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Electrical conductivity of an insulator matrix (alumina) and conductor particle (molybdenum) composites

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Abstract

Different concentrations of molybdenum (from 5 to 35 vol.%) were added to alumina matrices and the resulting mixture hot-pressed to produce dense metal toughened-ceramic composites. Their resulting electrical properties were measured using two-probe impedance spectroscopy, in the range 25–1000 °C. Experimental and theoretical studies were done to examine how the volume fractions and the morphology of the embedded metal particles affect the electrical behaviour of these composite materials. Due to the percolation effect, a sharp increase in the electrical conductivity of these composites was observed for compositions with molybdenum contents higher than 20 vol.%. The experimental data were fitted into the GEM equation. It was shown that the conductivity of these metal-toughened-ceramic composites is strongly affected by the amount, and less by the size of the metal particles. For low concentrations of molybdenum only one semicircle was readily identified with impedance spectroscopy analysis. This indicates that the matrix is still the main conductor phase. For higher concentrations of molybdenum, two readily resolvable arcs were present. For concentrations of metal higher than 30 vol.% the second semicircle might be an overlapping of two semicircles and therefore the impedance spectra for these composites can be resolved with three semicircles. The presence of this third semicircle can be explained in terms of molybdenum clusters. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In many areas of scientific research and engineering a key problem is the prediction of the effective physical properties of composite media from the properties and the microstructure of the constituents. For example when two powders with different electrical conductivity are mixed the resulting composite often has an electrical conductivity that is unpredictable in practice. In this respect our work deals with the electrical conductivity of cermets because they can have a variety of important technological applications such as heaters, ignites, heat exchangers, resistors, sensors, transducers, electromagnetic shielding of electronic components, electrical stress relief in high voltage devises, electrodes for fuel cells and potentially also as crucibles for vacuum induction furnaces.[1–4] Moreover if the electrical conductivity of these composites is high enough it is feasible to use electrical discharge methods (EDM), an economical way to prepare complex shapes of very hard materials. Recently, cermets with controlled electrical conductivity have been used for replacing metal parts in electrical and electronic devices, improving not only the performance of the components but also the temperature of their applications.[5,6] In particular alumina/molybdenum composites have been used in electrical applications in which different electrical properties are required, for instance, the lowest metal content that still provides low resistivily is needed when using these composites as electrical feed through.[7] In another case, a high molybdenum content with high resistivity is aimed to increase the dielectric constant in decoupling capacitors.[8]

As regards electro ceramics the main interest is the improvement of both electrical and mechanical properties. In this respect the design of a composite and especially metal-ceramic composites is usually a compromise between the desire to raise the conductivity as much as possible and to retain refractoriness, hardness and stiffness that will be depleted by the embedded metal particles.

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Metals particles are also used in ceramic matrices to increase their toughness. In this case, the maximum toughening effect is reached with addition of particles in the range 15–20 vol.%.[9] However, often the amount of metal in these cermets, in order to have enough electrical conductivity for technological applications, is above 20–30 vol.%. Therefore, in order to design composites for specific applications it is useful to be able to model the properties theoretically based on knowledge of the constituent phases and their relative distribution.

Usually at a certain threshold value of volume fraction of the metals particles, they are sufficiently close-packed to form an unbroken conducting pathway through the composites and the conductivity of the material increases sharply. This threshold is known as the percolation limit. A way of maximizing composite conductivity while retaining the good properties typical of ceramic materials would be to control not only the amount but also the shape and size of the embedded particle in order to reach the percolation limit at relatively low volume fractions.

So far, not many cermets have been tested for their electrical properties: Al_2O_3/TiN,[10] Si_3N_4/TiN,[11] Si_3N_4/TiN-TiC,[12] $Si_3N_4/MoSi_2$,[13] Si_3N_4/TaN,[14] SiC/TiB_2[15] SiC/ZrB_2[6,16] and even less metal-toughened ceramics ZrO_2/(Ti or Ni)[1] SiO_2/Mo,[17] BaTiO3/Ag,[18] $BaBi_8O_{13}$/Ag.[19]

For these reasons, Al_2O_3/Mo composites can be ideal for applications where two distinct properties, toughness and electrical conductivity, need to be combined in the same material. Therefore this system was chosen, in this study, as a convenient model to begin a systematic investigation of electrical properties related to the amount and also to the size of the metal particle.

2. Experimental procedure

2.1. Materials

Molybdenum is a silvery-white, hard transition metal. Because of its unique set of physical and electrical properties, it was chosen as the dispersoid in the Al_2O_3 matrix. Increasing amounts (from 5 to 35 vol.%) of molybdenum powder (Japan New Metals Co., Japan) were mixed with high purity alumina powder (AKP-53, Sumitomo Chemical LTD., Japan). The influence of the metal particle size was studied preparing several compositions using two different molybdenum powders: the first with average particle size = 0.56 μm the other with average particle size = 10 μm. The ceramic-metal powder mixtures were attrition milled in isopropyl alcohol for 5 h. After drying, samples of each composite were hot-pressed in a graphite die with its inner walls coated with a BN slurry to avoid any interaction between specimens and graphite die. The hot press atmosphere was argon. For all the composites, the maximum hot-pressing pressure was 30 MPa. The selected sintering temperature and time were 1640 °C and 1 h, respectively. The samples were then slowly cooled down (200 °C/h) to room temperature. Hot-pressed samples were in the form of discs with diameter and thickness of 50 and 10 mm, respectively. The density, measured by Archimede's method, was >98.5% of its theoretical value calculated from the rule of mixture. To enable micro structural parameters that describe the distribution of phases within the composites to be measured, all specimens were ground and polished using diamond pastes. After polishing the metal particles were clearly visible even with an optical microscope. However, to reveal alumina grain boundaries the specimens were also etched for 40 min at 1400 C in argon. Scanning electron microscopy (SEM) coupled with a microanalysis was then used to characterize mainly porosity, the matrix and the metal grain size and phase distribution. The quality of the molybdenum particles dispersion was assessed by using an image analyser.

2.2. Electrical characterization

Electrical resistivity (ρ) was measured by a two-probe ac impedance spectroscopy. Samples were prepared from the hot-pressed discs. Discs were sliced, using a low speed diamond saw, into samples of 10×10×10 mm. The surfaces of the samples were polished using diamond pastes. The direction of measurement was always perpendicular to the hot pressing axis. Platinum paste electrodes (Platinum conductive enamel, Johnson Matthey E8310) were painted onto the specimens and dried at 1000 °C for 2 h before mounting the conductivity cell.

The impedance measurements were carried out with an HP 4192A Impedance Analyzer in the frequency range 5 Hz to 13 MHz and in the temperature range 250–1000 °C. The temperature dependence of the resistivity was investigated by heating the sample in a furnace up to 1000 °C. Temperature increments of 50 °C were used, the temperature was reached and hold for 30 min. before testing the sample. Measurements were carried out at $p_{O_2} = 10^{-5}$ atm. obtained by using N_2 at a flow rate of 100 ml min^{-1}.

The conductivity of the composites was estimated by using an analogue circuit method. The composite is visualized as 100% dense compact of Al_2O_3 matrix grains and conducting Mo particles both of which are polyhedra with nearly spherical geometry. The total conductivity of the composites is treated as the sum of the effective interface and lattice conductivity.

3. Results and discussion

The microstructure of the hot-pressed composites are shown in Fig. 1(a,b). The respective grain size distributions of the Mo particles after hot pressing were assessed by image analysis on scanning electron micrographs [Fig 2 (a, b)]. SEM and microanalysis reveal that in all materials the hot-pressed process gives rise to a microstructure with α-Al_2O_3 grains and Mo particles.

The microstructural observations showed that the mixing procedure gave reasonably good dispersed fine homogeneous microstructures without residual porosity or macro defects. The Al_2O_3-matrix grains were typically in the size range ≅3–10 μm in all composites (Fig. 3). However keeping the Mo volume fraction constant, the average alumina grain size was always slightly larger when coarse Mo was used (see Table 1). A morphological change of the Mo particles after hot pressing was noticed in both kinds of composites and attributed to the attrition milling process as well as to plastic deformation occurred during hot-pressing. Image analysis showed that when finer Mo particles were used, the final average grain size of the metal particles was ≅3.0 μm, whereas for the coarse Mo powder the final grain size distribution after hot pressing was broader with a low fraction < than 3 μm and with average grain size

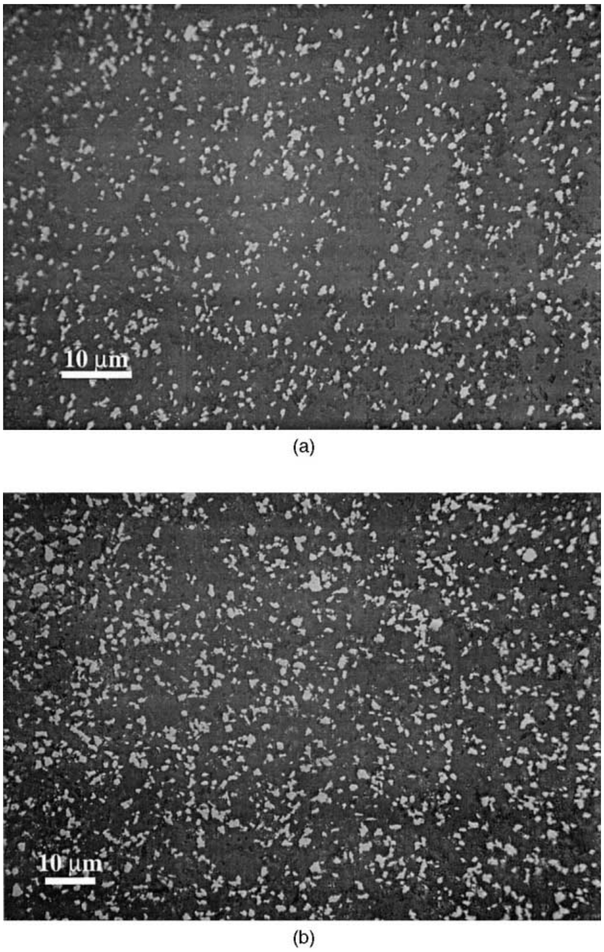

Fig. 1. SEM micrographs showing cermets microstructure (a) alumina/10 vol.% of fine Mo powder, (b) alumina/20 vol.% of fine Mo powder.

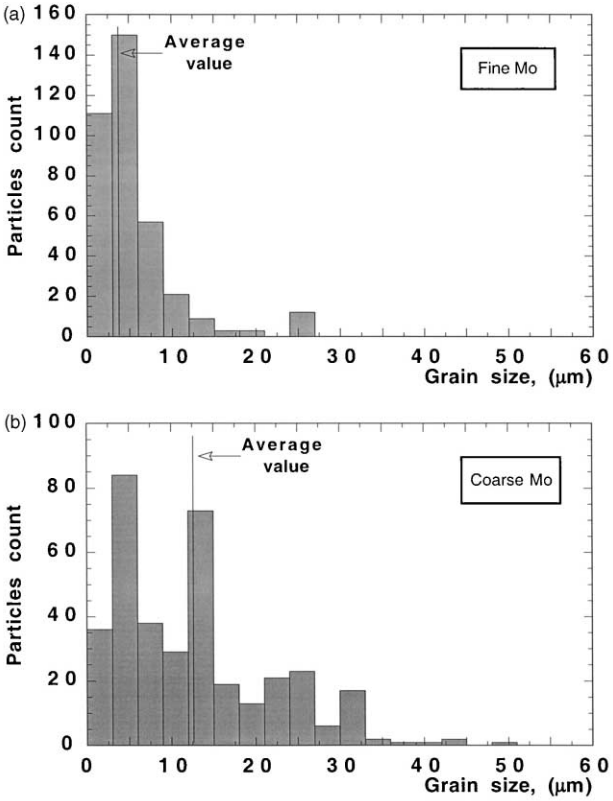

Fig. 2. Grain size distributions of the metal particles after hot pressing in cermets with 20 vol.% of molybdenum (a) composites with fine Mo powder (b) composites with coarse Mo powder.

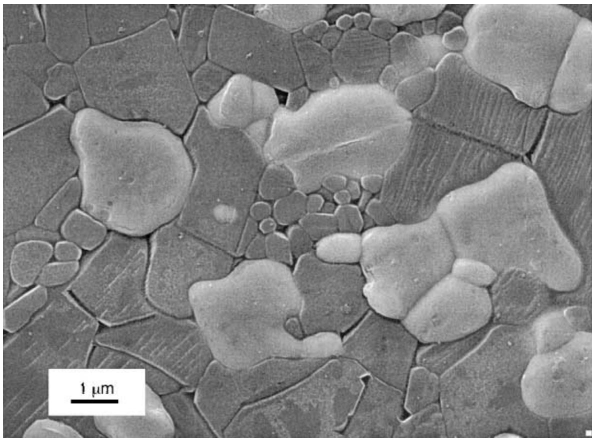

Fig. 3. SEM micrograph of a microstructure showing the alumina grain size.

Table 1
Value of the Al_2O_3 average grain size in the cermets

Materials	Al_2O_3 average grain size (μm)
Al_2O_3 + 5 vol.% of fine Mo	7.5
Al_2O_3 + 5 vol.% of coarse Mo	10
Al_2O_3 + 30 vol.% of fine Mo	3
Al_2O_3 + 30 vol.% of coarse Mo	5

≅12 μm. An important microstructure feature of this latter composite was the presence of many elongated metal particles with length up to 25 μm (see Fig. 4). In particular, when finer dispersoids were used, 65% of the total fraction of metal particles had a size of ⩽3 μm, whereas for the case of larger particles, only 20% were ⩽3 μm. In both kinds of composites only a few and very small (nanosized) particles were dispersed within the alumina matrix grain, whereas the majority of the particles (above 1 μm) were located at the grain boundaries of alumina.

Microstructure evaluation also showed that, for a given series of composites (either small or large Mo particles), the size of the metal particles (or metal clusters) in the composites increases as the metal content increases. This effect can be seen when comparing the microstructures presented in Fig. 1 (a) and (b). Both composites were made using fine Mo powder but the one with 20 vol.% of metal exhibits larger average metal particles.

However, the metal particles inhibit the matrix grain growth and therefore the matrix grain size slightly decreases for higher metal volume fraction (see Table 1).

The typical electrical behaviour of these composites is shown in Fig. 5. The electrical conductivity is plotted as a function of the molybdenum content for three different temperatures (500, 750 1000 °C). For Mo amount lower than 20 vol.% the electrical conductivity rises with temperature, but the behaviour is still similar to that of pure alumina. As the Mo amount is raised, the original insulating composite becomes a conductor. The critical Mo volumetric fraction (or percolation limit) for all composites is in the range 20–30 vol.%. However, the electrical conductivity of composites depends on the Mo volume fraction and the size of the metal particles. When coarse molybdenum particles were used, the conductivity increased remarkably at a Mo volume fraction of about 20–25 vol.% while when composites with finer particles are tested, the conductivity rises also with the temperature and volume fraction of the metal added but the percolation limit is slightly higher (25–30 vol.%). Moreover the relationship between conductivity and Mo content shows an S-shaped curve, which is typically seen in conductor/insulator mixtures.[20,21]

It should however be noted that although the conductivity rises when metal particles are in contact, it does not necessarily follow that a fully connected network of Mo is formed. McLachlan[22] showed that at volume fraction just below the percolation limit, conducting particles would be arranged in such a way to form large, but finite interconnected clusters which do not span the entire specimen. The resistivity measurements indicate that a properly formed, well-bonded network of molybdenum does not actually occur up to a volume fraction higher than 30 vol.% of Mo, as this is when the conductivity is typical of that of pure molybdenum.[23,24]

In the range 5–20 vol.% of Mo the apparent activation energies calculated from the slopes of the Arrehnius plots are close to 98 kJ/mol, which is in agreement with that of the conductivity of Al_2O_3 sintered and tested in a low partial oxygen pressure.[25] This implies that in this volume fraction range the composite conductivity is basically through the matrix phase. When Mo exceeds 20 vol.% the activation energy is much lower (≈6 kJ/mol) and the mechanism in this range should be the scattering of electrons by the geometric constraints on the current flow due to the meandering structure of the metal continuum.

Even when the conductivity is mainly due to the presence of molybdenum, composites with coarser metal powder have a slightly higher conductivity because larger metal particles results in a reduced electron scattering and a shortening of the current paths.

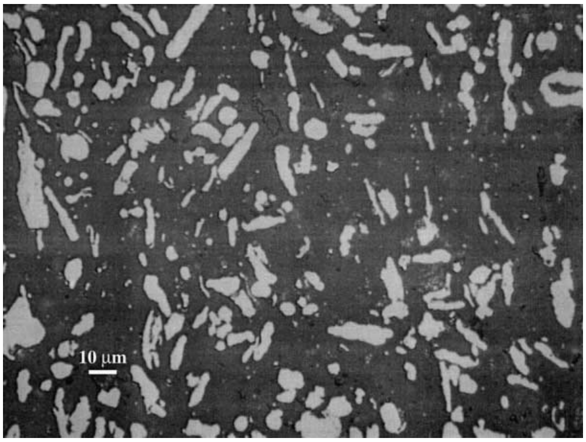

Fig. 4. SEM micrograph of a microstructure showing the presence of many elongated molybdenum particles with length up to 25 μm.

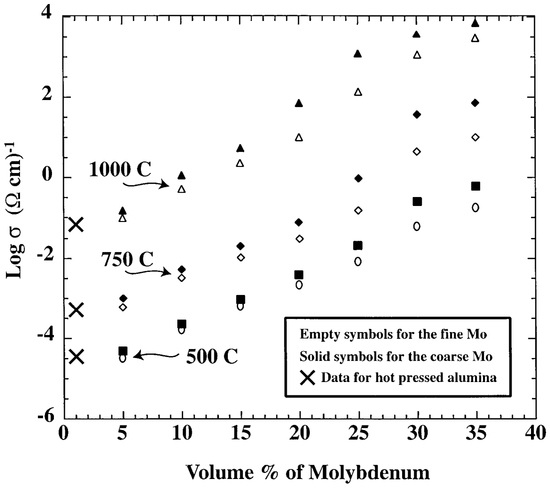

Fig. 5. The electrical behavior of alumina/molybdenum composites made with fine or coarse metal powders.

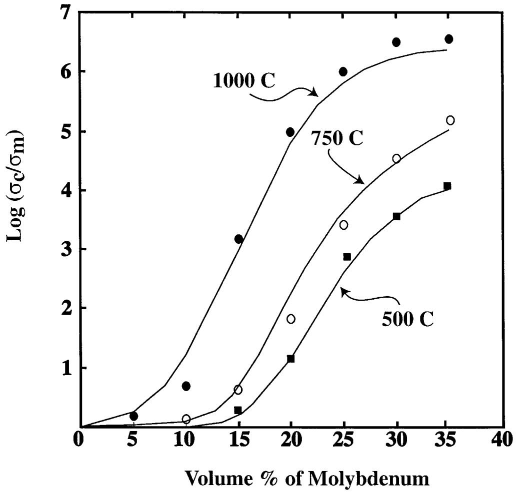

Fig. 6. A GEM fitting of a set of experimental data for composites with fine Mo particles and temperatures up to 1000 °C, σ_m is the matrix conductivity, σ_c is the composite conductivity.

The experimental data were fitted with the General Effective Media (GEM) equation.[22]

$$\frac{(1-f)\left(\sigma_m^{1/t}-\sigma_e^{1/t}\right)}{\sigma_m^{1/t}-A\sigma_c^{1/t}}+\frac{f\left(\sigma_p^{1/t}-\sigma_c^{1/t}\right)}{\sigma_p^{1/t}-A\sigma_c^{1/t}}=0 \tag{1}$$

$$A=\frac{1-V_c}{V_c} \tag{2}$$

where, in our case, f is the volume fraction of alumina, σ_m is the alumina conductivity, σ_p is the molybdenum conductivity, σ_c is the composite conductivity, V_c is the percolation limit.

The GEM equation gives complete information on how the volume fraction of components will affect the composite conductivity by taking into account the intrinsic conductivities and geometries of both component and their arrangement and orientation. In the equation, "t", is the exponent term, which represents the morphological variable and is related to the size and shape of the second phase, and it is equal to the product of the percolation limit and "m" a particle shape factor, which has the a value of 3 for spheres and greater than 3 for elliptical particles.

In Fig. 6, a GEM fitting of a set of experimental data for composites with small Mo particles and temperatures up to 1000 °C is shown. The experimental data was nicely fitted with the GEM equation up to 1000 °C. In Table 2 the "t" values used in the GEM equation are reported. The morphological variable "t" decreases and thus the slopes of the electrical conductivity curves became steeper as the temperature increases, moreover, at the same temperature, "t" is always lower for the composites with coarser metal particles. This is reasonable since easier percolation is expected for elongated metal particles. In fact the percolation limit has been related to the excluded volume of the conductive particles.[26] The excluded volume of an object is defined as the volume around an object into which the centre of another similar object is not allowed to enter if overlapping of the two objects is to be avoided. If the excluded volumes of two conducting particles overlap, there is a certain probability that they will form a conducting link. The theoretical calculation[26] showed that the aspect ratio (AR) of the conducting particles dependence of the percolation limit is $V_c \, \alpha \, (\mathrm{AR})^{-1}$. In our case, not only composites with coarser Mo particles have a larger metal average grain size but also many elongated metal particles with length up to 25 μm. The average aspect ratios calculated from the elongated length and width data from the particle size and shape analysis ranged between 1.7 for composites with only 5 vol.% of molybdenum (net particles shape nearly spherical) to 4.35 for those with 35 vol.% of metal added (far from spherical). This also has important implications for the mechanical properties of these materials because, if the same amount of molybdenum is used, the toughness of a cermet will always be higher if elongated metal grains are used.[9] Moreover, the alumina average grain size can also play a role, even if small, in the overall conductivity. When coarser alumina grain size is present (composites with coarser Mo particles), the Mo cluster has larger excluded volume per cluster and therefore higher conductivity.

Table 2
Value of 't' that fits the GEM equation

500 °C fine Mo	$t=2.4$
500 °C large Mo	$t=2.1$
750 °C fine Mo	$t=2.3$
750 °C large Mo	$t=1.85$
1000 °C fine Mo	$t=2.12$
1000 °C large Mo	$t=1.7$

A typical impedance spectrum, for these composites, is presented in Fig. 7(a–c). In this so-called "Nyquist plot" the imaginary part of impedance is plotted versus the real part. Frequency increases from the right to the left. For the range of frequencies investigated, for compositions up to 10 vol.% and low temperatures (up to 500 °C), only one semicircle was readily identified, which indicates the presence of a unique conductor phase (Fig. 7a). For higher amounts of molybdenum, it can be seen that there are two readily resolvable arcs (Fig. 7b). The high frequency arc corresponds to the low-conductivity continuous phase (alumina). The low frequency arc corresponds to the added second metallic phase. This arc is non-ideal (i.e. its centre being below the real axis) because it is composed of three relaxations

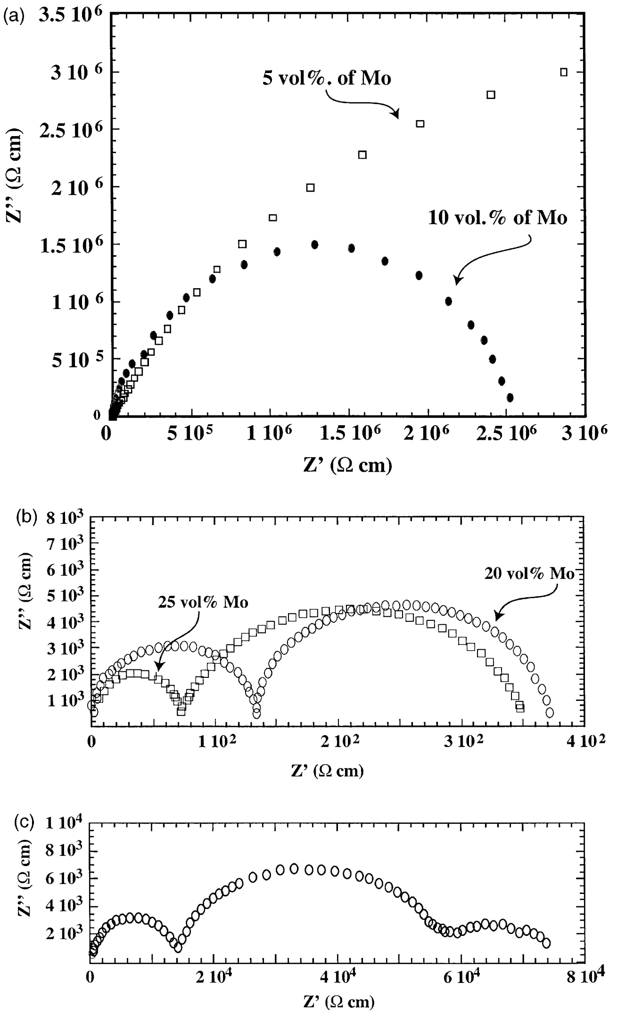

Fig. 7. Impedance spectrum for composites with (a) 5 and 10 vol.% of molybdenum added, at 500 °C, (b) 20 and 25 vol.% of coarse molybdenum at 800 °C, (c) 35 vol.% of coarse molybdenum at 500 °C.

corresponding to the three possible orientations of the elongated particles. As can be seen from Fig. 7b as the metal fractions increase, there is an increase in the low frequency semicircle whilst the high frequency semicircle is progressively overlapped, showing that the molybdenum conductivity is becoming predominant for higher amount of molybdenum present.

For amounts of metal as high as 30–35 vol.% the second semicircle might be an overlapping of two semicircles and therefore the impedance spectra for this composites can be resolved with three semicircles (Fig. 7c). The presence of the third semicircle can originate from the presence in the composite microstructure of metal elongated clusters oriented in the direction of the preferred current line (i.e. those arranged perpendicular to the electrodes). This third semicircle was predicted for a two-component system from computer simulation.[27]

4. Conclusions

Composites of alumina and molybdenum (from 5 to 35 vol.%) were hot pressed to produce dense metal-toughened-ceramic composites. In order to exploit the influence of the conducting particles size two different molybdenum powders were used. The mixing procedure gave reasonably good dispersed fine homogeneous microstructures without residual porosity or macro defects. However when finer Mo particles were used 65% of the Mo in the composite were <3 μm and when coarser Mo particles were used, only 20% of them were <3 μm, after sintering. Electrical conductivity is increasing as temperatures are increased but also, due to the percolation effect, a sharp increase in the electrical conductivity of these composites is observed for compositions with molybdenum higher than 20%. The GEM equation is effective for modelling the electrical properties of these composites. Not only the amount of Mo influences the percolation limit but also the size of the metal particles. Elongated molybdenum grains always reduce the percolation limit. Activation energies were close to those of pure alumina for compositions with Mo less than 20 vol.% while they were much lower for higher amounts of molybdenum. Impedance spectroscopy shows that for low amounts of molybdenum only one semicircle was readily identified, which indicates that the matrix is still in the main conductor phase. For higher amounts of molybdenum, two readily resolvable arcs were present. For amounts of metal higher than 30 vol.% the presence of a third semicircle can be explained in terms of molybdenum clusters.

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References

1. Martinelli, J. R. and Sene, F. F., Electrical resistivity of ceramic-metal composite materials: application in crucibles for induction furnaces. *Ceram. Intern.*, 2000, **26**(3), 325–335.
2. Martin, C., Mathieu, P. and Cales, B., Electrical discharge machinable ceramic composites. *Mater. Sci. Eng.*, 1989, **A109**, 351–356.
3. Tressler, J. F., Alkoy, S. and Dogan, A., Functional composites for sensors, actuators and transducers. *Compos. Part A-Appl. S.*, 1999, **30**(4), 477–482.
4. Mogensen, M., Primdahl, S., Jorgensen, M. J. and Bagger, C., Composite electrodes in solid oxide fuel cells and similar solid state devices. *J. Electroceramics*, 2000, **5**(2), 141–152.
5. Onitsuka, K., Dogan, A. and Tressler, J. F., Metal-ceramic composite trasducer, the Moonie. *J. Intel Mat. Syst. Str.*, 1995, **6**(4), 447–455.

6. Jimbou, R., Takahashi, K., Matsushita, Y. and Kosugi, T., SiC-ZrB_2 electroconductive ceramic composites. *Adv. Ceram. Mater.*, 1986, **1**, 341–345.
7. Kramer, D. P., White, K. and Kelly, M. D., Effect of sintering parameters and composition on the resistivity of a cermet used as an electrical feedthrough. *Ceram. Eng. Sci. Proc.*, 1982, **3**(9–10), 512–518.
8. Ogawa, M., Yamasaki, K., Hirano, M., Schmitt, M.A. and Bhattacharyya, B.K., U.S. Patent no. 5099–388, 1992.
9. Sbaizero, O. and Pezzotti, G., The influence of the metal particle size on the toughness of an Al_2O_3/Mo composite. *Acta Materialia*, 2000, **48**(2), 985–992.
10. Mukerji, J. and Biswas, S. K., Synthesis, properties and oxidation of alumina-titanium nitride composites. *J. Am. Ceram. Soc.*, 1990, **73**(1), 142–145.
11. Bellosi, A., Gucciardini, S. and Tampieri, A., Development and characterization of electroconductive Si_3N_4/TiN composites. *J. Eur. Ceram. Soc.*, 1992, **9**, 83–93.
12. Petroovsky, Ya.V., Use of conducting composite based on Si3N4 in broadband electric heaters. *Powder Metall. and Metal Ceram.*, 1998, **37**(3–4), 174–181.
13. Kao, M. Y., Properties of silicon-nitride molybdenum disilicide particulate ceramic composites. *J. Am. Ceram. Soc.*, 1993, **76**(11), 2879–2883.
14. Petroovsky, V.Ya. and Rak, Z. R., Densification, microstructure and properties of electroconductive Si_3N_4-TaN composites. Part II: electrical and mechanical properties. *J. Eur. Ceram. Soc.*, 2001, **21**, 237–244.
15. McMurtry, C. H., Boecker, W. D., Seshadri, S. G., Zanghi, J. S. and Garnier, J. E., Microstructure and material properties of SiC-TiB2 particulate composites. *Am. Ceram. Soc. Bull.*, 1987, **66**, 325–329.
16. Takahashi, K. and Jimbou', R., Effect of uniformity on the electrical resistivity of SiC-ZrB_2 ceramic composites. *J. Am. Ceram. Soc.*, 1987, **70**, C369–C373.
17. Ishibashi, H., Tobimatsu, H. and Matsumoto, T., Characterization of Mo-SiO_2 functionally graded materials. *Metall. Mater. Trans.*, 2000, **A31**(1), 299–308.
18. Zhou, J., Li, L. T. and Gui, Z. L., Sol-gel derived $BaTiO_3$ thin films with embedded silver nanoparticles: preparation and dielectric properties. *Nanostruct. Mater.*, 1997, **8**(3), 321–328.
19. Lee, T. H., Yang, Y. L. and Jacobson, A. J., Electrical conductivity and oxygen permeation of Ag/$BaBi_8O_{13}$ composites. *Solid State Ionics*, 2000, **134**(3–4), 331–339.
20. Gurland, J., *Trans. Metall. Soc. AIME*, 1966, **236**, 642.
21. Malliaris, A. and Turner, T., *J. Appl. Phys.*, 1971, **42**, 614.
22. McLachlan, D. S., Blaszkiewicz, M. and Newnham, R. E., Electrical resistivity of composites. *J. Amer. Ceram. Soc.*, 1990, **73**(8), 2187.
23. Northcott, L., In *Metallurgy of the Rarer Metals: Molybdenum*. Butterworths Sc. Publ., 1956, p. 28.
24. Khanna, S. N. and Jain, A., *J. Phys. F: Met. Phys.*, 1974, **4**, 1982.
25. Kitazawa, K. and Coble, R. R., Electrical conduction in single crystal and polycrystalline alumina at high temperature. *J. Am. Ceram. Soc.*, 1974, **57**, 245–250.
26. Balberg, C. H., Anderson, S., Alexander, N. and Wagner, Excluded volume and its relation to the onset of percolation. *Phys. Rev. B*, 1984, **30**(7), 3933–3943.
27. Han, D. G. and Choi, G. M., Impedance spectra for a 2-D conductor insulator composite by computer simulation. *J. Electroceramics*, 1998, **2**(1), 57–66.