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Impedance Analyses of Alumina-Molybdenum (Al_2O_3-Mo) Composites

S. Hussain[1,*] and O. Sbaizero[2]

[1]*Department of Physics, University of Dhaka, Dhaka 1000, Bangladesh*

[2]*Department of Materials Engineering, University of Trieste, Trieste 34127, Italy*

Abstract

The microstructure and electrical properties of Al_2O_3-Mo composites were investigated. Different amounts of molybdenum (5, 10, 20, 25 vol%) were added to alumina matrix and the resulting mixture was hot pressed to produce dense metal toughened-ceramic composites. The electrical properties of the composites were examined using impedance spectroscopy in the temperature range 250°C - 1000°C at 50°C temperature intervals. From the analysis, two readily resolvable arcs were found to be present: the one at higher frequencies is the intragranular (grain) response of the bulk; the other is the intergranular (grain boundary) response caused in the internal surfaces of polycrystalline specimens at low frequencies. The effects of grains and grain boundaries on the electrical properties of the composites vary with the composition and temperature. The temperature and composition dependence of grain and grain boundary conductivities are explained by the microstructure.

I. Introduction

Alumina ceramics is the most widely used fine ceramics material. This material has superb material characteristics such as high electrical insulation, high mechanical strength, high wear and chemical resistance. However, its application is severely limited due to its brittleness and poor machining properties [1]. Therefore, alumina toughening is a hot issue that has been attracting much attention of scientists in materials science in recent years. Incorporation of appropriate functional materials into alumina matrix can introduce new physical properties into the composite system realizing the so-called "functionally structural material". Composites are used in many different applications, for their unique properties (electrical, thermal, mechanical, or optical) which are difficult to predict and highly dependent on the composite microstructure.

It is well-accepted that the fracture toughness of the brittle Al_2O_3 can be increased through the incorporation of ductile metal [2]. But the higher electrical conductivity of the insulating material can also be achieved by the incorporation of conductive filler into the matrix. The conductivity in such systems is obtained only above a certain filler concentration, so called percolation threshold (φ_c), at which a continuous network of conductive particles is formed [3]. Composite materials with positive temperature coefficient can be used in manufacturing devices sensible to temperature variation. If the material shows non-linear current voltage behaviour in the percolation region, varistors can be produced [4].

The present work deals with the correlation of the microstructures of Al_2O_3-Mo composites with the electrical properties. The aim of this paper is to investigate the electrical behaviour of the Al_2O_3-Mo composites and the microstructural studies, in order to correlate the composite microstructure with the experimentally determined electrical properties. Since it is well-known that the constituents' (both matrix and filler) properties greatly affect the overall composite behaviour, the objective of this work is to carry out a systematic study to investigate the dependence of the composite performance on the constituent's characteristics and respective volume fractions of the filler. In particular, by using a microstructure based studies, it is possible to gain a deeper insight of the impedance analysis. Moreover, different volume fractions (5–25 vol%) of second phase can be analyzed.Impedance spectroscopy is an excellent nondestructive method of predicting the microstructure of the composite. Impedance spectroscopy (IS) can be used to separate the contributions to the electrical resistivity in solid materials; these contributions are mainly due to grains (bulk) and to the different internal surfaces like grain boundaries, pores and second phases [5]. IS uses AC signals which are highly affected by interfaces, whether between a material and the electrode, between different grains, or between different phases in a material [6]. In general each complex resistivity spectrum consists of three major arcs whose relative magnitude depends on temperature. The three arcs can be represented by three equivalent circuits connected in series. In order of increasing frequency arcs 1, 2, and 3 are due to electrode effects (LF-Low frequency), the grain boundary effect (IF-Intermediate Frequency), and the lattice(grain) effect (HF-High Frequency)) respectively [7**].** The important point is the existence of arc 2, generally related to a high resistivity or blocking layer along grain boundaries. Complex impedance plot showing three arcs together with the three equivalent circuits is shown in Fig. 1. The arrow indicates the direction of increasing frequency. For each specimen, the arc on the left is due to the intragrain resistivity and the arc on the right is due to the intergrain resistivity. The difference of intercepts of each arc on the real or X impedance axis gives resistivity associated with the intra or intergrain process.

*Corresponding author: (S. Hussain): sabinaphy@gmail.com

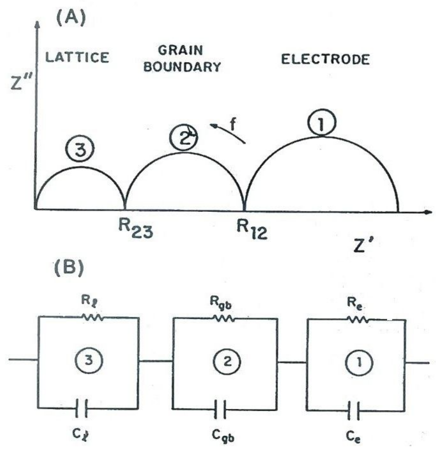


Fig. 1. Complex impedance plot with equivalent circuit.

II. Experimental

Materials

Increasing amounts of molybdenum powder (5 to 25 vol%) were mixed with high purity alumina powder (AKP-53, Sumitomo Chemical LTD., Japan). The average particle size of Mo was 0.56 μm. The ceramic-powder mixtures were attrition balled in isopropyl alcohol for 5h. After drying, the samples were hot-pressed in a graphite die. The hot press atmosphere was argon. For all the specimens, the maximum hot-pressing pressure was 30 MPa. The selected temperature and time were 1640°C and 1 h, respectively. The samples were slowly cooled down (200°C) to room temperature. Hot pressed samples were in the form of discs with diameter and thickness of 50 mm and 10 mm, respectively. To enable microstructural parameters, all specimens were ground and polished using diamond pastes. 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, the metal grain size, and the phase distribution. The quality of the molybdenum particles was assessed by using an image analyzer.

Electrical characterization

Electrical resistivity (ρ) was measured by a two-probe ac impedance spectroscopy. Samples were prepared from hot-pressed discs. Discs were sliced, using a low speed diamond saw, into samples of 10mmx10mmx10mm. The impedance measurements were carried out with an HP 4129 Impedance Analyzer in the frequency range 5 Hz to 13MHz and in the temperature range 250- 1000°C. The temperature dependence of the resistivity was studied by heating the samples in a furnace up to 1000°C with 50°C temperature interval.

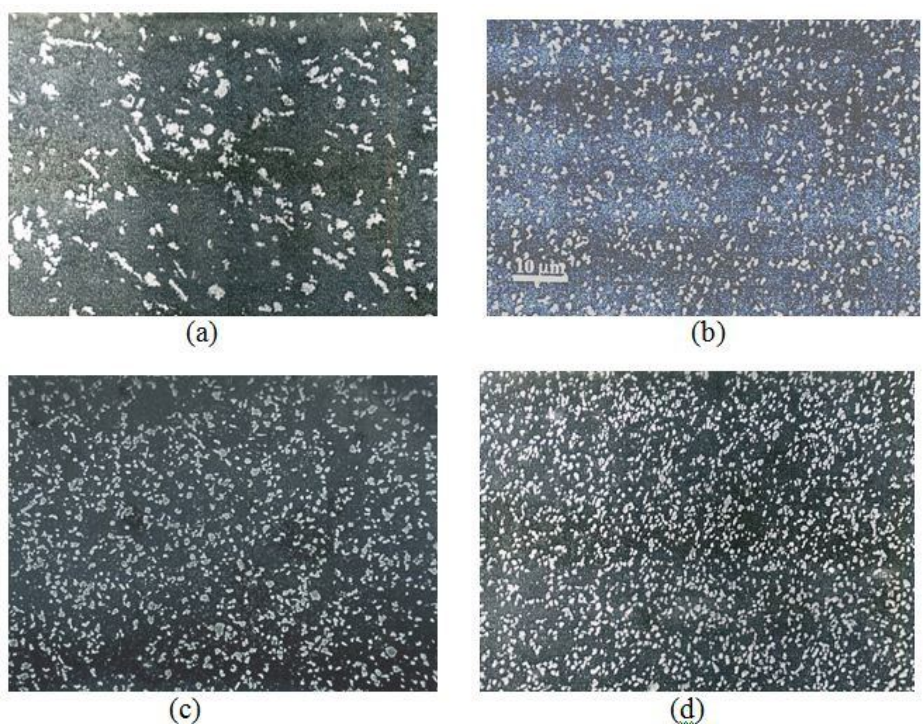


Fig. 2. Microstructures of Al_2O_3 matrix with different volume percentages of Mo particles: (a) 5 vol.%, (b) 10 vol.%, (c) 20 vol.% and (d) 25 vol.%.

III. Results and Discussion

Microstructures*:* SEM and microanalysis reveal that in all specimens the hot pressed process gives rise to a microstructure with α-Al_2O_3 grains and Mo particles. Very seldom there is also another phase identified as α-Mo_2C located close to the edges of the samples which might be due to a reaction between the metal particles and the graphite die. The metallic inclusions are located in the white regions and the ceramic matrix is the grey region in the pictures. Pores are represented by black spots. Figure 2 shows the microstructures of Al_2O_3 matrix with 5 to 25 volume percentages of Mo particles. From the figures it is observed that the size of the metal particles or metal clusters increase as the metal content increases. The metal particles inhibit the matrix grain growth and therefore the matrix grain size slightly decreases for higher volume fractions of metal particles inclusion [8]. Control of grain size is also a means of enhancing fracture strength in polycrystalline ceramics [9]. For 5 volume% of Mo inclusions, metal clusters are formed but no continuous path is observed, but for relatively higher volume fractions of Mo, few continuous paths are seen to be formed.

The respective grain size distributions of the Mo particles after hot pressing were assessed by image analysis on scanning electron micrographs (Fig. 3). Image analysis showed that for 20 vol.% of Mo particles inclusion in Al_2O_3, the average grain size of the metal particles was 3μm. The Al_2O_3-matrix grains were typically in the size range 3-10μm in all composites (Fig.4).

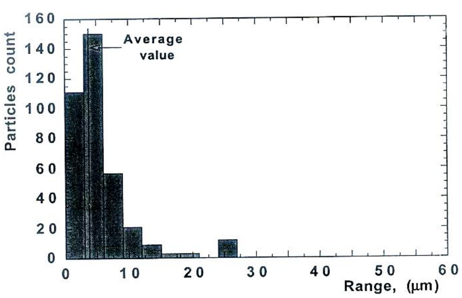


Fig. 3. Grain size distributions of the Mo particles.

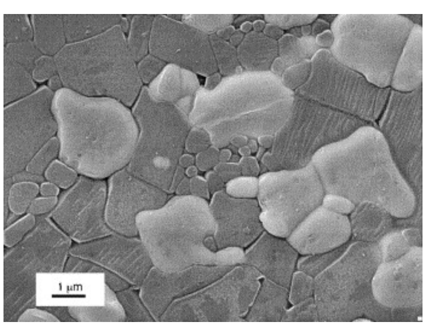
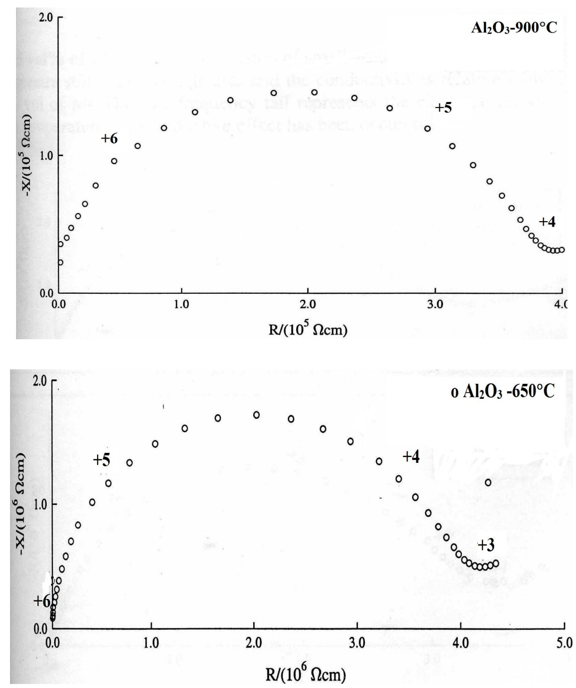


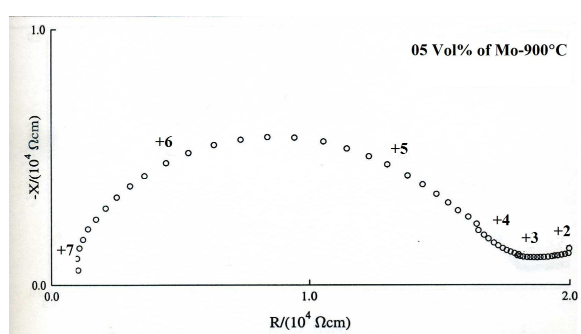
Fig. 4. Grain size of Al_2O_3-matrix

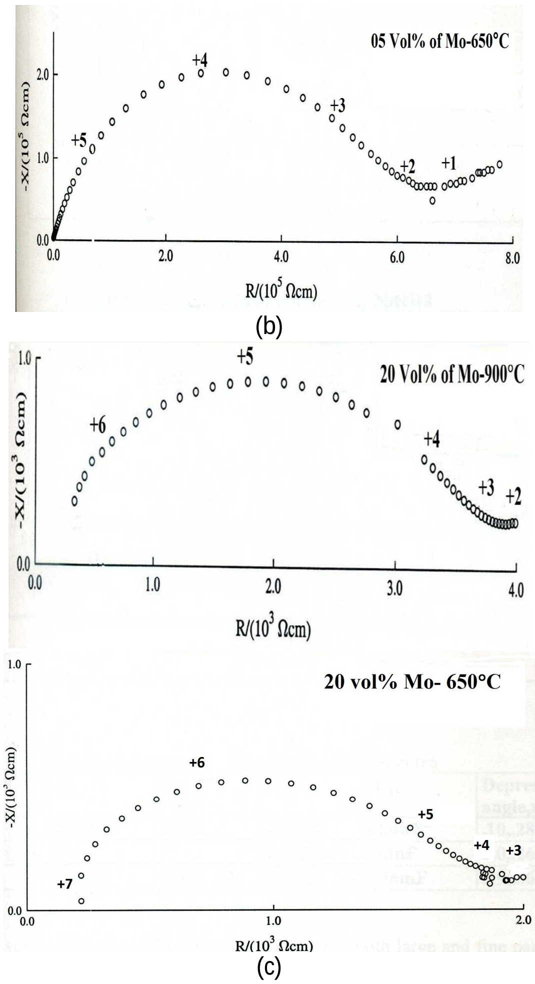
ImpedanceAnalysis

Figure 5 shows the impedance diagrams obtained at temperatures ranging from 550-900°C for different vol.% percentages of Mo. Through this technique it was possible to separate the contribution of the grain and the grain boundary resistivities. Even though the impedance plots consisted of one semicircle, the appropriate circuit analysis shows that the semicircle consists of two arcs due to the contribution of grain and grain boundary. In all cases the grain boundary conductivity is found to be quite high compared to the grain conductivity.



(a)





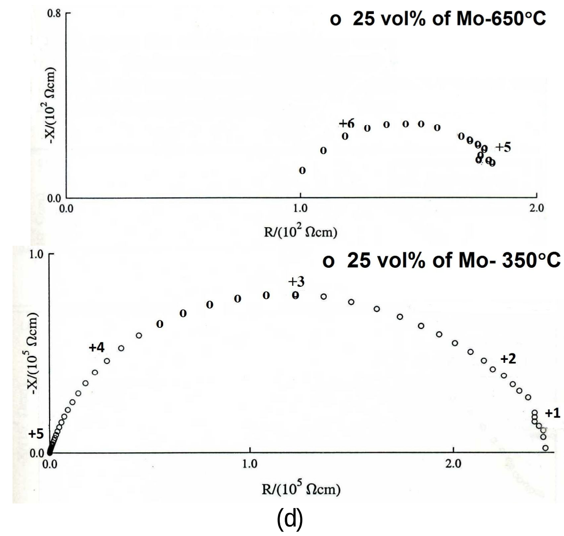


Fig. 5. Impedance diagrams obtained at temperatures from 550-900°C for (a) 00 vol% of Mo, (b) 05 vol% of Mo, (c) 20 vol% of Mo, and (d) 25 vol% of Mo.

It can be observed that with increasing volume percentages of Mo inclusion in Al_2O_3, electrical resistivities of grain and grain boundary of Al_2O_3 decrease when compared with those of the matrix Al_2O_3. Table 1 shows the circuit parameters used to simulate the impedance spectra for different volume percentages of Mo inclusion in Al_2O_3.

Table. 1. Circuit parameters used to simulate the impedance spectra

Vol% of Mo	Temperature (°C)	R_g	C_g	R_{gb}	C_{gb}	Depression angles(n_g, n_{gb})	Blocking factor, α
00	650	3.7 MΩ	4.0pF	0.7 MΩ	0.42 nF	0.08, 0.17	0.16
	900	0.40 MΩ	5.8pF	0.44 KΩ	1.0nF	0.09, 0.15	0.001
05	550	2.7 MΩ	0.15nF	1.2 MΩ	28nF	0.18, 0.27	0.30
	650	0.7 MΩ	0.20nF	0.30 MΩ	26nF	0.17, 0.26	0.30
	900	13 KΩ	0.50nF	6.7 KΩ	0.60 μF	0.19, 0.56	0.34
10	500	0.3 MΩ	0.52nF	82 KΩ	87nF	0.16, 0.37	0.21
	650	0.24 MΩ	4.6nF	0.02 MΩ	0.003 μF	0.17, 0.26	0.07
	900	-	-	0.30 KΩ	0.06 μF	0.19, 0.56	-
20	350	0.20 MΩ	21nF	0.20 MΩ	4.4nF	0.10, 0.28	0.50
	650	-	-	1.6 KΩ	13nF	0.0, 0.26	
	900	3.6 KΩ	67nF	1.9 KΩ	0.36μF	0.19, 0.56	0.30
25	350	0.20MΩ	2nF	77KΩ	0.10μF	0.10, 0.28	0.27
	600	-	-	0.16KΩ	88 nF	0.0, 0.26	

From the impedance analysis, the effects of grains and grain boundaries on the electrical conductivity of the composites have been observed to be varied with the composition and temperature. In all cases, the grain was more resistive than the grain boundary. With increasing amount of Mo, the high frequency semicircle shifted towards intermediate frequency region means that the high and intermediate frequency semicircles started overlapping. It indicates the dominance of Mo filler particles. The presence of Mo particles decreased the sample electrical resistivity of grain and grain boundary when compared with Al_2O_3. In order to impart electrical conductivity to insulating ceramics, dispersions of conducting second-phase particles have been considered without losing insulator's high thermal conductivity. In such composites, conducting particle contents of above 12–20 vol.% are necessary to produce a conducting ceramics. However, the addition of large amounts of second phase is undesirable, as this can potentially compromise the excellent properties of the matrix ceramic. If the grain boundary phase can be used as a conducting pathway, a grain boundary phase content of a few vol.% may be sufficient to impart electrical conductivity to insulating ceramics [10]. Thus electrically conductive ceramics with high thermal conductivity were obtained by incorporating Mo particles as a conducting pathway at the grain boundaries.The influence of the grain boundary conductivity in the total conductivity can be evaluated through the blocking factor (α_R) defined from the impedance diagram parameters by: $\alpha_R= R_g/(R_g+R_{gb})$, where R_g and R_{gb} are grain and grain boundary resistances, respectively [11]. This factor gives the fraction of the electric carriers being blocked at the impermeable internal surfaces (grain boundary) with respect to the total number of electric carriers in the sample. Table 2 shows the blocking factors as a function of temperature for all compositions.

Table. 2. Blocking factors as a function of temperature.

Composition	$\alpha_{350°C}$	$\alpha_{550°C}$	$\alpha_{650°C}$	$\alpha_{900°C}$
00 vol.% Mo	-	-	0.16	0.001
05 vol.% Mo	-	0.30	0.30	0.34
10 vol.% Mo	-	0.21	0.07	-
20 vol.% Mo	0.50	-	0.30	-
25 vol.% Mo	0.27	-	-	-

The lowest blocking factor was observed for 00 vol.% of Mo in Al_2O_3 at 900°C. It can be inferred that polycrystalline alumina maintains the insulator properties when it contains small amounts of impurities; but when the impurity concentration is large enough, the conductivity at high temperature increases [12]. It has been reported that alumina is a mixed conductor. Partial ionic and electronic conductivities depend on temperature and oxygen partial pressure [13]. In the present study it can be assumed that an electronic mechanism governs the electrical conductivity of polycrystalline alumina.

IV. Conclusion

Addition of different volume percentages of Mo (05-25 vol%) into Al_2O_3 increase the grain conductivity at a relatively lower temperature. Besides for increasing volume fractions of Mo, the high frequency semicircle and the intermediate frequency semicircle started overlapping suggests the dominance of Mo filler particles at the grain boundaries. With metallic concentrations above 20 vol%, electronic conducting paths are generated by touched metallic clusters.

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*Corresponding author: (S. Hussain): sabinaphy@gmail.com