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Relationships between microstructure and electrical properties of liquid-phase sintered silicon carbide materials using impedance spectroscopy

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Abstract

A range of liquid-phase sintered silicon carbide (LPS SiC) materials were produced, using hot pressing and gas pressure sintering. The densified materials were further heat-treated at the sintering temperature, 1925 °C. The ac electrical properties were measured and impedance spectroscopy used between room temperature and 330 °C. The investigated LPS SiC materials could be classified into three groups, with different electrical properties, which could be related to the grain boundary phases present in the materials. The temperature dependence of the log of the dc conductivity of hot pressed (HP) and gas pressure sintered (GPS) materials, $1/T^{0.25}$, showed that the conduction mechanism in these LPS SiC materials was variable range hopping conduction of electrons between defect sites. This non-Arrhenius behaviour showed that SiC did not contribute to the impedance spectra, which could be shown to be due to the aluminates and silicates that are known to be present from XRD results.

Keywords: Hot pressing; Electrical conductivity; Impedance; SiC; Conductivity–temperature dependence

1. Introduction

LPS SiC as a structural ceramic has only been studied extensively for the past 10 years. SiC is a well-known semiconductor material, of which a lot is known in terms of the electrical properties of single crystals of SiC.[1] Understanding of the relationships between the microstructure and the electrical properties of LPS SiC materials is very limited. Volz et al.[2–4], Martin, Adler and Ihle[5,6,7] have studied the electrical properties of dense LPS SiC with the Y_2O_3–Al_2O_3 sintering additives system. However, none of these groups did conductivity–temperature dependence measurements. The aim of this work was to investigate some relationships between composition, microstructure formation and electrical properties of hot pressed and gas pressure sintered LPS SiC materials.

2. Experimental

Commercially available powders alpha-SiC (UF-15, H.C. Starck), Y_2O_3 (fine grade, H.C. Starck) and Al_2O_3 (AKP-50, Sumitomo) were used as the starting materials.

Compositions with 10 wt.% sintering additives and varying mole ratio (Y_2O_3:Al_2O_3—1:4, 3:5, 1:1, 4:2 and 4:1) were milled in a planetary ball mill for 2 h. Materials were hot pressed (HP) at 1925 °C, 30 min and gas pressure sintered (GPS) at 1925 °C for 60 min at final Ar gas pressure of 80 bar, in graphite crucibles. Additional heat treatments were carried out on the HP samples at 1925 °C for 1.5, 5 and 8 h, in graphite crucibles.

Density was measured using the Archimedes method. Phase analysis was carried out using, RD7 (Seifert-FPM) XRD apparatus and calculated quantitatively using Rietveld analysis (Autoquan). Four-point impedance spectroscopy (impedance versus frequency (ω) measurements) was done using a *Solartron SI 1260 Impedance Analyzer* for samples with total resistances less than 100 MΩ and using a two-point *Solartron SI 1260/Novocontrol broad band dielectric converter (BDC) system* for samples with higher resistances. The complex con-

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ductivity of each sample σ^* ($\sigma' - \mathbf{i}\sigma''$) is calculated from the measured complex impedance Z^* ($Z' + \mathbf{i}Z''$) to which it is related by $\sigma^* = \mathrm{I}/(Z^* \times G)$ where G is the sample geometric factor (area/thickness).

3. Results and discussion

Rietveld calculations of the SiC polytypes showed that there was no significant difference in the SiC polytype ratios between the different as-sintered materials, despite the fact that Al is expected to stabilize 2H and 4H.[8] In hot pressed materials the formation of crystalline silicates was observed. In GPS materials, silicates did not form, instead aluminates formed. This can be related to the differences in densification between hot pressing and gas pressure sintering: in hot pressing densification is much faster and therefore less decomposition occurs, in comparison to gas pressure sintering.[9]

A pseudo-percolation model is proposed to describe the conduction path of electrons in the LPS SiC materials. In the ideal pseudo-percolation model the electrons follow the path of least resistance through the maximum number of thin intergranular layers, but cannot avoid some thicker intergranular layers, which probably dominate the resistance (illustrated in Fig. 1).

Fig. 2 shows that the conductivity results at all frequencies separate into three broad conductivity bands (which are indicated in the caption), with different magnitudes and somewhat different dispersive behaviour. XRD results show that there is a relationship between the conductivity curves and, from X-ray analysis, the following crystalline grain boundary phases were found in the different materials:

(1) The lowest conductivity materials are all hot pressed materials, containing silicates and alumina.
(2) The materials (in the broad middle band) with intermediate conductivity contain aluminates: YAG in some materials and YAG, YAP and YAM in others.
(3) The materials with the highest conductivity (the heat-treated materials) contain only the aluminates YAP and YAM.

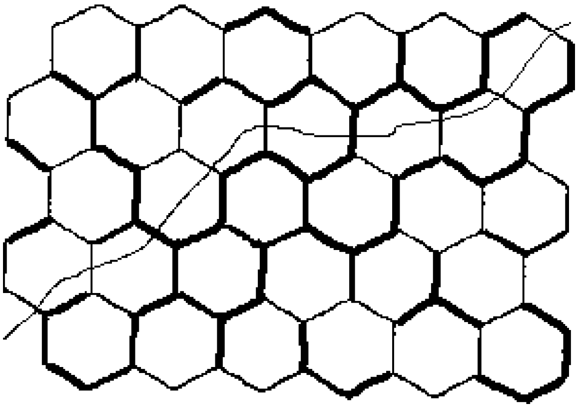

Fig. 1. Illustration of one of the proposed most favourable paths for conduction electrons in the pseudo-percolation model.

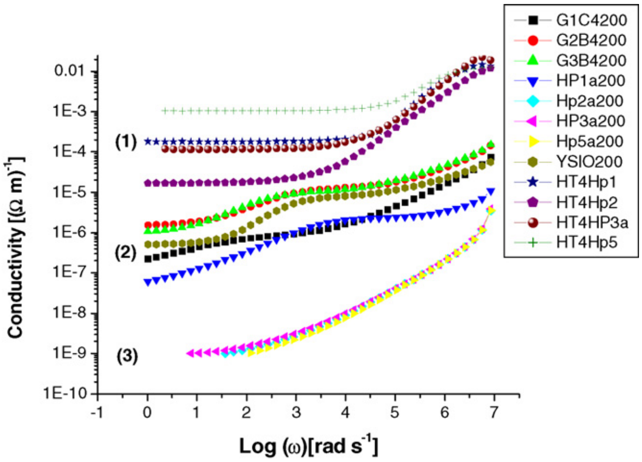

Fig. 2. Graph of the electrical conductivity as a function of the log of angular frequency at 200 °C. In the labels of this figure: 1 = 3Y5Al, 2 = 4Y2Al, 3 = 1Y1Al, 4 = 4Y1Al, 5 = 1Y4Al and groups:

(1) Heat-treated HP: aluminates and grain growth,
(2) GPS + HP: YAG aluminates,
(3) HP: silicates and small grains.

This supports the proposed pseudo-percolation model in which the electrical conductivity of the phases making up the layers separating the silicon carbide grains, play the major role in the bulk conductivity of the material.

For contiguous sintered semiconductors log(conductivity) $\propto$ $1/T$,[10] which is not observed in the investigated LPS SiC materials. The actual temperature-dependence of the log of the low frequency (dc) conductivity phases (with log conductivities less than 10^{-5}) were found to be predominantly $T^{-0.25}$. This is typical for many insulating materials in which the conduction mechanism is three-dimensional variable range hopping.[11,12] The electrical conduction through the liquid-phase sintered silicon carbide material therefore occurs by electrons "hopping" from one impurity site to the next, in the multi-phase grain boundary layer. This supports the argument that there is most likely not a continuous path of silicon carbide grains, as assumed by other authors.[2–6] Even if a core–rim structure exists in the SiC grains, as reported by Sigl and Kleebe[14], this results in the core SiC being surrounded by a doped SiC layer, which is still very conducting compared to the grain boundary material. Therefore this would have a minor influence on the pseudo-percolation path chosen by the electrons. The arcs observed in the Cole–Cole plots (an example of which is given in Fig. 3) are therefore not due to silicon carbide (which is very conducting), but due to grain boundary phases in the LPS SiC materials. It is known that a higher frequency is required to observe the effects of the more highly conductive silicon carbide, than which was available with current instrumentation.[13]

Three factors are proposed to contribute to the increase in conductivity of the HP materials when they were heat-treated (observed in Fig. 2):

(i) The formation of, presumably more conducting, aluminates.

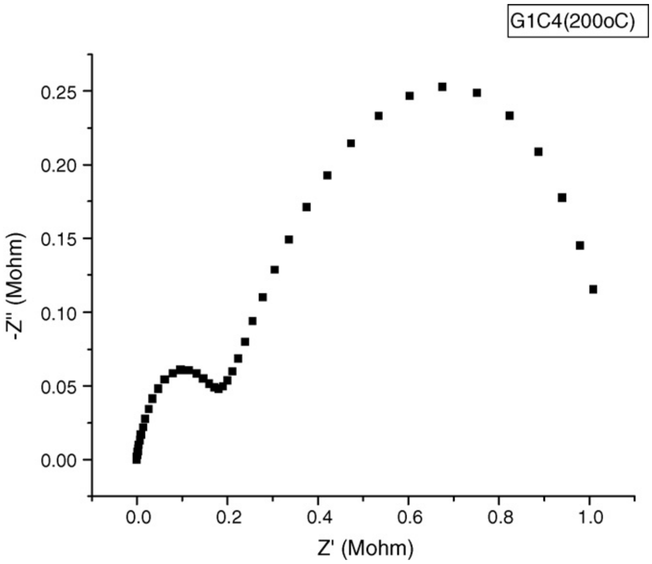

Fig. 3. Cole–Cole plot of the GP3Y5Al material.

- (ii) The decrease in the number, area and maybe the thickness of the separation layers between the conducting silicon carbide grains, due to the increasing grain size.
- (iii) The removal of amorphous and crystalline silicates.

The double Cole–Cole arcs observed for the HP3Y5Al and GP3Y5Al materials (illustrated in Fig. 3), in which only the YAG phase was identified as a crystalline grain boundary phase, was evidence of a second phase. This must be amorphous (most likely silicates) as it did not show up in X-ray analysis. Arguments were presented to show that amorphous material could be present in the GPS materials, which appear in the middle conduction group.

4. Conclusions

The non-Arrhenius behaviour, the wide range of $1/T^{0.25}$ excitation energies for the conductivity and the Cole–Cole characteristic frequency values, led to the conclusion that none of the phases observed in the impedance arcs were silicon carbide. The single arcs in the Cole–Cole plots of the hot pressed and heat-treated hot pressed materials and the double arcs in the gas pressure sintered materials must therefore be due to grain boundary phase or mixtures of grain boundary phases. This is in contradiction with the conclusions of other groups,[2–6] who claim that there are impedance arcs in their spectra due to silicon carbide. A pseudo-percolation model was proposed to describe the conductivity in the LPS SiC materials.

Three groups of materials with different grain boundary phase compositions and thickness found in each group, was evidence of the fact that the grain boundary phase had the major influence on the conductivity of these LPS SiC materials.

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References

1. Irmscher, K., *Mater. Sci. Eng.*, 2002, **B91–92**, 358.
2. Volz, E., Roosen, A., Hartung, W. and Winnacker, A., Electrical and thermal conductivity of liquid phase sintered SiC. *J. Eur. Ceram. Soc.*, 2001, **21**, 2089–2093.
3. Volz, E., Roosen, A., Albrecht, M., Wang, S.-C., Wang, S.-C. and Wei, W.-C., Microstructure and Electrical Resistivity of SiC Ceramics, Poster. In *104th Annual Meeting of the Amer. Ceram. Soc.*, 2002.
4. Volz, E., Korrelation zwischen den elektrischen Eigenschaften und dem Gefuge von SiC-Keramiken. PhD Thesis. University of Erlangen; 2003.
5. Martin, H.-P. and Adler, J., Design of electrical and thermal properties of liquid phase sintered silicon carbide. In *Proceedings of the Materials Week 2001, Symposium K5—Multifunctional Ceramics*, 2001.
6. Martin, H.-P. and Adler, J., Design of electrical properties of LPS-SiC. In *Proceedings of the Materials Week*, 2001.
7. Ihle, J., Martin, H. P., Herrmann, M., Obenaus, P., Adler, J., Hermel, W. and Michaelis, A., The influence of porosity on the electrical properties of liquid phase sintered silicon carbide. *Int. J. Mat. Res. (Z. Metallkunde)*, 2006, **97**(5), 649–656.
8. Riedel, R., *Handbook of Ceramic Materials*. Wiley-VCH, 2000, p. 687.
9. Can, A., Herrmann, M., McLachlan, D. S. and Sigalas, I., Densification of Liquid Phase Sintered Silicon Carbide. *J. Eur. Ceram. Soc.*, 2006, **26**(9), 1707–1713.
10. Alexander, S. and Orbach, R., *Physica B*, 1981, **107**, 675.
11. Mott, N. F., *J. Non-Cryst. Solids*, 1968, **1**(1).
12. Mott, N. F. and Davis, E. A., *Electronic Processes in Non-crystalline Materials*. Clarendon, Oxford, 1971.
13. McLachlan, D. S., Hwang, J.-H. and Mason, T. O., Evaluating dielectric impedance spectra using effective media theories. *J. Electroceram.*, 2000, **5**, 37.
14. Sigl, L. S. and Kleebe, H. J., *J. Amer. Ceram. Soc.*, 1993, **76**, 773.