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Electrical resistivity of Cr–Al_2O_3 and Zr_xAl_y–Al_2O_3 composites with interpenetrating microstructure

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Abstract

AC and DC resistivity of Cr–Al_2O_3 and Zr_xAl_y–Al_2O_3 composites with varying metal content were measured. A strong percolation behavior was observed in the Cr–Al_2O_3 system, where the AC resistivity varied nine orders of magnitude close to the percolation threshold of 28 vol.%. AC measurements were less dependant on the contact resistance than DC measurements. The best reproducibility was obtained at a frequency of 100 kHz. AC resistivity values of insulating composites differed from DC values and may also be frequency-dependant. DC measurements up to 600 °C indicate that the intermetallic phases $ZrAl_3$ and ZrAl are PTC conductors. The electrical properties of Zr_xAl_y–Al_2O_3 samples with a metal content of 29 vol.% were anisotropic, with a much higher resistivity in the pressing direction.

Keywords: Electrical resistivity; Composites; Al_2O_3–Cr; Al_2O_3–Zr,Al; Metalic inclusions

1. Introduction

The thermomechanical behavior of metal-ceramic composites with interpenetrating networks is dominated by the ceramic matrix, i.e. good wear and oxidation resistance as well as high-temperature strength, while the metal phase can improve the fracture toughness. A novel pressureless reaction sintering process was presented for the fabrication of alumina-aluminide alloys (3A).[1–3] Full densification was achieved by inert-atmosphere heat treatment of compacts prepared from high-intensity milled mixtures of aluminum and metal oxide powders. The process takes advantage of the higher oxygen affinity of aluminum compared to other metals, described by the general reaction scheme:

$$Me_aO_b + Al \rightarrow Me_xAl_y + Al_2O_3.$$

Similar exothermic reactions seem to enhance the densification behavior of mixtures of Al_2O_3 with different refractory metals and small additions of aluminum powder. Thus Al is thought to reduce passivating oxide layers on metal surfaces. For example, highly dense Cr–Al_2O_3 composites with chromium contents up to 50 vol.% were fabricated by pressureless sintering.[4]

Depending on the total metal content, the resulting metal-ceramic composite consists of either isolated metal particles in a ceramic matrix or interpenetrating metal-ceramic networks. At the percolation threshold, one cluster of metal phases is percolating through the composite.[5] The metal content, where the metal phases are homogeneously connected, is more important from a technological point of view. Macroscopically, a dramatic change in the electrical and thermal conductivity is observed in this region while the mechanical properties change only gradually.[6] Particularly, if the ceramic matrix is a good insulator like Al_2O_3, the specific electrical resistance can vary over several orders of magnitude.[7] Percolation of the metal phase does not necessarily occur at the same metal content in different composites but varies significantly with metal phase size and shape and also with the ratio of metal to ceramic phase sizes.[8–13] A good review of different percolation models can be found in McLachlan et al.[14]

In this study, the electrical resistivity of two different composite materials was measured at RT and elevated temperatures. The metal phase consisted of Cr, Zr-aluminides (Zr_xAl_y) or Mo. Different models were evaluated in order to predict the measured resistivity data.

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Table 1
Details of the starting powders used

Powder	Producer	Trade name	d_{50} (μm)
α-Al_2O_3	Condea Inc.	Ceralox HPA0.5	0.5
m-ZrO_2	Z-Tech Corp.	SF Extra	0.8
Al	Fa. Eckart	AS 081	20
Cr	Alfa Aesar	Cr 99.8%	5
Mo	Alfa Aesar	Mo 99.95%	16

2. Experimental procedure

Details of the starting powders and the investigated compositions in the systems Zr_xAl_y–Al_2O_3, Cr–Al_2O_3 and Mo–Al_2O_3 are given in Tables 1 and 2, respectively. The powder mixtures were attrition milled for 5–7 h in acetone using 3 mm TZP balls. After drying and sieving, rectangular bars were first uniaxially (25 MPa), then cold-isostatically pressed (900 MPa) and sintered in argon atmosphere (1500 °C for 2 h) in a graphite furnace. Reaction between Al and metal oxides, e.g. ZrO_2, takes place between 500 and 800 °C and is highly exothermic. Low heating rates up to 800 °C had to be applied for compositions with high aluminum contents. For composition "Al44" in the Zr_xAl_y–Al_2O_3 system (see Table 2), the heating rate was kept below 1.5 °C/min (between 500 and 800 °C) to avoid loss of Al and damage of samples. Above 800 °C, all samples were heated up to 1000 °C at the rate of 10 °C/min, then to 1500 °C at the rate of 20 °C/min. Table 2 also gives the compositions after sintering, calculated theoretical density (t.D.) and average final density determined by Archimedes measurement (in%t.D.). In the Cr–Al_2O_3 system, samples with metal contents between 10 and 50 vol.% were prepared.

After sintering, the samples were ground using a 107 μm diamond grinding disk to remove any sintering skin and to obtain parallel surfaces. Low contact resistance for electrical measurements was achieved by a sputtered gold layer (30–40 nm thickness) followed by coating with silver paint.

The ohmic resistance R was measured at room temperature by DC (multimeter Voltcraft VC227) as well as AC measurements (LCR meter Hewlett Packard 4284A, $f=100$ kHz, 4-point contact). The electrical resistivity was then calculated from $\rho = R \times A/L$, where A is the sample cross-section area and L is the sample length. The DC resistance of a Zr_xAl_y–Al_2O_3 sample was also measured at elevated temperatures (up to 600 °C, argon atmosphere) by 4-point contact method on a plate-like sample geometry (7 × 7 × 1 mm^3). The resistivity values were calculated analogous to Refs. 15 and 16.

The effective metal content of each sample was calculated by considering the apparent porosity determined from density measurements of ground samples. For example, a theoretical metal content of 50 vol.% and a residual porosity of 5% resulted in an effective metal content of 47.5 vol.%.

3. Results and discussion

DC measurements at RT were found to be less reproducible than AC measurements. The DC resistance varied up to 50% between repeated measurements and will, therefore, not be quoted here. The observed variation of the DC data is probably caused by a higher sensitivity of this measurement method to contact problems. The AC resistance varied less than 10%, even when the contact layers had been completely removed and renewed. A measurement frequency of 100 kHz gave the lowest variation.

The AC resistivities calculated from AC resistance measurements are listed in Table 3. In all investigated

Table 2
Details of the investigated compositions

Material system		Zr_xAl_y–Al_2O_3		Cr–Al_2O_3		Mo—Al_2O_3
	Powder	"Al10"	"Al44"	"Cr10"[a]	"Cr50"[a]	"Mo30"
Starting powder mixture	Al_2O_3 (vol.%)	83.1	36.0	89.5	47.4	68.5
	ZrO_2 (vol.%)	6.9	20.0	–	–	–
	Al (vol.%)	10.0	44.0	0.5	2.6	2.2
	Cr (vol.%)	–	–	10.0	50.0	–
	Mo (vol.%)	–	–	–	–	29.3
	Density (g/cm^3)	3.961	3.754	4.279	5.521	5.793
After sintering	Al_2O_3 (vol.%)	94.6	71.1	90.1	50.4	70.8
	ZrO_2 (vol.%)	–	–	–	–	–
	Zr_xAl_y (vol.%)	5.4	28.9	–	–	–
	Cr (vol.%)	–	–	9.9	49.6	–
	Mo (vol.%)	–	–	–	–	29.2
	t.D. (g/cm^3)	4.036	4.156	4.285	5.543	5.810
	Density (%t.D.)	94.0	91.2	99.4	95.0	94.1

[a] Equivalent to these samples: compositions "Cr15", "Cr20", "Cr25", "Cr30", "Cr35".

Table 3
AC resistivity of different compositions at RT ($f = 100$ kHz)

Effective metal content (vol.%)	AC resistivity 100 kHz (Ωm)
Cr–Al_2O_3	
10.0	5.8E+05
14.5	3.6E+05
18.6	3.2E+05
22.9	2.2E+05
27.8	8.3E+04
28.3	2.8E+04
32.6	2.1E+04
44.8	1.7E+04
Zr_xAl_y–Al_2O_3	
5.4	2.8E+05
28.9	3.9E+04
Mo–Al_2O_3	
29.2	1.6E+04

systems, samples with low metal content were electrical insulators with high resistivity in the range of 1E+05 Ωm. Samples with high metal content were conductors with resistivity around 1E-04 Ωm. The percolation threshold lies at around 28 vol.% in the Cr–Al_2O_3 system. The percolation thresholds in the other two systems are equal or smaller than that. When comparing the resistivity for a metal content of around 29 vol.%, it can be seen that it is significantly lower in the metallic Cr–Al_2O_3 and Mo–Al_2O_3 systems than in the intermetallic Zr_xAl_y–Al_2O_3 system. This behavior was expected and can be explained by the ordered structure of intermetallic phases. XRD measurements indicate that the main constituents were Zr_4Al_3 in the case of "Al10". and $ZrAl_3$ respectively ZrAl in the case of "Al44".

A sharp percolation threshold is obvious in the Cr–Al_2O_3 system (see Fig. 1). The resistivity decreases gradually with increasing metal content in the insulating region. A sharp drop of eight orders of magnitude occurs at a metal content of 28 vol.%. At higher metal contents, the resistivity again decreases gradually with increasing metal content. Different models were applied trying to predict the resistivity values, but only the GEM (general effective media) equation[14] describes a sharp drop in the resistivity at the percolation threshold. A theoretical resistivity[17] of 1.5E-07 Ωm for Cr was used for the calculations. For pure α-Al_2O_3, a resistivity around 1E+12 to 1E+14 Ωm is quoted in the literature.[18–21] However, the resistivity is also reported to decrease several orders of magnitude when Al_2O_3 forms

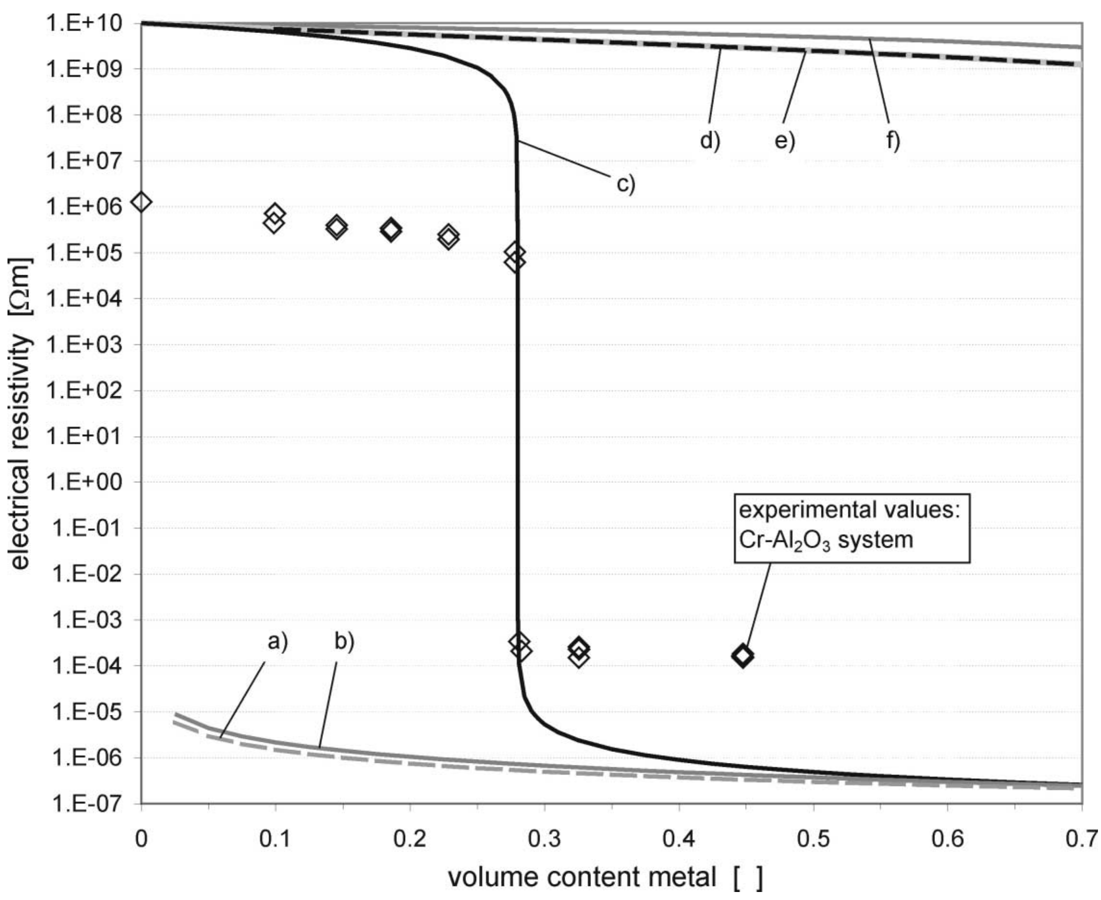

Fig. 1. Influence of the metal content on AC resistivity of Cr–Al_2O_3 samples (by 4-point contact method at $f = 100$ kHz); theoretical calculations based on different models: (a) parallel resistors, (b) Hashin–Shtrikman lower bound, (c) GEM—general effective media equation, (d) Weiner's rule, (e) Hashin–Shtrikman upper bound and (f) serial resistors.

a solid solution with Cr_2O_3[22] or is sintered in carbon-rich atmosphere.[23] For high Cr content, diffusion of Cr into Al_2O_3 does occur in the Cr–Al_2O_3 system leading to a shift of the Al_2O_3 XRD peaks. In addition, all samples were sintered in a carbon-containing atmosphere, so that a theoretical resistivity of $1E+10$ Ωm was assumed for the Al_2O_3 phase in the composites.

Even far off the percolation threshold, the experimental values differ considerably from the theoretically calculated values (see Fig. 1). This is probably due to artifacts of the experimental setup. At high metal contents, the overall resistance of the samples was so low that a considerable influence of the contact resistance can be expected. At low metal contents, the resistance is very high, so that the contact resistance is negligible but adsorbed moisture can have a significant effect. It appears that the AC resistivity of insulating composites can be quite different from DC data, which became obvious when measuring the AC resistivity of Al_2O_3 (see data point at 0 vol.% in Fig. 1). In addition, the AC resistivity of electrical insulators may vary significantly with measurement frequency.

At the percolation threshold, small changes in metal content cause big changes in resistivity. This could result in anisotropic electrical properties. The ohmic resistance of samples with metal contents close to the percolation threshold was measured in three orthogonal directions. One direction was parallel to uniaxial pressing force. The calculated resistivity values are shown in Fig. 2. When considering the Cr–Al_2O_3 and Mo–Al_2O_3 samples, the resistivity is approximately isotropic. In contrast, the Zr_xAl_y–Al_2O_3 samples exhibit significantly higher resistivity in the pressing direction (two orders of magnitude lower perpendicular to the pressing direction). This can be explained by the flaky particle shape of milled metal powders. Especially the highly ductile Al particles are deformed into flakes which align during uniaxial pressing. As a result, the connectivity of the intermetallic phases after reaction sintering can be far lower in pressing direction at metal contents close to the percolation threshold.

Preliminary measurements of DC resistance at elevated temperatures for a conducting Zr_xAl_y–Al_2O_3 sample (effective metal content: 29 vol.%) seem to indicate that the contained intermetallic phases ($ZrAl_3$ and ZrAl) are PTC conductors. This assumption is supported by electrical heating experiments where the sample resistance increased with temperature so that the electrical power had to be controlled by constant voltage to achieve stable conditions.

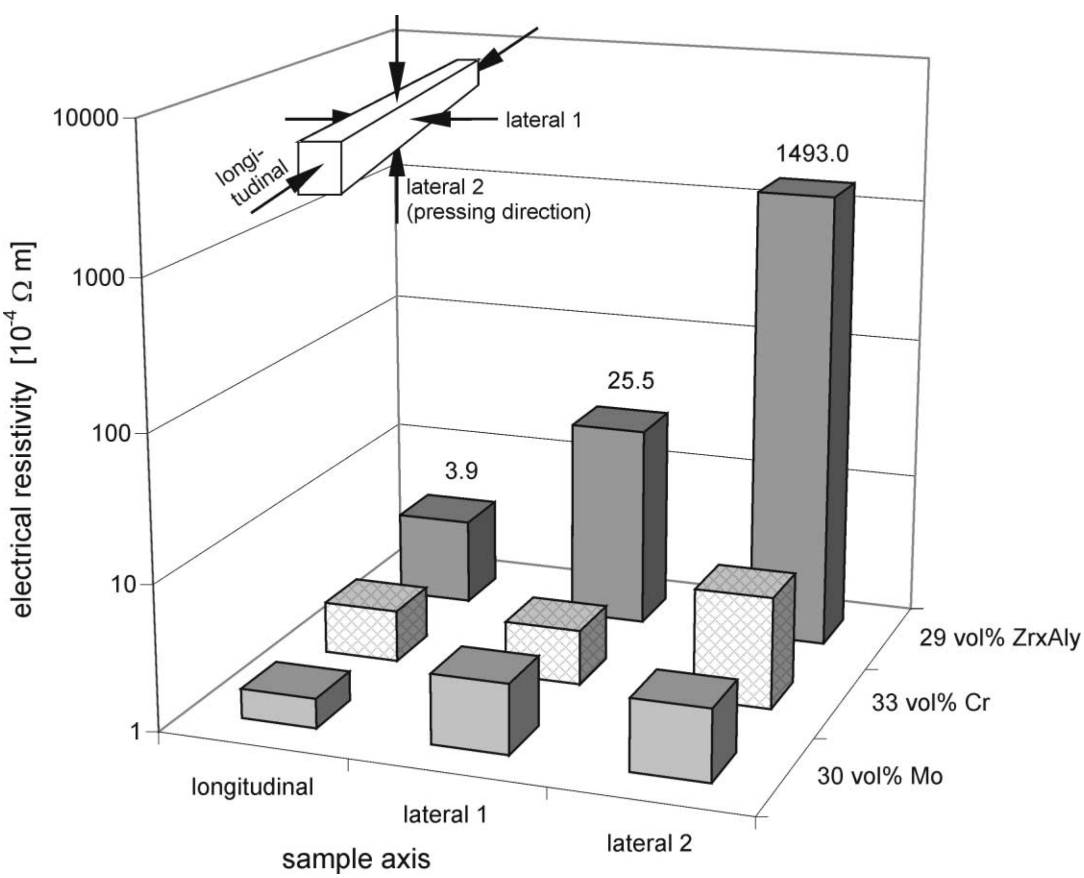

Fig. 2. AC resistivity of different metal–Al_2O_3 composites parallel ("lateral 2") and perpendicular ("longitudinal" and "lateral 1") to uniaxial pressing direction, resistance measurement by 4-point contact method; $f=100$ kHz.

4. Conclusions

AC resistivity measurement is a good tool for characterization of metal-ceramic composites with interpenetrating networks. The values obtained differ from DC values and are also dependant on the frequency. Further knowledge of AC resistivities and their dependence on the frequency is necessary, e.g. for the design of AC resistance heaters.

A sharp percolation threshold was observed in the Cr–Al_2O_3 system ($\pm$4 orders of magnitude). This drastic change in resistivity for small variation in composition could be used to tailor the electrical properties of functionally graded materials. Even multicomponent compounds with layers or inner structures of a conductive phase may be possible as the variation in composition seems to be small enough to enable successful co-sintering in reactive systems.

Pressed Zr_xAl_y–Al_2O_3 samples with a metal content close to the percolation threshold exhibited anisotropic electrical properties due to alignment of flaky particles during uniaxial pressing. This effect may be useful to achieve a high dielectric strength in one direction, while the material is highly conductive in the other directions. But it is still questionable whether the compliance with certain resistivity values is possible close to the percolation threshold, as a sudden change in the electrical properties is expected in this material system, as well.

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