5.3 Relationships between microstructure and electrical properties

5.3.1 Proposed conduction path

Electrons will follow the most favourable conduction paths in any sample, leading to the highest conductance between any two points (electrodes). In two or three phase crystalline or granular composite materials, this will be the percolation path through the more conducting grains, which is silicon carbide in the case of LPSSiC materials. If there are no high silicon carbide-silicon carbide contact resistances, the SiC grains will form a true percolation path. The percolation threshold is the critical volume at which the conducting phase first forms a continuously connected network and there is a sudden increase in conductivity. Note that at about 90 volume-%, the SiC component is well above the percolation threshold, which could be about 16 volume-% (commonly observed in conductor-insulator percolation systems[213]), as long as the SiC is uncoated so that the SiC grains make good intergranular contact, and the insulating grains are the same size[213]. Figure 5.48 gives an example of a percolation system, with conducting and insulating grains of similar size, which is not directly applicable to the LPSSiC system.

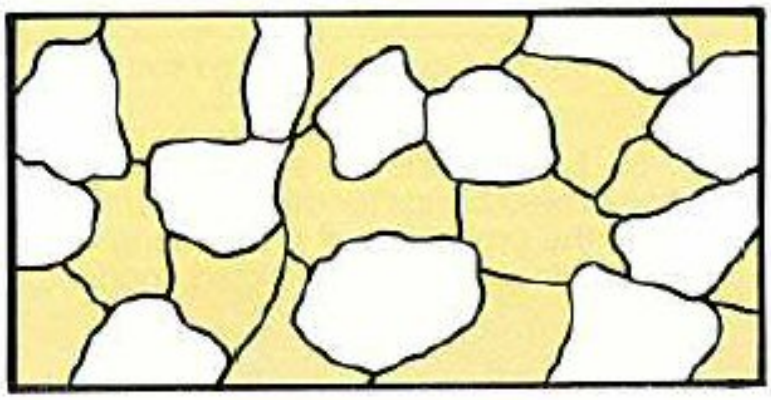

Figure 5.48 Example of a percolation model, where the yellow phase is the conducting component and the white phase is the insulating component of equal grain size[213]

However, because there is such a wide range in conductivities for the lowest and highest conductivity samples (with a log conductivity range of approximately 10^5 as seen in Figure 4.17 and 4.18), there cannot be a direct percolation path through the silicon carbide grains, especially in the low conductivity samples. If there were pure SiC percolation paths through the samples, the curves would lie in a much narrower log conductivity band, which is not observed in Figure 4.17 and Figure 4.18, which are reproduced later as Figure 5.50 and 5.51.

If there was a direct conduction path through SiC-SiC contacts, the temperature-dependence of the conductivity would be 1/T, characteristic of semiconductors, which is not observed. Also, it is accepted that in sintered silicon carbide there is almost always a layer of intergranular material (crystalline and/or amorphous) between the grains[41,111]. This is illustrated in Figure 2.14. The characteristic frequency for the higher frequency (higher conductivity) phase in the Cole-Cole plots of all the GPS materials, varies over a wide range: between 400Hz and 17 000Hz (seen Figure 4.29). This is too wide for this phase to be a single phase like silicon carbide. This also supports the argument that the phase corresponding to the high frequency arc is most likely not silicon carbide, but in fact a grain boundary phase, which can vary from sample to sample in terms of conductivity of the compounds (which are probably substoichiometric) and their connectivity.

Hence, the optimum paths chosen by the current in the LPSSiC samples are pseudo-percolation paths, going through the silicon carbide grains which have the largest nearest neighbour contact areas, and which are separated by the thinnest layers of grain boundary or secondary phase material. Figure 5.49 gives a simplified illustration of this. Considering that the silicon carbide grains in the LPSSiC material consists of a more resistive core SiC region and more conducting rim region of Al-doped SiC,

the conductive path through the SiC part of the structure, illustrated in Figure 5.49, would be most likely along the rim part of the SiC grains.

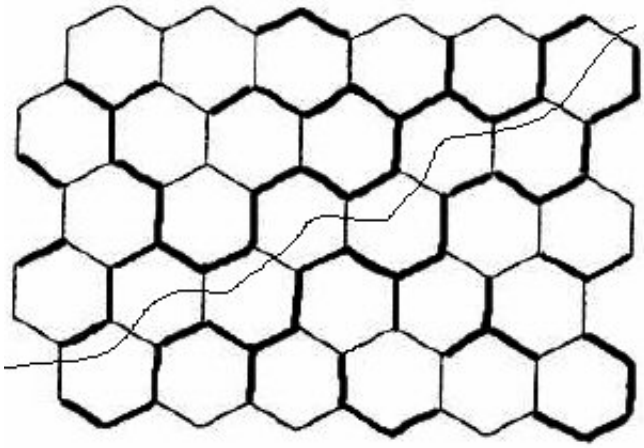

Figure 5.49 Illustration of the proposed favoured path of conduction in the pseudo-percolation model.

If pseudo-percolation paths are the favoured paths for conduction, this means that the nearest distance between silicon carbide grains, the area of nearest contact, and the number of points of nearest contact between silicon carbide grains, have the major influence on the paths of the electrons through the LPSSiC materials. Grain growth in a LPSSiC material during sintering or post-sintering heat treatment results in larger grains. These larger grains mean fewer and larger area of nearest neighbour contact between the silicon carbide grains and larger triple junctions, which contain most of the secondary phase. The remainder of the secondary phase is “squeezed” between the grain faces, into very thin intergranular layers. Larger grains would therefore lead to higher conductivity in a multi-phase material with the same grain boundary phases. Longer heat treatments would also result in increased Al- doping of the SiC grains, which which increase the conductivity of the silicon carbide grains.

Note that an electron on any one of the pseudo-percolation paths will pass through a large number of intergranular contacts with different areas and thicknesses. The more resistive of these contacts will determine the conductivity of the materials.

This means that 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. Also, following this pseudo-percolation model, the grain boundary composition of the material in the triple junctions is not of importance in determining the conductivity (in agreement with references 19 and 20). Instead the composition and contiguity in the thinner separation layers between the silicon carbide grains is of major importance.

Even if a Core-Rim structure exists in the SiC grains, as reported by Sigl *et al.*[41], 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. Note that in the cubic brick layer model[214] this corresponds to the current passing through bricks (the silicon carbide grains) and cement/mortar (the intergranular material) layers alternatively, and virtually no current goes along the square pipe which surrounds this alternating structure.

Recall that the log conductivity- temperature dependence for contiguous sintered semiconductors would be $1/T$[197], which is not observed in the investigated LPSSiC 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 $T^{-0.25}$, indicative of insulating materials. As already explained in the results section (4.5.3), a log conductivity temperature dependence of $T^{-0.25}$ indicates that the conduction mechanism is three-dimensional variable range hopping[191,192].

This means that the electrical conduction through the liquid phase sintered silicon carbide material 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. For example Volz *et al.*[17,18] believed that the arc appearing in their Cole-Cole plots was silicon carbide, and that when pressureless sintering between 1850^{o}C and 1950^{o}C the secondary phase had no influence on the resistivity of the LPSSiC material, which is not consistent with results of this work and the above model. They also explained the increase in conductivity (by eight orders of magnitude) when sintering at higher temperature to be due to the solution-reprecipitation of silicon carbide grains. This is also not in agreement with the findings in this thesis. Volz *et al.*'s assumptions were made without doing temperature-dependence measurements, and actually observing the log conductivity versus 1/T response typical for semiconductors.

Variable range hopping is a bulk phenomenon and this implies at least ten variable range hops between the SiC grains, or a intergranular distance/ thickness of order 10 nm. If the thickness of the layers was less than the hopping distance direct tunneling would dominate. Previous TEM investigations[41,19,20] conclude that the thinnest layers between SiC grains is of order 2nm. The conductivity-temperature dependence results for the LPSSiC materials with log conductivities below 10^{-5}, strongly supports the fact that intergranular material at least 10 nm thick is present in these materials. i.e. it is the thicker grain boundary layers on the pseudo-percolation path that determine the bulk resistivity of the LPSSiC materials. Along the pseudo-percolation path some grain boundaries may be negligible, resulting in some tunneling, others are thick with variable range hopping conduction in them. Also recall that, the pseudo percolation model does not require that all the electrons pass through 10 nm or thicker layers, but that there can be few of these and a large number of thinner grain boundary layers on any pseudo-percolation path of the electrons.

5.3.2 Influence of grain boundary phases on log conductivity behaviour

Figures 5.50 and 5.51, previously given as Figure 4.17 and 4.18, show that the conductivity results separate into three broad conductivity bands, with different magnitudes, and somewhat different dispersive behaviour. XRD shows that from the bottom to the top of the conductivity curves the following crystalline grain boundary phases are found:

(1) the lowest conductivity materials contain silicates and alumina (all hot pressed materials)

(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) and the materials with the highest conductivity (the heat-treated materials), contain only the aluminates YAP and YAM.

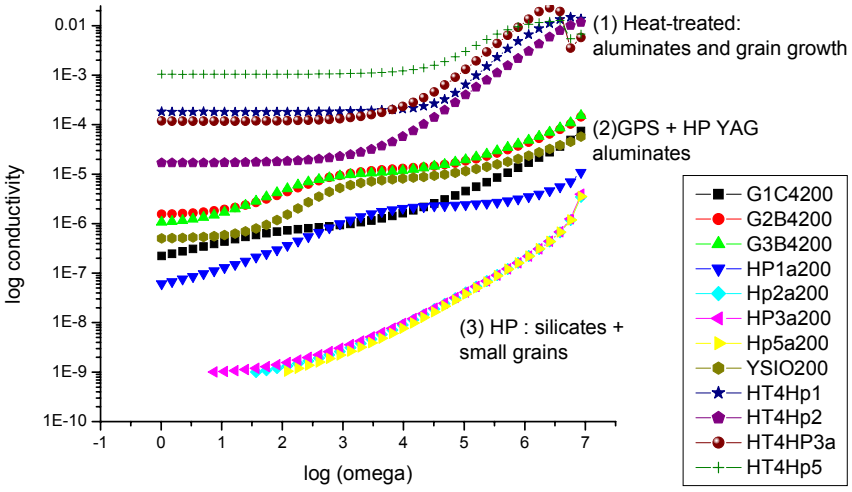

Figure 5.50 (also 4.17) Graph of the log of electrical conductivity as a function of the log of angular frequency at 200°C. In the labels of this figure: 1 = 3Y5Al, 2 = 4Y2Al, 3= 1Y1Al, 4 = 4Y1Al, 5 = 1Y4Al

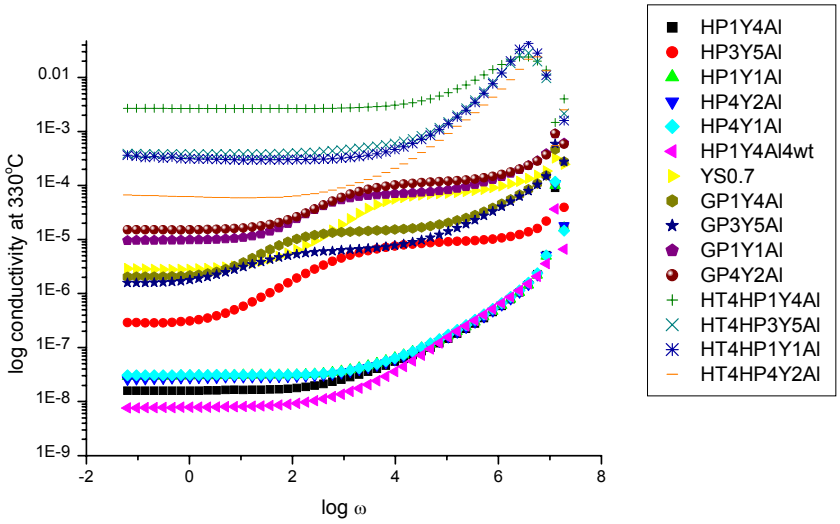

Figure 5.51 (also 4.18) Graph of the log of electrical conductivity as a function of the log of angular frequency at 330°C

One general trend in the microstructure from bottom to top of Figures 5.50 and 5.51 is an increase in grain size. In line with the previous discussion, this indicates an increase in nearest neighbour contact area, and a decrease in thickness of the grain boundary (separation) layer from bottom to top of the ac conductivity curve. Silicon carbide contiguity results in Table 4.14 confirm that contiguity of SiC is lowest in the HP materials, and higher in the HTHP materials. This means that the distance between the silicon carbide grains, and hence the distance which the charge carriers have to traverse the grain boundary in order to go through the conducting silicon carbide, is expected to be smaller in the HTHP materials. This would lead to the higher conductivity, which is observed in the heat treated materials. However, it is believed that change in composition is the more dominant effect (from the variable range hopping energy results to be discussed).

The lack of consistent barrier hopping conductivity in the heat treated (HT4) highest conductivity materials, could be due to the onset of some

direct tunneling through still narrower barrier layers in the heat treated HP materials.

A quantitative understanding of the influence of the grain boundary layer on conductivity is very difficult from the temperature –dependence of the conductivity. The calculated excitation energies associated with variable range hopping are shown in Figure 5.52 (calculated using equation 2.28 with the actual values given in Table 4.20). There was a definite trend observed in the calculated characteristic energies, which was in agreement with the log conductivity plots (shown above in Figures 5.50 and 5.51). Three groups of materials were observed in terms of similar characterization energies- the lowest energies were observed in the heat treated materials (which have the highest conductivities), the middle group of energies corresponded to all the materials in the middle conduction band, and the highest energies were seen in the lowest conductivity HP materials.

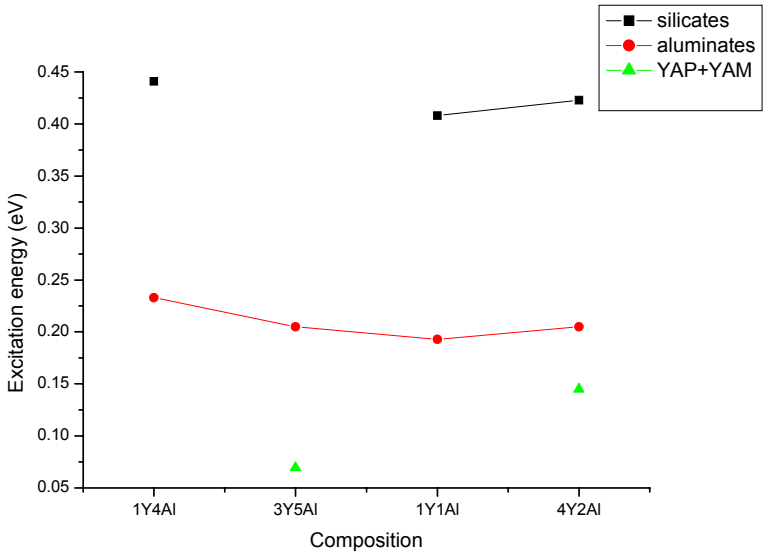

Figure 5.52 Excitation energies of the higher frequency phase observed in the LPSSiC materials

These energies would not be related to the thickness of the grain boundary layers, but rather to energy differences and distances between the hopping sites. The characteristic energy differences between the materials, therefore confirm that silicon carbide is most likely not being observed in the electrical data, and that it is the multi-phase grain boundary materials that are determining the conductivity. As will later be shown, this implies that silicates form more insulative grain boundary phases than the aluminates.

The phases in the grain boundary or secondary material resulting from the sintering additives, was determined using X-ray diffraction and Rietveld analysis. One limitation of this technique is that it is only able to detect the crystalline phases present in the material. Any amorphous phases will go undetected, and the secondary phases are almost certainly mixtures of amorphous and crystalline material. SEM micrographs show (in section 4.4), that most of the grain boundary material is not in the narrow separating layers (thin films between the grains), especially in the case of the heat treated materials. This means that XRD analysis primarily determines the composition of the triple junction material and not the intergranular layers. If it is assumed that the composition of the triple junctions are similar to that of the thin films between the grains, the X-ray diffraction will give the grain boundary phase chemistry of the crystalline phases in the secondary material (although TEM studies would be needed to confirm the composition of the thin films). There are three exceptions to this statement, namely the GP4Y2Al and heat treated (HT) HP4Y2Al and heat treated GP4Y2Al materials, in which the grain boundary phases were observed to be segregated, i.e. inhomogeneously distributed. (The discussion of these microstructures is given in section 5.1).

The only hot pressed material, which does not contain crystalline silicate phases, is the HP3Y5Al material, where the grain boundary phase material is primarily YAG. This material lies at the bottom of the middle conduction

band. The other materials in the middle conduction band are all GPS materials. According to XRD, all of the materials in the middle conduction band have aluminates as their primary crystalline grain boundary phases. The two lowest conductivity materials in this middle band are the HP3Y5Al and the GP3Y5Al, which both, according to XRD, have only YAG as their grain boundary phase. Therefore the thin films containing primarily YAG probably have lower conductivity than those containing primarily YAP and YAM aluminate phases. The results of the Rietveld calculations confirm that with heat treatment, the YAG tends to decompose to the $Y_4Al_2O_9$ and $YAlO_3$ phases. This probably serves as a partial explanation as to why the heat treated HP materials (in the upper band), which only contain YAP and YAM, have higher conductivities than the GPS materials (in the middle band), which contain YAG, YAP and YAM.

The fact that the log conductivity plots of the HP materials in the lowest conductivity band all lie on top of each other at 200^{o}C, indicates that their grain boundary compositions, structures and contiguity must be very similar. Microstructural image analysis and Rietveld calculations discussed in section 5.1 confirm this.

HP3Y5Al has a similar microstructure to the other hot pressed materials in the bottom conduction group. Yet, it does not have similar conductivities, instead groups with the GPS materials, and has conductivities similar to the GP3Y5Al material, which contains the same crystalline grain boundary phase, namely YAG. This, together with the wide low frequency conductivity range of approximately 10^5, is clear evidence of the fact that the silicon carbide grain size is not the only contributing factor to the trends observed in conductivity, but rather the grain boundary has the major influence on the conductivities of these LPSSiC materials. From these results it is evident that silicates are more insulative than aluminates. There is no clear evidence for this difference in the literature. This could be due to the fact that the conductivity of non-stoichiometric silicates and aluminates is dependent on their stoichiometry, which can change from

sample to sample, making experiments very irreproducible. In this case, the author is confident of the trend in conductivity increasing as the materials move from silicates to aluminate phases in this system.

The model proposed by Martin *et al.*[19,20] differs from the present model, in that they propose conduction purely along the Al-doped sites in the SiC grains situated at the edges of the SiC grains. Martin *et al.* suggest that the improvement in conductivity of the LPSSiC material on heat treatment is because of broadening of this impurity-containing grain boundary region. This is in contradiction with the present model, where the secondary phase material that lies off the pseudo-percolation path plays only a small role, and the thinner secondary phase material barriers along the pseudo-percolation path plays the major role in the determination of the bulk conductivity. They also made the assumption that the two arcs observed in their Cole-Cole plots corresponded to the silicon carbide and grain boundary components, which is not in agreement with the present work from which it appears that the effect of the silicon carbide can only be detected at higher frequencies than those available[215]. A shortcoming in their work, was that they, as previous other authors, did no temperature-dependence conductivity measurements of the phases observed in the Cole-Cole plots.

One might argue that the variable range hopping mechanism determined in this project is associated with hopping between aluminium sites in the sub-stoichiometric silicon carbide lattice. However, there are a number of arguments to counter this. Variable range hopping refers to hopping between sites variable distances apart or of variable energy states. The variable range hopping fit was best for the hot pressed materials, which had the lowest silicon carbide contiguity (shown in Table 4.14), and consistent variable range hopping was not observed in the HT4HP materials, in which Al-doping would be expected to be the highest (according to TEM studies by Martin *et al.*[19,20]).

Additionally, the grouping of the materials in terms of their grain boundary phases in the log conductivity plots, is also evidence that the grain boundaries, and not silicon carbide, are dominating the conductivity of the materials. For example, as already discussed, the hot pressed material, HP3Y5Al, which did not contain crystalline silicates, but that underwent the same time of sintering and had a similar microstructure as the other HP materials, does not lie in the conductivity group with the other HP materials, which did contain crystalline silicates. Instead it lies in the middle conduction band next to the GP3Y5Al material, which contains the same grain boundary phase (YAG), but underwent a longer sintering time (different conditions), and has a different SiC contiguity and microstructure. If the solution-reprecipitation process was dominating in these materials, a difference in conductivity behaviour would be expected between the hot pressed HP3Y5Al material and the gas pressure sintered GP3Y5Al material. This is additional evidence that the variable range hopping mechanism is most likely referring to hopping in the grain boundary phase material.

5.3.3 Further discussion of the dispersion curves and Cole-Cole plots

All of the arguments thus far have dealt with the low frequency (dc) conductivity behaviour of the LPSSiC materials. However, the shapes of the conduction dispersion curves (log conductivity curves vs log ω) give further information about the electrical behaviour and the composition of the grain boundary phases. The shape of the lowest and highest conductivity materials are typical for two-phase percolation systems, as seen by Wu *et al.*[216] and Chiteme *et al.*[217], and is characteristic of systems above their percolation threshold, or the critical volume Φ_c. In a two-phase system, if the more conducting phase is contiguous, it is above its percolation threshold. In a three phase percolation system consisting of one conducting and two insulative phases, the two insulative phases are often treated as a single phase. An example of this is given in a paper by

Wu and Mclachlan[216], in which their materials had considerable amount of porosity (20%), which was considered to be part of the insulating phase.

At 200°C and 330°C the classical percolative behaviour- two phase curvature of the log conductivity plots, is clearly observed in the heat treated HP materials, as well the lowest conductivity group HP materials (more so at 330°C), although only one arc is clearly observed in Cole-Cole plots. Note the fact that more than one crystalline phase in the upper and lower conductivity group materials does not give rise to complex dispersion curves and more than one arc in the Cole-Cole plots of these materials.

The dispersion observed in the log conductivity curves can probably be related to percolation phenomena. The frequency of the point of upturn (inflection) is related to the closeness to the percolation threshold (decreasing as the system gets closer to its percolation threshold), as well as the ratio of conductivities of the two phases[216,217]. Figure 5.3.4 shows that the higher conductivity component, which gives rise to the flat region is more dominant (in all three conduction groups) at 330°C than at 200°C. This leads to an upturn at higher frequency, which makes this percolation-type behaviour more apparent at 330°C. This is especially observed in the lower conductivity group, where the upturn for the HP materials moves from possibly being observed at 200°C, to being clearly observed at 330°C. The reason why the exact point of upturn is seen at one temperature and not the other, is that the ratio of the two conductivities has changed.

The shape of the middle group of materials indicate a more complex grain boundary phase system, where the effects of two grain boundary phases could be examined using the Impedance Spectroscopy apparatus, appearing as double arcs in the Cole-Cole plots. This means that at least two insulating phases are contributing to the bulk conductivity. The GPS

materials maintain their complex dispersion curves and double Cole-Cole arcs between 200^{o}C and 330^{o}C. According to XRD results, the HP3Y5Al and GP3Y5Al materials only contain the YAG phase in their grain boundaries. However, the presence of the double arc in the Cole-Cole plots of these materials, means that there must be at least one other phase present in the HP3Y5Al and GP3Y5Al grain boundaries, not detected by the XRD. This is most likely an amorphous silicate or aluminate phase, since any amorphous phases would not be detected by XRD.

To support the existence of amorphous phases, Rietveld calculations in this project showed that there was 6 .5 mass-% crystalline phase detected in the HP3Y5Al material (details are shown in section 4.2). Since approximately 10 mass-% grain boundary phase is expected from the sintering additives used (and weight loss during hot pressing is minimal), this is further evidence of some amorphous phases present in the grain boundary. The evidence of amorphous phases in similar systems in the literature[41] means that amorphous phases almost certainly contribute to the curvature of the dispersion curves and double arc in the Cole- Cole plots of the remaining materials in the middle conduction group.

The fact that the conductivity of the GPS materials is two to three orders of magnitude lower than the heat treated HP materials, supports the fact that there is most likely still some amorphous aluminate/silicate phase coating the secondary phase in the GPS materials, keeping their resistivities high. Removal of amorphous silicate from the grain boundaries, by evaporation of SiO during heat treatment of the hot pressed materials, would continuously decrease the resistivity of the grain boundary material. The amorphous silicate phases also directly wet the silicon carbide grains, in which case evaporation of SiO during heat treatment or gas pressure sintering would bring the conducting SiC grains and less conducting aluminate phases into better electrical contact. However, it is possible that

there are amorphous layers of aluminates left in the narrow silicon carbide interfaces in the heat treated materials.

SUMMARY

The non-Arrhenius behaviour, and the wide range of $1/T^{0.25}$ excitation energies and Cole-Cole characteristic frequency values, led to the conclusion that most probably 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 were said to be most likely due to grain boundary phases or mixtures of grain boundary phases. This is in contradiction with other groups in the literature[16-20], who claim that there are impedance arcs in their spectra due to silicon carbide. It is proposed that a higher frequency is required to observe the effects of the silicon carbide, than what is available with current instrumentation[215]. A pseudo-percolation model was proposed to describe the conductivity in the LPSSiC 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 LPSSiC materials.

Three factors are proposed to contribute to the increase in conductivity of the HP materials when they were heat treated:

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

The double Cole-Cole arcs observed for the HP3Y5Al and GP3Y5Al materials, in which only the YAG phase was identified as a crystalline grain boundary phase was evidence of the fact that there must be amorphous phases (most likely silicates) present in their grain boundaries. Arguments were presented that amorphous material could be present in the other GPS materials in the middle conduction group.