Journal of the European Ceramic Society **19** (1999) 875–878

PII: S0955-2219(98)00335-5
0955-2219/99/$ - see front matter

New Experimental Approaches to Characterise Silicon Carbide Hot Rods

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Abstract

A four-point technique has been developed for the resistivity measurement of industrial SiC rods. The superficial oxidation of SiC pellets has been characterised using the impedance spectroscopy technique, thermogravimetric analysis and S.E.M micrography.

Keywords: characterisation, corrosion, electrical properties, impedance, SiC.

1 Introduction

Silicon carbide is widely used as a heating rod material in industrial furnaces up to 1500°C. To insure adequate control of the electrical power supplied, it is necessary to know its electrical resistivity variations. However, this resistivity varies with temperature and time and shows high discrepancies between polycrystalline SiC resistors used for industrial applications. These variations appear exceedingly large and unpredictable due to polytypism, and impurities. This is partly due to the lack of appropriate measurement techniques implementable on large samples at high temperature.

In this paper, we describe several experimental approaches, including thermogravimetry analysis and impedance spectroscopy, to characterise the electrical properties of silicon carbide rods and to monitor their superficial oxidation at high temperatures.

2 Samples

The investigated industrial samples are polycrystalline materials with different noncubic polytypes,[1,2] referred to as α-SiC in the literature. Porosity of such materials is about 20 to 30%, and grain size ranges from 0·1 to 1 mm. The amount of impurities (B, Al, etc.) is of the order of 1%. Other SiC (α or β) samples were made in the laboratory to insure higher purity, homogeneity, and greater final density (above 90%).

3 Electrical Measurements

The variation of the electrical resistivity of 1 m long industrial SiC rods with temperature was measured, up to 1700°C, using a modified non-destructive four-point technique [Fig. 1(a)]. A special furnace was built for our purpose: it was specially designed to provide a wide chamber with homogeneous temperature (less than 5°C variation along x and y axes, at 1500°C).

As shown in Fig. 1(a), four probes, of the same composition as the tested resistor, are held in contact with the resistor by metal springs. These probes are 5 cm apart. Two counter-probes are used to prevent the resistor from bending at high temperature. A dc current is passed through the tested rod. The mean resistivity of the rod is calculated from the measured potential differences between the probes. As shown in Fig. 1(b), a resistivity minimum was observed at about 800°C. The electrical resistivity is about $3\times10^{-3}\,\Omega$m at room temperature, decreases down to $5\times10^{-4}\,\Omega$m at 800°C (referred to as ρ_0) and then increases slowly for higher temperatures (up to 1500°C).

The electrical resistivity, at room temperature, of laboratory-made samples was $2\times10^{-2}\,\Omega$m and $1{\cdot}4\times10^{-2}\,\Omega$m for α- and β-SiC, respectively.

4 Oxidation Characterisation

The main interest of silicon carbide is its ability to be protected against further oxidation by a silica layer formed under appropriate conditions

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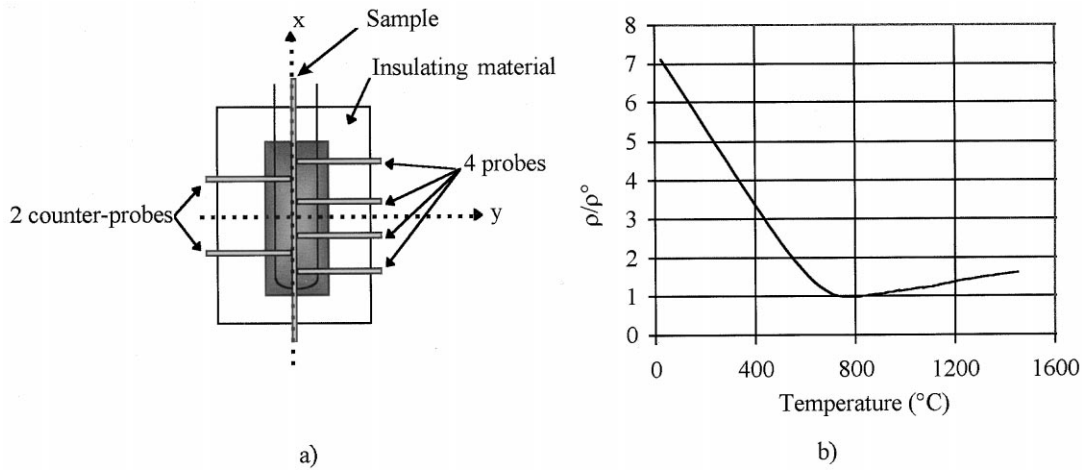


Fig. 1. (a) Schematic representation of the modified four-point technique for non-destructive measurement of the electrical resistivity of industrial hot rods. (b) Relative resistivity versus temperature of an industrial α-SiC rod.

of temperature and oxygen pressure. This property has been widely studied.[3–6] However, the reported data show large discrepancies which can be ascribed to the investigated materials (polytypes, impurity contents) and to the elaboration procedures (sintered pellets, CVD thin films, etc.).

4.1 Thermogravimetry under controlled oxygen partial pressure

In this study, the oxidation kinetics were characterised up to 1500°C by thermogravimetry, using a Setaram thermobalance (TAG 24 S) with a 1 μg sensitivity. Oxygen partial pressure in flowing argon or helium was controlled between 10^{-6} and 1 bar by coupling an electrochemical oxygen pump and a zirconia oxygen sensor to the T.G. equipment. Figure 2 shows a typical plot with simultaneous recording of the temperature, the zirconia sensor voltages upstream and downstream (corresponding to the oxygen pressures), the T.G. set-up and the mass variation of the sample (Δm) after changing the flowing gas composition (from pure helium to dry air).

Figure 3 shows a S.E.M. micrograph and three X-filtered images (C, O, Si) of the oxide scale formed on a α-SiC sample annealed at 1200°C for 55 h in dry air. As shown at the bottom right of Fig. 3, the scale was about 1 μm thick, which is in agreement with the thermogravimetric results. Figure 3 also indicates that oxygen is located both in the silica scale and in the sample pores. As shown in Fig. 4, few cracks can be observed in the scale.

4.2 Impedance spectroscopy study

Previous works have demonstrated the interest of impedance spectroscopy for ceramic characterisation and especially for the detection and characterisation of thin impurity layers.[7,8] Impedance measurements were performed using two impedancemeters (HP 4194 A and Autolab-Ecochemie) in the frequency range 10^{-2} Hz–40 MHz. Platinum electrodes were deposited by sputtering to ensure the best ohmic contact on SiC or SiO_2 at temperature less than 1000°C.[2]

In order to illustrate the effect of thermal annealing on the electrical characteristics of industrial samples, impedance diagrams, plotted at room

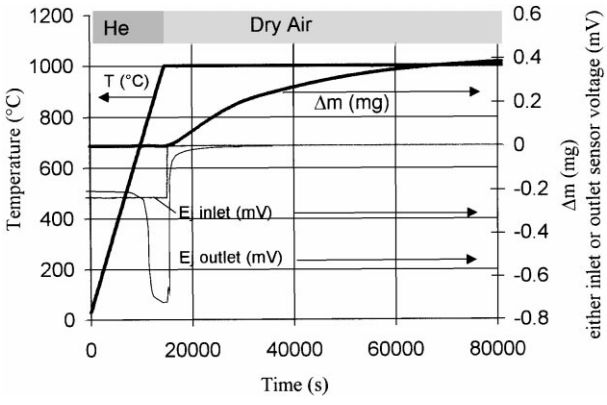


Fig. 2. Typical mass variation plot of a α-SiC pellet at 1000°C in dry air.

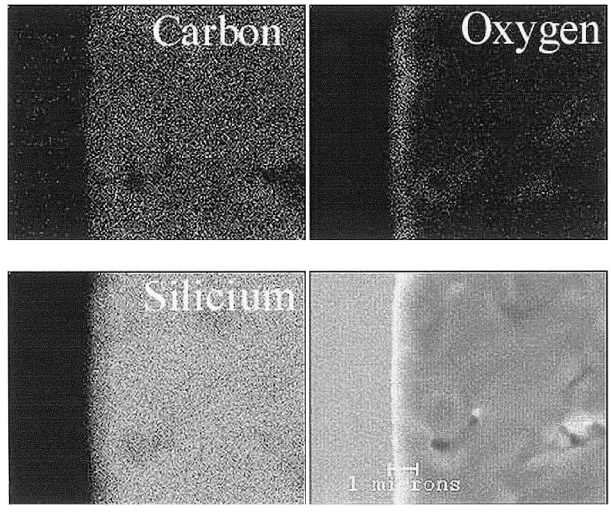


Fig. 3. S.E.M. and X-filtered images of oxide scale formed on a α-SiC sample annealed at 1200°C for 55 h in dry air.

temperature, for two samples annealed at 1300°C for 500 h, in wet air (20 wt% of water in air) are shown in Fig. 5(a). Measurements were made after polishing, which eliminated the SiO_2 outside layer, and electrode deposition.

A noticeable increase of the sample impedance was observed after annealing, i.e. $4{\cdot}5\times10^{-2}\,\Omega$m, compared with $3\times10^{-4}\,\Omega$m for the initial sample. Although the impedance variations are different for the two samples, both diagrams show a homotetic frequency distribution. This behaviour could indicate that the same blocking effect is predominant whatever the oxidation degree. The modulus representation [M'' versus log(frequency)] is used in Fig. 5(b) and indicates the same behaviour for both samples at high frequency (above 1 MHz).

A typical impedance diagram, plotted at room temperature, on a laboratory-made α-SiC sample annealed at 1200°C for 55 h in dry air is shown in Fig. 6.

Note that

- the total impedance is higher than with the bare sample,
- the diagram is composed of at least two semicircles,
- When the scale is removed by polishing, the initial impedance obtained before annealing is restored.

From the thermogravimetric analysis, S.E.M. investigations, and the sample geometry, the resistivity of the scale was estimated to be $3\times10^{5}\,\Omega$m.

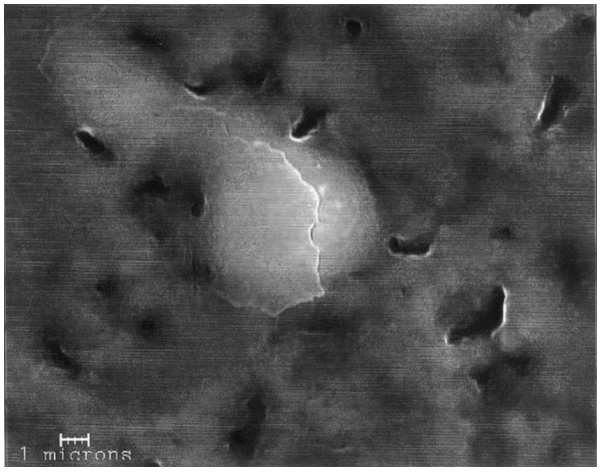


Fig. 4. S.E.M. micrograph of the SiO_2 scale formed on α-SiC in dry air.

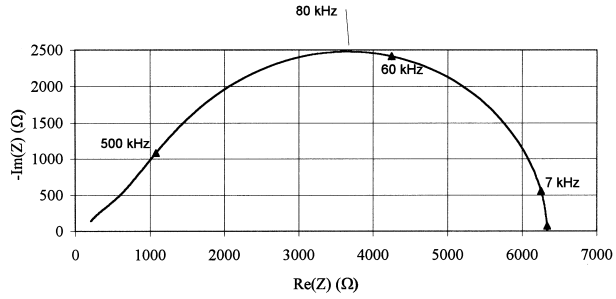
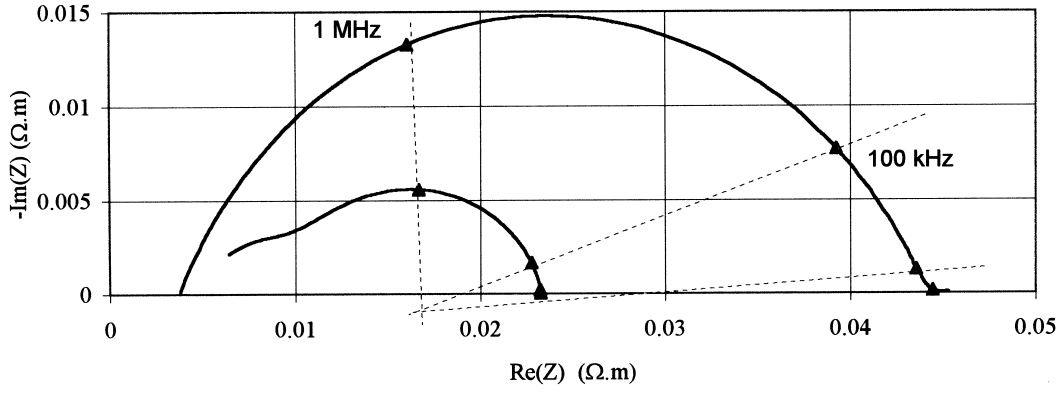
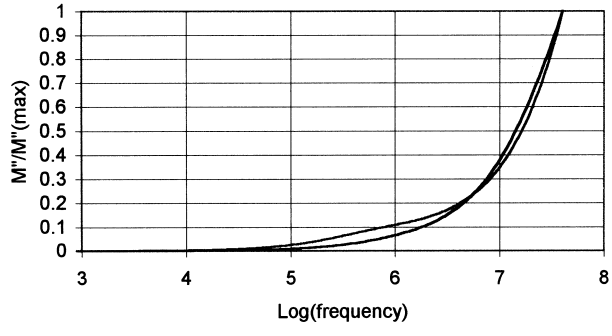


Fig. 6. Impedance diagram of a laboratory-made α-SiC pellet annealed at 1200°C for 55 h in dry air.



(a)



(b)

Fig. 5. (a) Normalised impedance diagrams of an industrial SiC pellet at room temperature. (b) Impedance modulus representation of an industrial SiC pellet at room temperature.

This value is small compared to the published resistivities of quartz or vitreous silica[9] (10^{14} to $10^{16}\,\Omega$m). However, according to Speers,[10] the resistivity for a silica film (electrochemically deposited on a metallic substrate) can be as small as $10^{8}\,\Omega$m, depending on the substrate material and the impurity level, especially for alkaline impurities.

On the same sample, without removing the scale, measurements were carried out over a range of temperatures (up to 380°C), in argon atmosphere (less than 2 ppm of oxygen). Figure 7(a) presents the evolution of impedance diagrams (100 to $1{\cdot}5\times10^{7}$ Hz). Figure 7(b) shows the same evolution in the modulus representation. Note that:

- the impedance variation is reversible along temperature cycles (at least for short annealing times at high temperatures),
- the total impedance decreases with increasing temperature,
- for temperatures above 122°C, a low frequency semicircle appears, and becomes well defined at high temperatures.

Figure 8 shows an impedance diagram at 380°C. Measurements were carried out from 10^{-2} to $1{\cdot}5\times10^{7}$ Hz. The total impedance increases with time, at a given temperature. The diagram exhibits three well defined semicircles. The high frequency semicircle is related to the dielectric response of the bulk SiO_2 (which relaxes at a frequency of about 3 MHz under the experimental conditions of Fig. 8). The intermediate response, referred to as MF, relaxes at about 5 kHz, could be ascribed to interface blocking at the SiO_2/SiC interface. Note that only the low frequency process changes: its magnitude increases with time, and its relaxation frequency decreases. This phenomenon requires further observations.

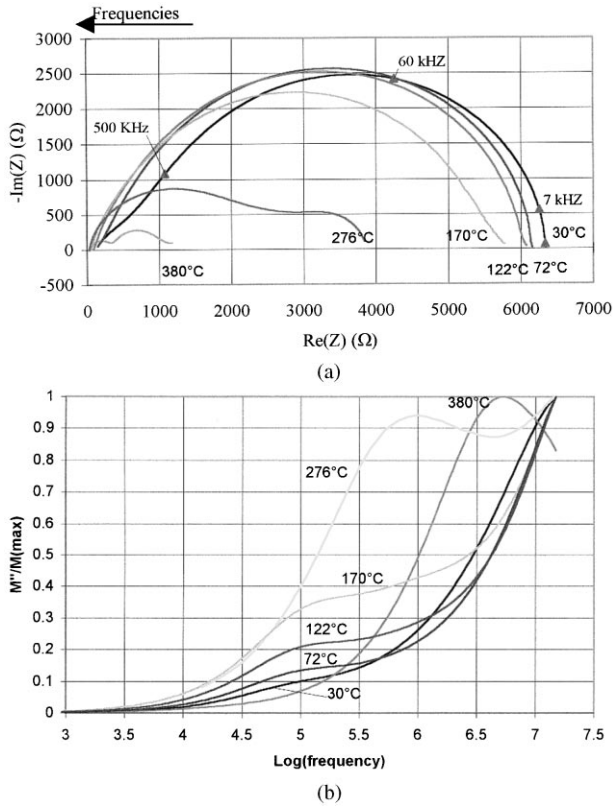


Fig. 7. (a) Variation with temperature of the impedance diagrams of an oxidised pellet of α-SiC in an argon atmosphere (oxygen mole fraction $<2\times10^{-6}$. (b) Variation with temperature of the impedance modulus of an oxidised pellet of α-SiC in an argon atmosphere (oxygen mole fraction $<2\times10^{-6}$).

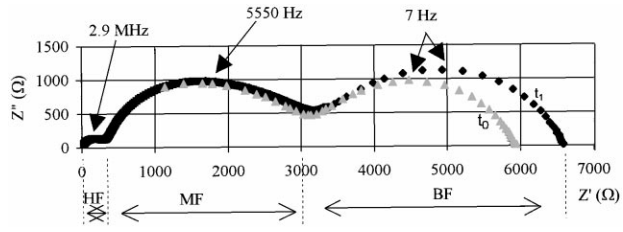


Fig. 8. Evolution with time, at 380°C, in dry air, of the impedance diagram of a α-SiC sample (t_0: initial measurement; t_1 annealing time = 3 weeks).

Acknowledgements

Dr Michel Kleitz is acknowledged for fruitful discussions. The work has been supported by Electricité de France, Direction des Etudes et Recherches.

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