent on the grain boundary composition. Higher grain growth and more “in-situ” toughened microstructures are observed for the materials with higher alumina content (1Y₂O₃:4Al₂O₃ and 3Y₂O₃:5Al₂O₃).

8) There appears to be a maximum in the strength observed for the hot pressed material containing only YAG as crystalline grain boundary phase. This is in agreement with other work in the literature⁽¹⁰⁸⁾. A stronger composition dependence of strength is observed in the GPS materials, where strength decreased with increase in Y₂O₃:Al₂O₃ ratio, due to higher defect sizes resulting from reduced densification of these materials.

9) The hardness appeared to be most influenced by the type of grain boundary present in the 10 mass-% LPSSiC material. The hot pressed materials with a silicate grain boundary showed a lower hardness than the

dense gas pressure sintered and the heat treated materials with aluminates at the grain boundary. The hardness decreased after heat treatment at higher temperature (1975°C) due to porosity from the decomposition of aluminates in the materials.

A strong reduction of the hardness measured at 1000 and 1200 °C in comparison to room temperature hardness was observed in the HP3Y5Al material. This is most likely due to softening of the grain boundary phase, the amorphous silicates in particular. No references of high temperature hardness measurements on LPSSiC materials were found in the literature but SSiC materials show a nearly constant hardness up to 1200- 1400 °C.

10) Only a few authors/groups have published work in the literature that describe electrical measurements (impedance spectroscopy in particular) on LPSSiC materials, with the $Y_2O_3-Al_2O_3$ system in particular. None of these groups did temperature dependence measurements on the LPSSiC materials, which was done in this project. The temperature dependence of the materials were determined to be $1/T^{0.25}$, which is characteristic of variable range hopping^(191,192) of electrons from one defect site to the other, indicating that insulating rather than semiconducting phases are giving rise to the Cole-Cole arcs.

The non-Arrhenius conductivity behaviour, and the wide range of excitation energies and characteristic frequency values, led to the conclusion that most probably none of the phases observed in the impedance arcs is silicon carbide, but most likely a second grain boundary phase or groups of grain boundary phases, with different distinct patterns of electrical behaviour. This is in contradiction with other results in the literature⁽¹⁶⁻²⁰⁾, who claim that silicon carbide is giving rise to the impedance arcs. It is proposed that a higher frequency is required to observe the effects of the silicon carbide, than what is available with current instrumentation⁽²¹⁶⁾.

11) Three groups of materials with different electrical conductivities and also different grain boundary phases were observed. This is evidence of the fact that the grain boundary phase has the major influence on the conductivity of these LPSSiC materials. The group of materials with the lowest conductivity were all hot pressed materials containing silicates in their grain boundaries; the group of materials with intermediate conduction were mainly GPS materials and the HP3Y5Al material- all containing crystalline aluminates (YAG, YAP and YAM) in their grain boundaries. The group of materials with the highest conductivity, were all heat treated HP materials, with the YAM and YAP phases in their grain boundaries.

12) A pseudo-percolation model was proposed to describe the conduction of electrons in LPSSiC materials. In this model the favoured path of electrons is through the thinner intergranular layers, with largest areas of nearest neighbour contact. Three factors were suggested to contribute to the increase in conductivity of the HP materials when they are heat treated:

- (i) the formation of presumably more conducting aluminates,
- (ii) the decrease in number and maybe thickness of separation layers between the conducting silicon carbide grains, increasing in contact area, and
- (iii) the removal of amorphous and crystalline silicates.

13) In the Cole-Cole plots of the hot pressed and heat treated hot pressed materials, only one arc was observed. i.e. only the effect of one phase could be observed in the frequency range measured. The GPS materials and the one HP material HP3Y5Al, yielded double arcs in the Cole-Cole plots.

The double Cole-Cole arcs observed for the HP3Y5Al and GP3Y5Al materials, in which only the YAG phase was identified as a crystalline phase, suggests that the contribution of amorphous phases (most likely silicates) present in their grain boundaries was being observed. Amorphous silicates in the other GPS materials could give rise to an arc in their Cole-Cole plots.

14) UHP materials sintered with 4 mass-%, 10 mass-% and 15 mass-% additives were fully dense. As expected, sintering at lower temperature (ca. 1550°C) using ultra-high pressure, resulted in a very fine grained non-equilibrium microstructure. However, the hardness values of the UHP LPSSiC material were not higher than that of the HP and GPS materials.

The fine-grained intergrown microstructures meant that quantitative microstructural analysis, both Rietveld and Image analysis could not be done on the UHP materials. High strain in the materials contributed to the broadening of the XRD peaks. A mixture of yttrium silicates, as observed in the HP materials, and aluminates, as seen in the GPS and heat treated materials, were also observed in the UHP materials. YAG was not observed in any of the UHP materials.

15) Special features observed in all the UHP microstructures were the large SiC grains scattered through the material and the core-rim structures of segregated grain boundary regions. These core-rim structures probably arise because the sintering temperature is not high enough, and sintering time not long enough for all the sintering additives to dissolve, and the Y_2O_3 in particular precipitates as a non-equilibrium phase, with the equilibrium yttrium silicate phases precipitating onto the Y_2O_3 , forming the rim of the structure⁽¹⁶⁹⁾. The core regions were observed to become smaller as the Y_2O_3 content in the material decreased.

In the high alumina content materials, a higher fraction of large SiC grains were observed. In these materials, each very large SiC grain was surrounded by a crack. These cracks most probably formed around the large SiC grains due to the presence of high residual tensile stresses, which were probably generated during rapid cooling.

16) The higher alumina content, 10 mass-% material, UHP1Y4Al, had a higher hardness than the other 10 mass-% materials. Hardness of the UHP LPSSiC materials increased, and fracture toughness decreased with decrease in grain boundary content (15-mass%, 10 mass-% and 4 mass-%). These results provide some insight into the behaviour of the liquid phase/ sintering additives during application of ultra-high pressures, since no other work has been reported in the literature in which silicon carbide is ultra-high pressure sintered with sintering additives.

In conclusion, a great deal of insight has been gained into the relationships between densification and microstructure, and consequent microstructure-properties relationships. In particular, the importance of the influence of the grain boundary phases, successfully quantified by Rietveld analysis arising from the different densification techniques, on the properties of the LPSSiC materials, was emphasised.

7.2 Future work

There are a number of experiments which could be done to gain even more understanding of the results obtained in this project.

(A) The hypothesis, that segregation of grain boundary material in the high yttria-content materials on heat treatment, was due to poor wetting of the YAM phase on the SiC grains, needs to be tested. An investigation into wetting characteristics of various phases, such as YAG, YAM and

YAP on silicon carbide, would be useful to provide further insight to formation of segregations.

(B) Further heat treatment experiments could be done. Heat treatment at 1925°C appears to be too low for significant anisotropic grain growth. The 5 hour heat treatment at 1975°C, did improve fracture toughness of the LPSSiC materials, but the porosity caused decrease in hardness. This suggests that perhaps heat treatments should be tried at 1950°C for different times and at 1975°C, for a shorter time. Hardness and fracture toughness could then be measured, to see if the same increase in toughness can be achieved, with less mass loss. i.e. optimize heat treatment conditions in order to improve both hardness and fracture toughness.

(C) TEM studies would be useful to determine the extent of Al-doping in the silicon carbide lattice. It would be useful to compare the HP, GPS and especially a material heat treated for 8 hours at 1925°C and compare these results to that of a material heat treated at 1975°C for 5 hours. Correlating these results to SiC polytype content and grain growth would prove or disprove the hypothesis that higher temperature (1975°C) was needed for the increased activation of Al-diffusion into the silicon carbide lattice. The status of Al substitution in the SiC lattice would also be useful in interpreting electrical data.

(D) The electrical measurements of heat treated GPS materials to observe if there is also a large increase in conductivity as was observed with the heat treated HP materials.

(E) Any effect of the suspected Al-doping in the HT5 materials (heat treated at 1975°C) could be studied by doing impedance spectroscopy studies of these heat treated materials.

(F) Further experiments have to be done to verify the conduction mechanisms and the reasons of the arcs appearing in the impedance spectroscopy. Especially a detailed TEM investigation of the measured materials can give some additional proofs of the mechanisms.

(G) Further optimization work on the UHP material sintering cycle is required to produce samples with less cracks (delamination) in them. A slower cooling rate may help to reduce internal stresses and delamination in the material.