JOURNAL OF MATERIALS SCIENCE 29 (1994) 1097–1100

Positive temperature coefficient of resistance effect in hot-pressed cristobalite–silicon carbide composites

DU WEI-FANG, TAN XU, DU HAI-QING
Institute of Materials Science and Application Chemistry, University of Hunan, ChangSha 410082, People's Republic of China

Conductive silicon carbide particles were incorporated into an insulating cristobalite ceramic matrix to produce composite materials with a sizeable positive temperature coefficient (PTC) effect. A large drop in resistivity with silicon carbide content at room temperature, or percolation behaviour, was observed. The PTC effect of the composites, which resulted from the thermal expansion of the cristobalite ceramic matrix, was a maximum with five orders of magnitude for the specimen with 25 vol% silicon carbide. The PTC transition temperature of the composites was at 260 °C, which coincided exactly the reversible high–low phase inversion temperature of the cristobalite ceramic matrix.

1. Introduction

Materials exhibiting a positive temperature coefficient (PTC) of resistance have been widely used in temperature sensors, protective switches, etc., which require a large positive temperature coefficient in a narrow region above the switching temperature and low resistivity below the switching temperature. At present, PTC thermistors are fabricated by doping the $BaTiO_3$ ceramics or dispersing the conductive particles (such as carbon black powders) in an insulating polymer matrix. Although most of the commercially available PTC thermistors are doped $BaTiO_3$ ceramics, composite thermistors have many advantages. First, they are more flexible than doped $BaTiO_3$ ceramics, and can be processed into a complex shape. Second, the fabrication of composite thermistors is very simple, so the fabrication costs are lower than for doped $BaTiO_3$ ceramics. These advantages of composite thermistors have attracted the interest of many materials researchers [1–6].

The mechanism of the PTC effect of a composite is completely different from that of doped $BaTiO_3$ ceramics. At room temperature, the conducting particles dispersed in the polymer matrix form a conductive path through the composite, so that it exhibits low resistivity. At the switching temperature of the composite, the volume of insulating polymer matrix expands abruptly, destroying the conductive path formed at room temperature and resulting in an abrupt rise of resistivity of the composite. Thus, a PTC effect occurs. The switching temperature of the composite is generally at the melting point of the polymer matrix of the composite, because only at the melting point can the volume of polymer matrix expand sufficiently. Therefore, the switching temperature of a composite thermistor is low, owing to the low melting point of the polymer. In addition, the oxidation resistance and corrosion resistance of a composite thermistor are also inferior.

We have studied hot-pressed SiC-based multiphase ceramics [7]. Hot-pressed SiC–SiO_2 has been manufactured and in previous experiments we found that the resistivity of the hot-pressed SiC–SiO_2 ceramics increased significantly between 250 and 260 °C. In view of the reversible high–low phase inversion of cristobalite with an extraordinarily large volume change between 230 and 270 °C, in the present work we chose cristobalite ceramic instead of polymer as the insulating phase for the matrix of a composite thermistor and silicon carbide powder for the conductive particles. The objective of this study was to investigate the PTCR characteristics in conducting silicon carbide–insulating cristobalite ceramic composites.

2. Experimental procedure

The purity of the silicon dioxide powder used in this experiment was 99.65%. To obtain cristobalite, the silicon dioxide powder was calcined in advance at 1300 °C for 3 h with a small amount of additive (CaO and K_2O with 2.4–3.1 wt %). The X-ray pattern of silicon dioxide powder, shown in Fig. 1, demonstrated that it was of the quartz form before calcination and was cristobalite form after calcination. The calcined SiO_2 powder was then ball-milled. The SiC powder used in this experiment as conductive particles was prepared by the sol–gel method [7]. The particle sizes of cristobalite powder and silicon carbide powder, which were analysed using a Micron Photosizer model SKC 2000 based on the light-scattering principle employing sedimentation, are shown in Fig. 2.

Homogeneous mixtures of insulating cristobalite powder and dispersed-phase SiC powder in the desired proportions were prepared, then hot pressed at

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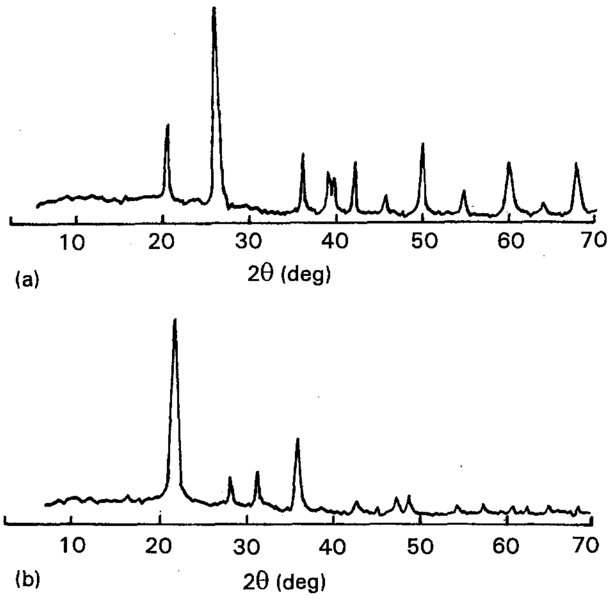

Figure 1 X-ray diffraction patterns for powders (a) before calcination, (b) after calcination.

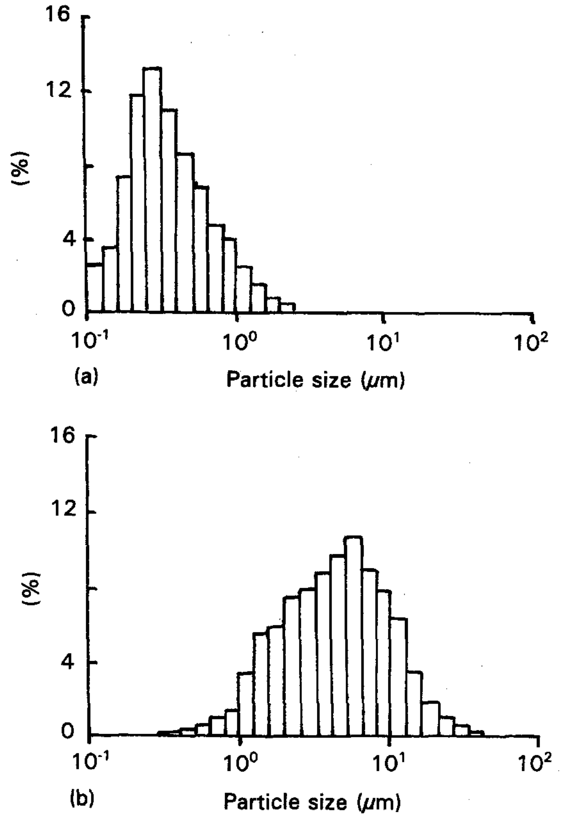

Figure 2 Particle-size distributions of (a) silicon carbide powder, and (b) cristobalite powder.

1300 °C for 1 h under 35 MPa. The dimensions of the disc-shaped samples were 20 mm diameter and 4–5 mm thick. All samples were polished and then electrodes produced with silver paste. The d.c. resistivity of the composites was measured as a function of temperature with a Keithley solid-state electrometer (model 610-C).

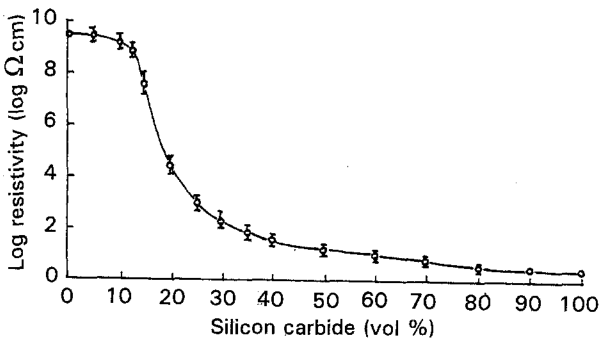

Figure 3 Room-temperature resistivity plotted against SiC concentration for cristobalite–SiC composites.

3. Results and discussion

Fig. 3 shows the dependence of room-temperature electrical resistivity on SiC volume concentration in cristobalite–silicon carbide composites. The specimens with low SiC volume concentrations have large resistivities which vary little with concentrations up to 12 vol %. However, at 12 vol % SiC, the resistivities of the composites begin to decrease drastically. A large drop in resistivities was observed in the composition range 12–35 vol %. Above 35 vol %, the resistivity approaches that of silicon carbide. A similar change in resistivity as a function of conducting particle concentration in conductor–polymer insulator composites was also found by Newham [2–5], Moffatt [6] amongst others, which was explained by the concept of percolation. That is, when the SiC volume concentration is low, the SiC conducting particles are separated by insulating cristobalite matrix, so the specimens exhibit large resistivities approaching that of the cristobalite. At 12 vol % SiC, termed the percolation threshold, the SiC volume concentration is large enough to form conductive paths. Thus, in the composition range between 12 and 35 vol %, termed the percolation region, the larger the concentration of SiC particles, the more conductive paths are formed through the composite, resulting in a large drop in resistivities for a small increase in SiC concentration. This region of filler concentration is usually where one would expect to see large PTC effects as the conductive paths through the composite in this region are easily destroyed by the expansion of the insulating matrix. Above the percolation region, there are so many conductive paths through the composite that it reaches a saturated state, therefore above 35 vol % SiC the composites exhibit low resistivities which vary little with change in SiC concentration.

The relationship between resistivity and temperature for cristobalite–silicon carbide composites containing various SiC contents is shown in Fig. 4. It can be seen that in the composition range between 20 and 35 vol %, a remarkable increase in resistivity is observed in the vicinity of 260 °C, which coincides exactly with the reversible high–low phase inversion temperature of cristobalite. Fig. 5 shows the thermal expansion behaviour of cristobalite prepared by the same method as the composite specimen; a dramatic increase in the expansion coefficient in the vicinity of 260 °C can be seen. This proves that there is a close connection between the thermal expansion of the cristobalite at its reversible high–low phase inversion temperature and the PTCR effects. We have shown in

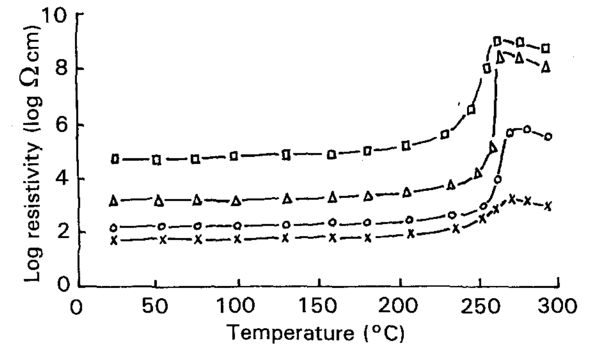

Figure 4 Electrical resistivity dependence of temperature for cristobalite–SiC composites prepared for different SiC contents: (□) 20 vol %, (△) 25 vol %, (○) 30 vol %, (×) 35 vol %.

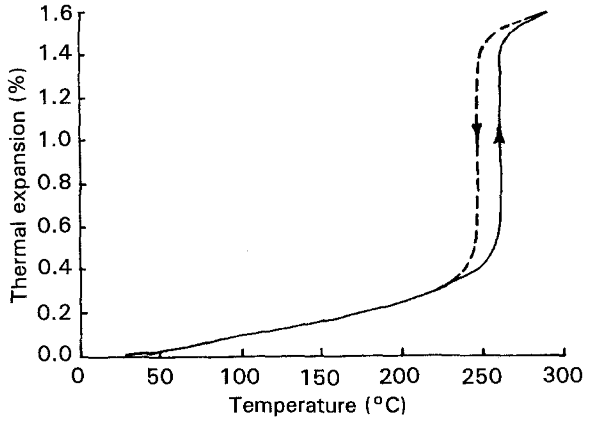

Figure 5 Thermal expansion of cristobalite.

Fig. 3 that in the composition range between 20 and 35 vol % SiC, the composites are in the percolation region, so the conductive SiC particles dispersed in the composite can form a number of conducting paths throughout the composite, resulting a relatively low resistivity at room temperature. When heated, the cristobalite matrix expands more quickly than the silicon carbide particles near 260 °C and this disrupts the conductive paths which are formed by the silicon carbide particles at room temperature, and eventually results in a rapid increase in the resistivity of the composite. Thus a large PTCR effect is observed at 260 °C, as shown in Fig. 4. The largest PTCR effect of up to five orders of magnitude was observed in the specimen containing 25 vol % SiC. As the SiC concentration is increased further, the PTCR effect gradually decreased: it is small at 35 vol % SiC. One interpretation is that the destructive effect of the thermal expansion of the cristobalite matrix on the conductive paths formed by the SiC particles is weakened as the volume concentration of cristobalite decreases, resulting in a decrease in the PTCR effect. The thermal expansion behaviour of composites containing various SiC contents is shown in Fig. 6. It can be seen that the thermal expansion of the composite decreases with increasing SiC content in the vicinity of 260 °C.

The reproducibility of the resistivity–temperature behaviour for 25 vol % SiC–cristobalite composite upon thermal cycling is illustrated in Fig. 7. The data exhibited excellent reproducibility with the PTC curves being almost the same from the first to the third run. However, in each cycle, the heating and the cooling curves do not coincide, as shown in Fig. 8. This is due mainly to the difference in expansion coefficient of cristobalite between heating and cooling in the vicinity of 260 °C, as shown in Fig. 5.

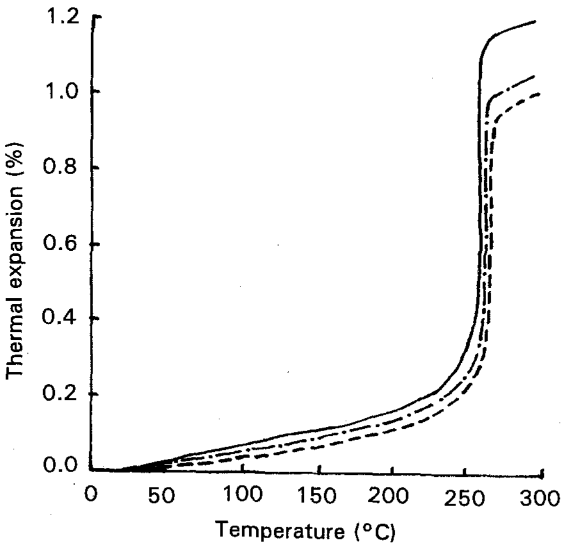

Figure 6 Thermal expansion of composites prepared for different SiC contents: (———) 25 vol %, (—·—) 30 vol %, (– – –) 35 vol %.

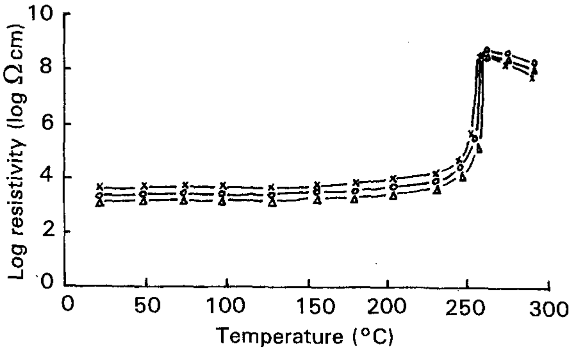

Figure 7 Reproducibility of the PTCR behaviour for 25 vol % SiC–cristobalite composite: (△) run 1, (○) run 2, (×) run 3.

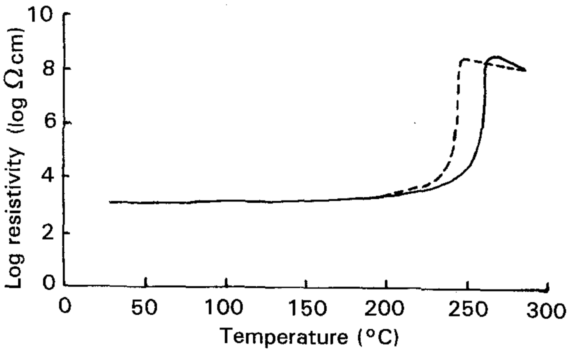

Figure 8 PTC behaviour of 25 vol % SiC–cristobalite composite in each thermal cycle: (———) heating, (– – –) cooling.

4. Conclusions

In a series of composites composed of conducting silicon carbide particles in an insulating cristobalite ceramic matrix, a large drop in resistivity with silicon carbide content at room temperature, which was accounted for by percolation theory, was observed. When the composition was in the percolation region, the composites exhibited a PTC effect with a constant PTC transition temperature of 260 °C, which coincided exactly with the reversible high–low phase inversion temperature of the cristobalite ceramic matrix. The PTC effect of the composites was maximum by five orders of magnitude for the specimen with 25 vol % silicon carbide, and the effect exhibits excellent reproducibility on cycling.

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Received 19 April
and accepted 9 July 1993