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Silicon Carbide Heating Elements

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Abstract: Silicon carbide is widely used as an electrical heating element because of its excellent thermal and mechanical properties and its electrical resistivity. However, the increase of the electrical resistivity with running time and temperature limits the industrial development of the SiC heating elements. The processes responsible for ageing are not well understood, but it is generally assumed that this phenomena is primarily associated with the oxidation. The present work is a review of the substantial effort that has been made to determine and understand the effects of oxidation with respect to the properties, performance and durability of various commercialized silicon carbide heating elements. This review encompasses measurements of the main characteristics (crystalline phases, composition, density, porosity, flexural strength, thermal conductivity, oxidation and electrical resistivity). © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Silicon carbide has been recognised as a high performance material for structural ceramics because of its unique combination of properties, such as high mechanical properties maintained at high temperature, high wear resistance, high thermal conductivity and its low electrical resistivity.[1–3] Silicon carbide is widely used as electrical heating element, in spite of the electrical ageing (i.e. increase of electrical resistivity) and of the non-linear electrical resistivity variation with running time and temperature. Ageing remains the main drawback of this type of heating element and limits its industrial development. Although the problem is known since 1930, the phenomena responsible for ageing is not well understood, but it is generally assumed that ageing is primarily due to the oxidation of the material.[4]

The present work is a review of the main characteristics of commercial silicon carbide heating elements in order to determine the major parameters which influence their electrothermal behaviour (corrosion and electrical properties evolution). The microstructure of the material (grain size and porosity),[5–7] and the nature of the crystalline phases (α and/or β), which both depend on the additive elements, are related to the properties of the heating elements at high temperature and particularly to the variations of the electrical resistivity.

2 EXPERIMENTAL

2.1 Starting materials

Eleven silicon carbide heating elements, produced by the main manufacturers, were characterised. According to origin, electrical heating elements were constituted either of α-SiC or β-SiC with a protective coating (amorphous), or of a α-SiC and β-SiC mixture. The design of the electrical heating elements were rod or tubular shape depending on the diameter, U type (α-SiC and α-SiC + β-SiC), or with a tubular spiral slot (β-SiC and α-SiC + β-SiC). The heating central section was referred as the hot zone and the two terminal sections were called cold ends (Fig. 1). They operated at furnace temperature between 900 and 1500°C.

2.2 Structural analysis

All the analyses were performed on the central heating material.

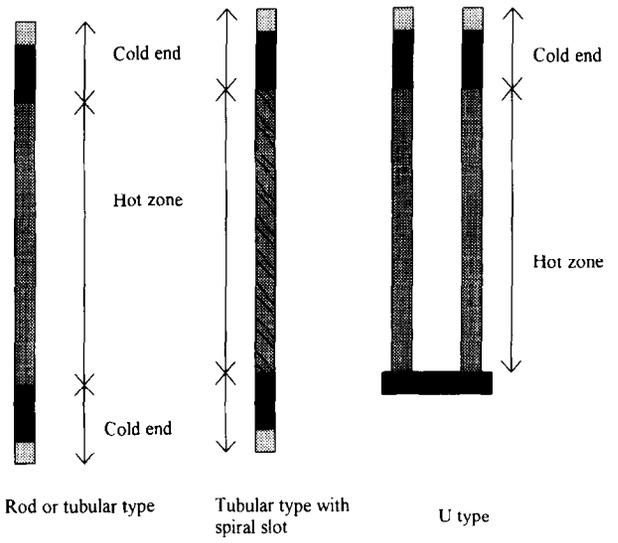

Fig. 1. Different shapes of commercial silicon carbide heating elements.

The crystalline phases present in the various heating elements were identified by X-ray diffraction. The shape and grain size were observed by scanning electron microscopy (Hitachi S2500). The porosity and the density of the SiC materials were measured using water intrusion and Archimedes' methods.

2.3 Thermal conductivity

The thermal diffusivity, a (m^2s^{-1}), of one sample constituted of α-SiC + β-SiC was measured, from 400 to 1300°C, with a laser flash method.[8] The thermal conductivity, λ(W m^{-1} K^{-1}), was then calculated according to the following relation :

$$\lambda = a\rho Cp \qquad (1)$$

where ρ (g cm^{-3}) is the bulk density and Cp (J kg^{-1} K^{-1}) the heat capacity of the sample. The values of heat capacity were given by Touloukian[9] for various temperatures (Cp increased from 680 J kg^{-1} K^{-1} at 20°C to 1400 J kg^{-1} K^{-1} at 1600°C).

2.4 Electrical resistivity

The electrical resistivity was determined in the hot zone of the heating elements using the 4-point method in order to avoid any electrical contact phenomena. This method, based on Ohm's law, consisted in measuring the voltage between two probes, separated by a distance l, on a sample crossed by a direct current which was applied between two other probes separated by a distance L (l < L) (Fig. 2).[10] The resistance R (Ω), for a sample of uniform cross-section S is given, at a temperature T, by the relation:

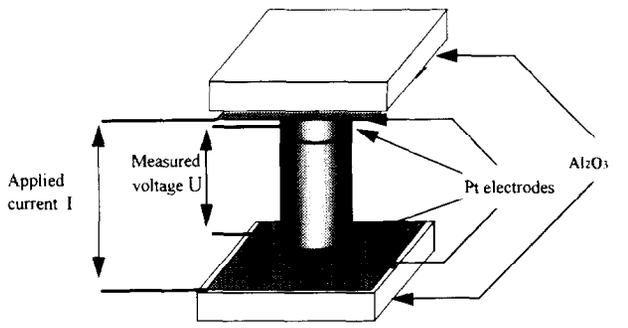

Fig. 2. Experimental device for the measurement of the electrical resistivity by the 4-point method.

$$R = \rho_e \frac{1}{S(1 + \alpha \Delta T)} \qquad (2)$$

where ρ_e(Ω cm) is the electrical resistivity of the material. The thermal expansion coefficient, α (m $m^{-1}°C^{-1}$) of the silicon carbide, between 20°C and 1200°C, was taken equal to an average value of $\alpha = 4.5\ 10^{-6}°C^{-1}$.

2.5 Oxidation behaviour

The oxidation mechanisms of SiC were determined by measuring the weight change during thermal cycles, from 20°C to 1000°C with a heating rate of 5°C min^{-1} and during isothermal treatments at 900°C and at 1250°C in air.

2.6 Flexural strength

The flexural strength of heating elements, which was related to their microstructure (mean grain size, porosity and density), was measured at room temperature using the 4-point bend test on 4×4×35 mm^3 bars. The given values correspond to the average of three tests.

3 RESULTS

3.1 Phase and structural analysis

Typical X-ray diffraction patterns of heating elements containing α-SiC and β-SiC as the major phases are represented in Fig. 3. The phases constituting the heating elements can differ from one manufacturer to another and even sometimes in the same production for a given manufacturer. Nevertheless, three types of heating elements can roughly be distinguished:

3.1.1 α-SiC elements

Their surface appearance was heterogeneous and rough. Equiaxe grains were bounded by a second

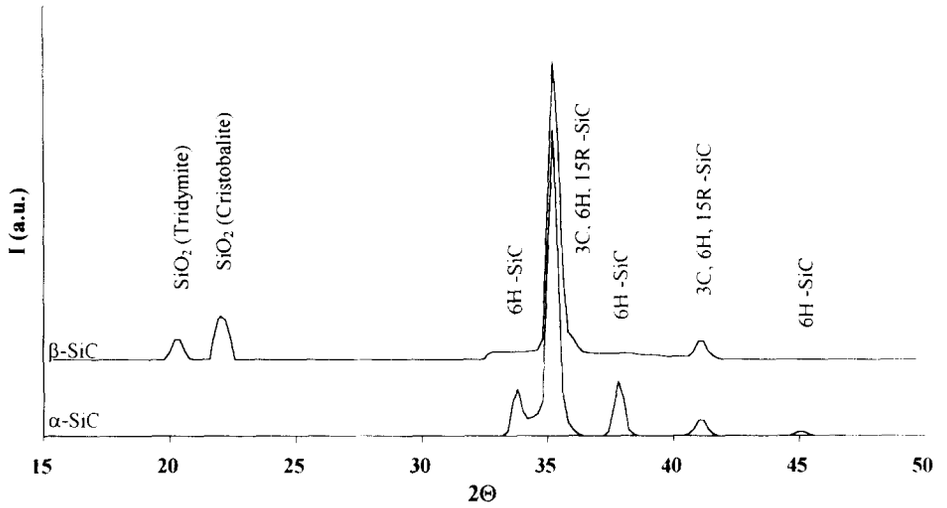

Fig. 3. X-ray diffraction patterns for heating elements containing α-SiC and β-SiC as major phases.

phase, the average grain size varied from 110 to 300 μm (Table 1).

3.1.2 β-SiC elements

The grain size was similar from one manufacturer to another (about 125 μm). The external appearance was homogeneous with the presence of a glass coating. This layer presented a large number of defects (bubbles) and enclosed acicular grains with an average size of 100 μm. SiO_2 picks, attributed to the presence of quartz, cristobalite or tridymite, appeared on X-ray diffraction patterns (Fig. 3).

3.1.3 α-SiC + β-SiC elements

The grain size was about 100 μm The appearance was the same as the one described for the α-SiC elements.

As far as the porosity was concerned, the porosity of samples containing α-SiC or α-SiC + β-SiC as the major phase is at least 28 vol% (apparent density varying from 2.3 to 2.4 g cm^{-3}) and the porosity of β-SiC samples, containing a significant amount of SiO_2 on the surface and inside the porosity, was close to 20 vol% (apparent density varying from 2.1 to 2.2 g cm^{-3}).

3.2 Flexural strength

Whatever the heating element studied, the average 4-point flexural strength is about 110 MPa.

3.3 Thermal properties

The variations, with temperature, of the thermal diffusivity of one α-SiC + β-SiC sample, calculated using different methods (Parker, Degio 1/3, Degio 1/2, Degio 2/3, and Moments)[8] are represented in Fig. 4. Taken the average values of a and the heat capacity values given by Touloukian,[9] the thermal conductivity was calculated between 400°C and 1300°C (Fig. 5). Due to the high porosity and to the poor homogeneity of the tested heating elements, the thermal conductivity values were relatively low, i.e. 45 W m^{-1} K^{-1} at 400°C and 23 W m^{-1} K^{-1} at 1300°C.

3.4 Oxidation behaviour

The oxidation behaviour was the main drawback of the silicon carbide heating elements. In addition to the obvious degradation effect, oxidation greatly

Table 1. Characteristics of the tested commercial SiC heating elements. Tox. is the temperature from which a weight gain was detected (heating rate : 5°C min^{-1}, from room temperature to 1000°C)

Phase	Grain size (μm)	Measured porosity (vol%)	Mean (vol%)	Tox. (°C)	Weight gain at 1000°C (%)	Mean (%)
α	110	33.6		280	0.32	
α	110	34.9		160	0.46	
α	125	28.6	32.7	90	0.40	0.39
α	125	28.7		60	0.40	
α	250	37.9		200	0.40	
α	300	32.6		280	0.35	
α + β	120	34.1		80	0.40	
α + β	125	33.5	33.8	160	0.30	0.37
α + β	125	33.8		290	0.40	
β	100	18.5		100	0.05	
β	100	22.4	20.4	100	0.23	0.14

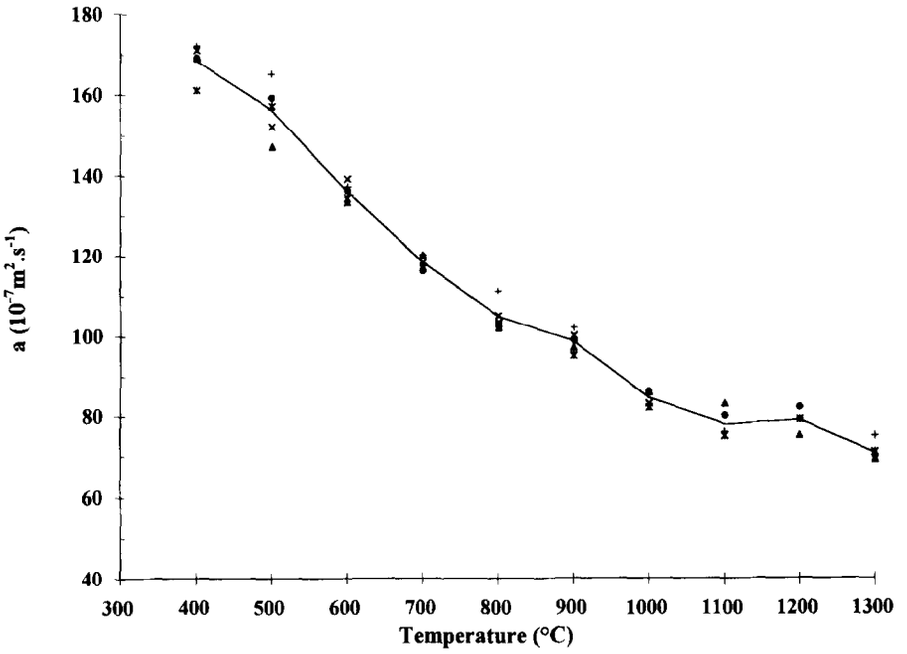

Fig. 4. Variation of the thermal diffusivity with temperature for one α-SiC + β-SiC commercial sample, using different methods for the calculation (▲ Parker, * Degio 1/3, × Degio 1/2, + Degio 2/3, • Moments).[8] The line corresponds to the average values of the thermal diffusivity taking into account the five methods of calculation.

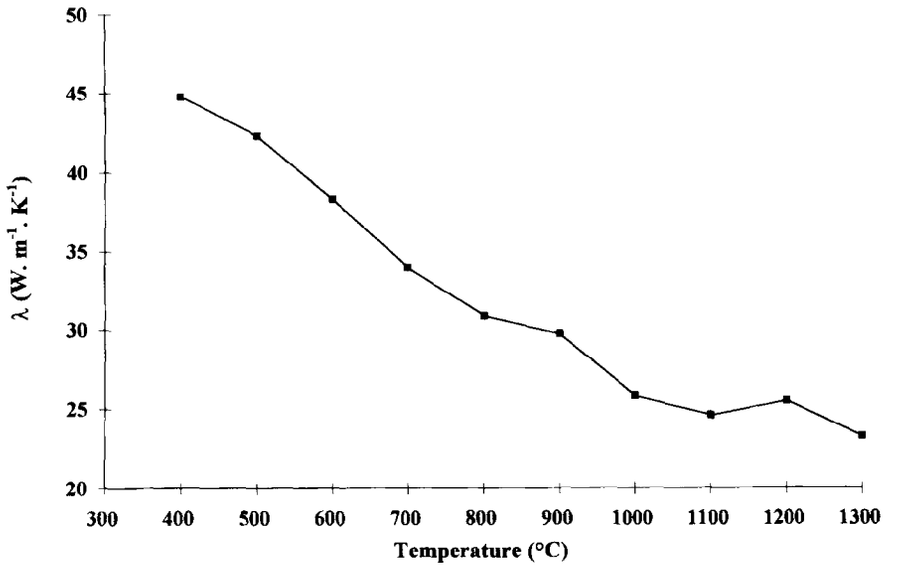

Fig. 5. Variation of the thermal conductivity with temperature, calculated from the average *a* values, for one α-SiC + β-SiC commercial sample.

influenced the variations of electrical and thermal properties during use. Some heating elements presented a weight gain at a temperature as low as 100°C and the weight gain at 1000°C (heating rate of 5°C min^{-1}) may reach 0.5% for the high porosity samples.

With regard to the influence of the nature of the major crystalline phase, we can notice the following principal evolutions (Fig. 6 and Table 1):

3.4.1 α-SiC elements

The mean weight gain of the α-SiC samples at 1000°C, with a mean porosity of 32.7 vol%, was about 0.40% of the initial weight. The temperature from which a weight gain was recorded varied from 60°C to 280°C.

The temperature of the beginning of oxidation of the materials containing the largest α-SiC particles (250 and 300 μm) was higher than 200°C.

3.4.2 α-SiC + β-SiC elements

When the α-SiC and β-SiC phases were combined, the mean porosity (33.8 vol%) and the mean weight gain (0.37%) were similar to those observed for α-SiC samples. The temperature from which a weight gain was recorded varied from 80°C to 290°C.

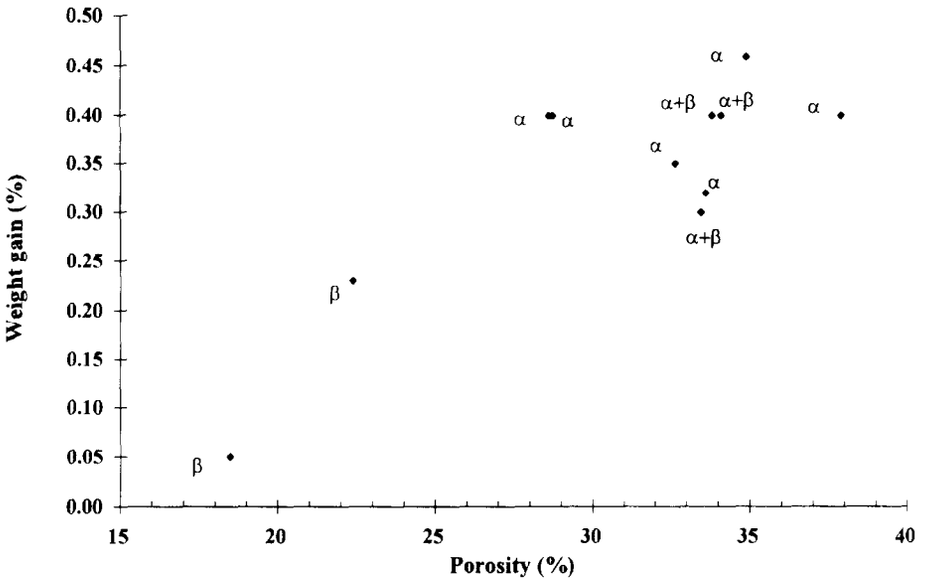

Fig. 6. Weight gain at 1000°C, measured by TGA with a heating rate of 5°C min^{-1}, for elements of different porosity values.

3.4.3 β-SiC elements

In the case of heating elements constituted of β-SiC phase, the global porosity (20.4 vol%) and the mean weight gain (0.14 %) were lower than for α-SiC and α-SiC + β-SiC samples. The temperature of the beginning of oxidation was as low as 100°C.

The oxidation kinetics of one α-SiC + β-SiC heating element was determined with isothermal experiments in air at 900°C and at 1250°C (Fig. 7). For a short oxidation period ($t < 3$ h), the weight gain was important (0.7% of the initial weight at 1250°C), then for longer times, the kinetics reduced (after 75 h, the total weight gain was about 1.0%).

3.5 Electrical characteristics

The electrical resistivity of the commercial SiC elements differed from one manufacturer to another in spite of identical commercial characteristics. The measured electrical resistivity values of the hot zone were varying from 0.05 to 0.5 Ω cm at room temperature (Fig. 8). The variations of the electrical resistivity with temperature, for different commercial products, were coherent with the results given by J. W. Evans *et al.*.[11] In any case, the temperature coefficient of electrical resistance for SiC heating elements was negative from room temperature up to 600°C. In this temperature range, the electrical conductivity was controlled by the presence of quite small amounts of impurities and/or doping agents,[12] which were responsible of the semi-conduction properties of the material. According to Kingery,[13] the temperature corresponding to the highest thermal conductivity squared with the maximum carrier mobility. Therefore, for temperatures higher than 600°C, all

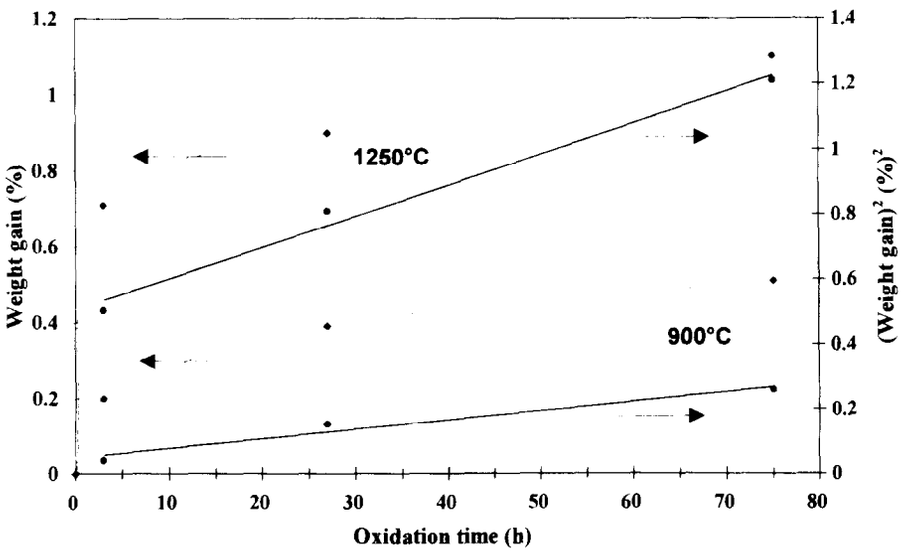

Fig. 7. Weight gain variation with time and oxidation kinetics at 900 and 1250°C temperature for one α-SiC + β-SiC commercial sample.

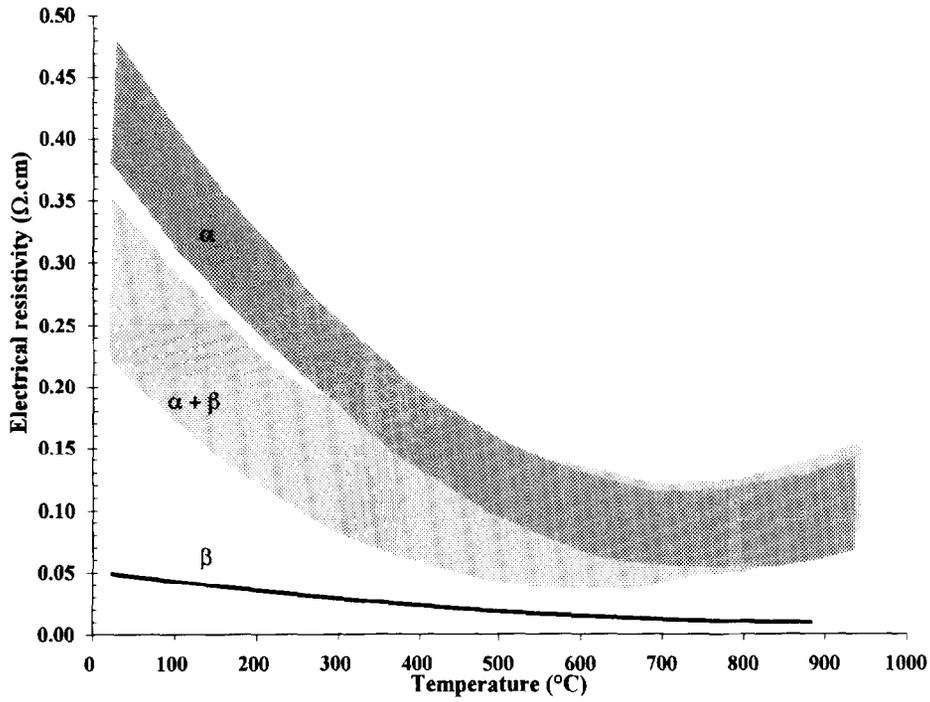

Fig. 8. Envelopes of the electrical resistivity values, between room temperature to 950°C, for commercial SiC heating.

commercial SiC elements showed a stable and small positive temperature coefficient of resistance. Above 600°C, the measurements become very delicate because of changes of the microstructure, and especially because SiO_2 formation took place at the surface part and in the porosity of the material. Then, the conductivity can be governed by different mechanisms and the chemistry of the system has to be taken into account to explain the positive temperature coefficient.

Two distinct classes of heating elements can clearly be distinguished in Fig. 8. On one hand, α-SiC and α-SiC + β-SiC mixtures exhibited electrical resistivity values ranging from 0.05 to 0.5 Ω cm and, on the other hand, the electrical resistivity values of β-SiC covered with a SiO_2 layer ranged from 0.01 to 0.05 Ω cm.

4 DISCUSSION

According to Taketa *et al.*,[12] thermal conductivity and electrical resistivity of SiC ceramics depend on the amount and on the nature of the second phase located at the grain boundaries and on the free carrier concentration in SiC grains. It is assumed that an important quantity of additives, then of intergranular phase, increased phonons scattering, and reduced the thermal conductivity. For instance, when the electrical resistivity of SiC was adjusted with alumina addition, the thermal conductivity values were relatively low ($\lambda = 23$ to 45 W m^{-1} K^{-1}). In other respects, Okamoto *et al.*[14] observed that thermal conductivity decreased when the sample porosity increased. This parameter is important for heating elements tested in this study which presented a porosity from 18 to 35 vol%.

Oxidation led to the formation of SiO_2 at the expense of SiC, according to the reaction:

$$SiC(s) + 3/2O_2 \rightarrow SiO_2(s) + CO(g) \quad (3)$$

At low temperature and/or for short treatment time, the formation of a protective layer of amorphous silica on the sample surface was observed. Then, the oxidation penetrated the material core by the open porosity and/or by species diffusion all along the grains boundaries.

The oxidation kinetics was studied on one α-SiC + β-SiC element at 900 and at 1250°C. For isothermal treatments longer than 3 h, when the silica protective layer was formed, the oxidation kinetics followed a parabolic law (Fig. 7):

$$\Delta m^2 = kt \quad (4)$$

where Δm is the weight gain and k is a kinetic constant. This parabolic law of the oxidation kinetics suggested a diffusional mechanism and the diffusion of oxygen through the protective SiO_2 layer, seemed likely to be the limiting stage of the reaction. In these conditions, the oxidation is passive.

For higher temperatures (> 1250°C), or for longer oxidation times (> 75 h), the amorphous silica layer crystallised into cristobalite leading to the cracking of the protective layer and allowing

the oxygen to freely enter in the material. In these conditions, the oxidation is named active.

The porosity was the major factor which influences the oxidation behaviour of the SiC heating elements because the surface exchange with the atmosphere, then the material reactivity, were increased. Other factors than the porosity may influence the oxidation behaviour of the SiC elements. The presence of small amounts of impurities or sintering additives (particularly CaO and MgO which react with silica to form eutectics) led to the formation of low viscosity intergranular phases which favoured the inwards diffusion of oxygen towards the bulk.[15] Moreover, the presence of impurities can influence the crystallisation of the cristobalite as well as others secondary phases.

Concerning the electrical behaviour of the SiC heating elements and whatever the predominant crystalline phase, two different domains were observed depending on the temperature. The electrical resistivity decreased from room temperature to 600°C, and increased in the usual temperature range (from 600 to 900°C). This behaviour can be related to the oxidation of the silicon carbide. The inwards migration of oxygen led to the formation of an insulating intergranular phase which affected the electrical behaviour.

5 CONCLUSION

The results concerned 11 silicon carbide heating elements provided by the main manufacturers. The electrical properties of the porous SiC heating elements directly depended on the oxidation behaviour of the material. The formation of an insulating intergranular phase, due to oxidation, greatly affected the electrical resistivity.

The oxidation was lower for the less porous β-SiC heating elements. At low temperature and/or for short treatment time, the limiting stage of oxidation was the diffusion of oxygen through the protective silica amorphous layer.

Finally, two possible ways to improve the electrothermal behaviour of SiC heating elements could be suggested (i) the elimination or the reduction of the open porosity, which implies a good selection of the raw materials and of the additives, and (ii) the modification of the surface of the SiC heating elements with a protective oxide layer in order to reduce the oxidation rate in the usual temperature range of use.

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