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ELECTRICAL CHARACTERIZATION OF ZIRCONIA-NIOBIUM AND ZIRCONIA-TITANIUM COMPOSITES

J.R. Martinelli and S.T. dos Reis

Energy and Nuclear Research Institute
Brazilian Nuclear Energy Commision
C.P. 11049 - Pinheiros - CEP 05422-970
S. Paulo, S.P. , BRAZIL

Zirconia-niobium and zirconia-titanium composites were made by powder mixing, cold pressing, and vacuum sintering at 1,600°C. The metallic particles were added in the proportion of 0 - 50% by volume. Electrical resistivity measurements were performed by the two probes and the four probes d.c. method as a function of metallic particle concentration. Electrical resistivity of these composites decreased sharply in the region of 30-40 vol% Nb or Ti, in agreement with the percolation theory. Tests in a vacuum induction furnace were performed to check the self-heating response of these composites.

INTRODUCTION

Zirconia has been used in high temperature environment applications (>1000°C) due to its high melting point and chemical inertness. Heating elements, cathodes for plasma torches and electrodes for MHD energy conversion can be made of zirconia (1). When used as heating elements in electric furnaces, zirconia requires pre heating to temperatures above 600°C to increase the ionic charge carrier mobility and thus promote self-heating by the application of an external electrical power source.

In the range of high oxygen partial pressures ($1-10^{-5}$ atm), the electrical conductivity of zirconia is essentially ionic. The main charge carriers are either thermally generated intrinsic oxygen vacancies (high temperature range) or extrinsic oxygen vacancies created by doping the matrix with aliovalent ions. Hence zirconia can only be used as an oxygen sensor or as heating elements, if previously heated.

The electrical conductivity of various solid electrolytes

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increases drastically upon the addition of a dispersed second phase (2). It is assumed that the charge carrier concentration in the interfacial layer (ranging from 10 to 30nm)and/or the degree of structural disorder in these regions is responsible for this electrical behavior. The percolation theory has been used to predict such behavior in metal-metal oxide composites (3). This considers that an inversion layer may be formed in the vicinity of the metal phase, which increases the probability of having electrons in the conduction band (2).

Percolation threshold has been predicted for different metal - ceramic powder mixtures considering the connectivity of a metallic phase distributed in an insulating phase (4). It has been shown that the addition of Ti particles in alumina matrix decreases the electric resistivity of this composite for a Ti volume fraction above 20% (5). Electrical resistivity in the titanium-carbonitrite-zirconia system has also been studied and values predicated by theoretical model have been used to compare with experimental results (6). The Landauer's model (7) assumes that in a dual phase system a particle of one phase is surrounded by particles of both phases, which are seen to be replaced by an uniform medium.Values predicted by this model approximate well with the experimental results. However composites containing high zirconia content deviate from this model because a little error on the volumetric fraction can lead to an important difference in the resistivity value (6).

In this paper electrical resistivity measurements for zirconia - titanium and zirconia-niobium composites are reported and correlated to their microstructure as well as to radio frequency(r.f.)response of an induction furnace. It is noted that composites that show decreasing resistivity, heat themselves when exposed to r.f..These composites may potentially be used as heating elements in electrical furnaces without being previously heated and as crucibles for melting reactive alloys in vacuum induction furnaces.

EXPERIMENTAL

Zirconia-6 mol% magnesia pellets with 0-50 vol% niobium or titanium were made by powder dry mixing, cold dry pressing and vacuum sintering.

Zirconium oxide* was produced by calcining zirconium hidroxide in ammonium sulphate solution* at 900°C in air.

This powder was wet mixed with magnesia powder**, dried at 110°C, compressed into a pellet and calcined at 1,000°C in air. The resulting pellets were crushed and ground with an agate mortar and pestle. The particle size distribution was determined by a sedigraph*** and found to be in the range of 1 to 10μm. This powder is suitable for preparing ceramic matrix composite since its particle size is lower than that of the metallic particles. The particle size distribution of Ti powder ranges from 10 to 100μm and that of Nb, 37 to 74μm.

Zirconia - 6mol% MgO powder was dry mixed with Ti or Nb powder during 10 min****, uniaxially pressed under 2 Ton during 15s in a steel die with a 12mm diam. and result in pellets 3mm thick.

The pellets were sintered at 1,600°C/1h in 10^{-5} torr vacuum in an alumina tube closed at one end and placed inside an electrical furnace. The open end was connected to a vacuum system. Sample densities were evaluated before and after sintering by the Archimedes' method.

Phase characterization was carried on by x-ray diffraction in which the CuKα line was used. The scanning rate was 2θ/min=1°/min.

Electrical resistance at room temperature measurements were done in the range of 10^3 - 10^{14} ohms by using the two probe dc method with a Keithley model 610C electrometer attached to a HP model 16008A resistivity cell. The four probe dc method was used to measure resistance in the range of 1 - 100 milliohms by using a HP model 4328A milliohmmeter. Gold was sputtered on to the surfaces of the pellets to act as electrodes. The electrical resistivity was determined from the expression $\rho = RS/L$ where L is the distance between the electrodes, S the crossectional area and R the resistance.

Specimens were prepared for scanning electron microscopic analysis. The pellets were polished with 15μm, 9μm, 6μm, 3μm and 1μm diamond paste successively and thermally etched at 1,500°C/20 min in argon. Thermal etching was done to reveal the grain boundaries by submitting the samples to r.f. to permit them to self-heat. The specimen were then covered with a thin carbon layer to avoid charge pile up during analysis. The analysis were done in a Philips model XL30 Scanning Electron Microscope.

To verify the response of the composite to radio frequency, the specimens were set inside a quartz tube surrounded by a copper coil 6 cm in diameter, connected to a 50KW generator operating in 450 KHz. Argon flow was used to prevent oxidation of the metal dispersoids. A pyrometer was used to monitor the temperature.

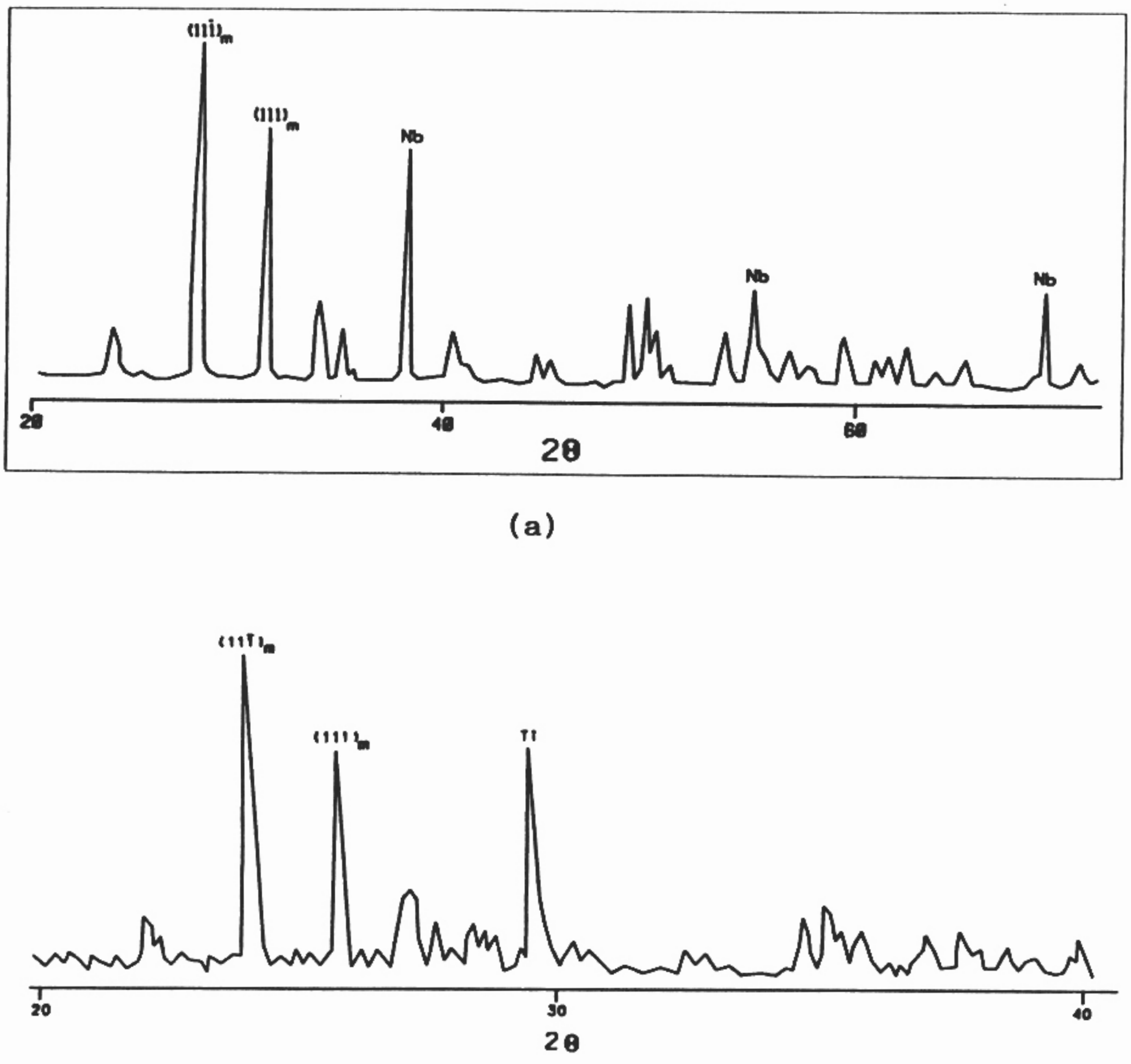
RESULTS AND DISCUSSION

Table 1 shows density values for zirconia-Ti and zirconia-Nb composites both before and after sintering. Densities for samples before sintering range from 60 to 64% of their theoretical values (TD). Densities after sintering range from 76 to 82% TD for zirconia -titanium composites. Even though these values are relatively small compared to others sintered ceramic bodies, they are comparable with density values reported by Breval et al. for alumina -Ni composites (8).

TABLE 1. Densities for zirconia -Ti composites and zirconia - Nb composites.

	Ti composite		**Nb composite**	
vol %	**green state density (%TD)**	**sintered density (%TD)**	**green state density (%TD)**	**sintered density (%TD)**
10	61.1	82.0	61.7	79.0
20	60.9	80.0	61.8	80.0
30	60.5	77.0	62.4	79.2
40	59.9	76.6	61.2	76.4
50	59.8	79.3	63.8	75.3

Figure 1 shows X-rays diffraction patterns for zirconia-Nb and zirconia-Ti composites. It can be noted that only diffraction lines corresponding of the zirconia monoclinic phase and the metallic phases are present. There is no evidence of the presence of stabilized tetragonal or cubic phases. This is an indication that MgO is not stabilizing zirconia and when samples are heated above 1,200 ^{o}C disruptive monoclinic-tetragonal transformation is prone to happen.



(a)

(b)

FIG.1 - X-rays diffraction pattern for: (a) Zirconia-Nb composite; (b) Zirconia-Ti composite. Cu Kα line) $(11\bar{1})_m$ and $(111)_m$ → monoclinic zirconia.

Figure 2 shows electrical resistivity values as a function of volume fraction of metallic phase in zirconia-Nb and zirconia-Ti . The resistivity values decrease as the volume fraction of metallic phases increase. It can be noted that this effect is pronounced above 30 vol% and is consistent with the percolation theory that predicts threshold in the range of 21 to 39 vol% (4).

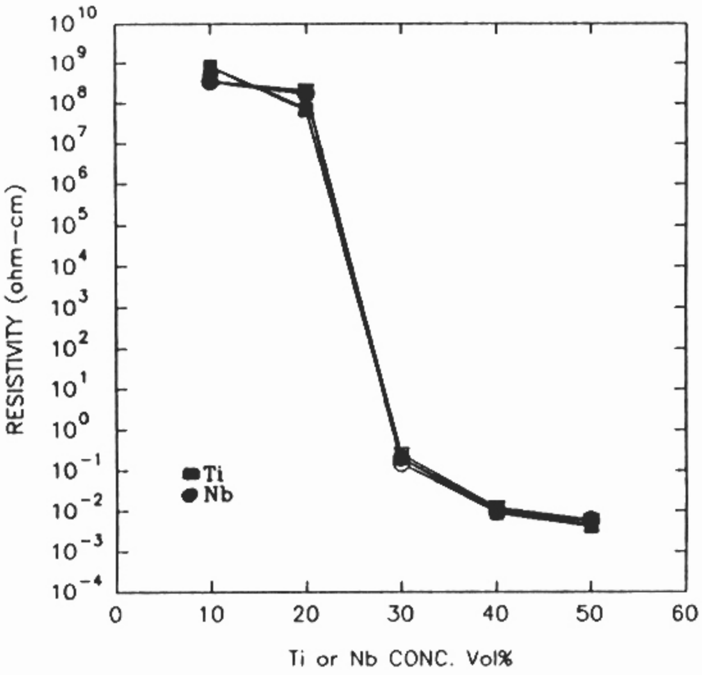


FIG.2 - Electrical resistivity of zirconia Ti and zirconia-Nb composites at room temperature as function of metallic dispersoids concentrations.

Landauers et al. (7) developed a model based on the percolation theory for composites with an insulating matrix and dispersed conducting phases and is given by the following equation for $\sigma_1 >> \sigma_2$.

$$\sigma_m = 1/2\ [3V - 1]\ \sigma_1$$

where σ_1 is the conductivity of the conducting phase

σ_2 is the conducitivity of the insulating phase

σ_m is the conducitivity of the composite

V is the columetric fraction of conducting phase.

In this investigation, the percolation threshold is 0.3, $V = 1/3$ and $\sigma = 0$. Therefore as already known this model does not apply in this particular situation. However for $V > 1/3$, the model gives values shown in Table 2 for zirconia-Nb and zirconia-Ti composites, and the experimental results are in good agreement with values predicted by the model.

TABLE 2. Comparison between experimental resistivity values and theoretical prediction for zirconia-Ti and zirconia -Nb composites (V_{Nb} and V_{Ti} represent volume fraction).

V_{Nb} vol% V_{Ti}	ρ_{Ti} ohm - cm Theor.	Exp.	ρ_{Nb} ohm - cm Theor.	Exp.
30	0	2.0×10^{-1}	0	2.0×10^{-1}
40	4.2×10^{-2}	1.0×10^{-2}	1.3×10^{-2}	1.1×10^{-2}
50	1.7×10^{-2}	4.3×10^{-3}	5.0×10^{-3}	6.0×10^{-3}

Table 3 shows temperatures monitored when specimens of the composites were under a r.f. field generated with different voltages. The frequency was kept constant. Only the transferred power was varied. Temperatures higher than 1,500°C were avoided for zirconia -Ti composites in order to avoid melting Ti dispersoids inside the ceramic matrix.

TABLE 3. Temperatures monitored on zirconia-Ti and zirconia-Nb composites under r.f.

Vol%	Specie Element	80V	100V	150V	200V
30	Ti	700°C	1,020°C	1,300°C	>1,500°C
	Nb	840°C	900°C	1,090°C	1,600°C
40	Ti	1,200°C	1,360°C	1,450°C	>1,500°C
	Nb	980°C	1,160°C	1,400°C	1,750°C
50	Ti	1,330°C	1,450°C	1,500°C	>1,500°C
	Nb	990°C	1,140°C	1,500°C	2,000°C

Sel-heating was observed for metallic volume fraction above 30% . That is also the percolation threshold. Therefore only above this limit is enough eddy current present inside the samples, to cause heating. Apparently Ti based composites are easier to heat than Nb based composites.

An attempt was made to check the r.f. response in specimen with 40 vol% of metallic dispersoids without sintering. No self-heating was observed under these condition. Therefore r.f. response depends not only on the metallic dispersoid concentration but also on the density and microstructure.

Since the response to r.f. starts at room temperature it is obvious that eddy current comes from electronic charges provided by the metallic inclusions. Work functions for Nb and Ti are approximately 4.3 eV. Electron affinity for zirconia is approximately 3.5 eV and gap energy is approximately 5 eV (monoclinic phase).It is possible that a negative charge layer is created in the ceramic-metal interface by the migration of electrons from the metal dispersoid surfaces to the ceramic matrix in order to level the fermi energy in that region. The overlapping of these layers may be responsible for the increase in the electrical conductivity of these composites. The type of charge carriers in the space charge layers surrounding metal particles differs from that of the zirconia matrix, since electrons are minority carriers in this material.

To promote a slight change in the metal particles surface,in order to alter the space charge layer, composite specimens were annealed at temperatures in the range of 200°C to 650°C for 1h in air. The electrical resistivity was measured to room temperature. Figure 3 shows the changes in resistivity values of a zirconia-40% vol Ti at room temperature after annealing at different temperatures.Large variations were observed for temperatures above 400°C.It is assumed that a thin layer of titanium oxide is created at the surface of Ti particles, changing the space charge layer surrounding these particles.

For Nb based composites, the oxidation reaction is more prominent and electrical resistivity values could not be determined at temperatures above 300°C. This fact is consistent with the Gibbs free energy for oxidation of both metals, which implies that niobium pentoxide (ΔG =-394 Kcal at 573K) is more stable than titanium dioxide (ΔG =-183 Kcal at 573K).

Figure 4 shows a SEM micrograph of a zirconia-50 vol% Nb specimen where touching metal particles are observed. In this situation the percolation cannot be treated as through overlapping space charge layers. Metallic clusters are also observed.These clusters prevent improved densification of this material.

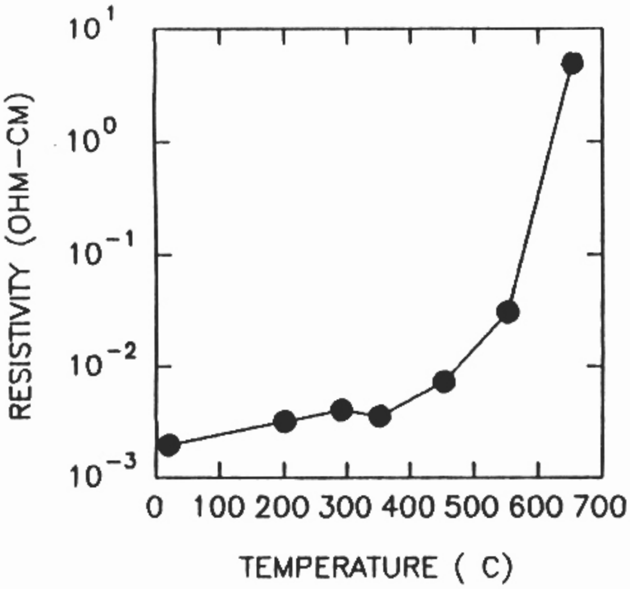


FIG.3 - Electrical resistivity of zirconia-40% vol Ti composite at room temperature after annealing at different temperatures.

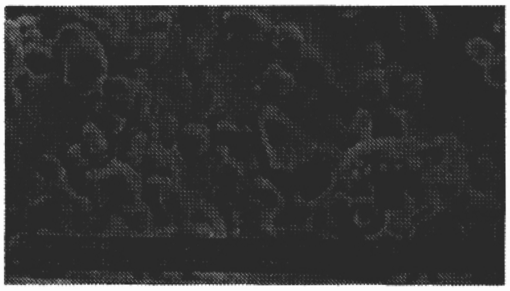


FIG.4 - SEM micrograph of a zirconia - 50 vol % Nb specimen. Touching metal particles are shown.

Figure 5 shows a SEM micrograph of a zirconia-50 vol% Nb specimen after exposing to r.f. Grain growth as well loss of Nb from grain boundaries is observed. These effects are a consequence of self -heating above 2,000°C.

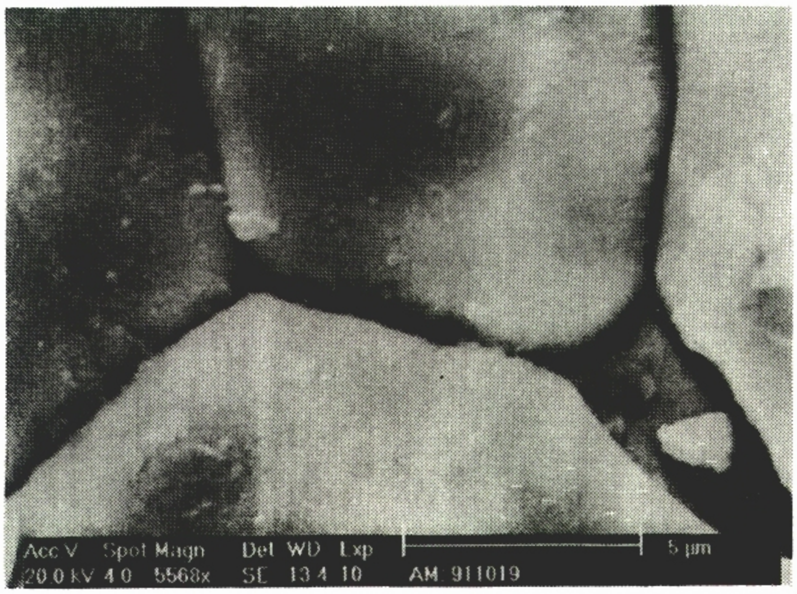
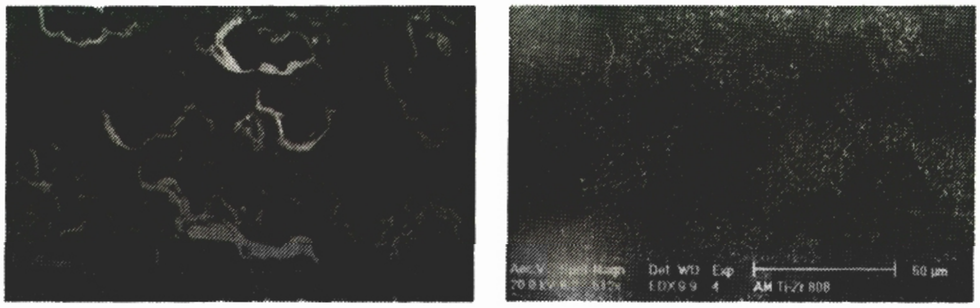


FIG.5 – SEM micrograph of a zirconia – 50 vol% Nb specimen after exposing to r.f. Grain growth and lost Nb from grain boundaries is observed.



(a) (b)

FIG.6 – (a) SEM micrograph of a zirconia – 50 vol% Ti sample after exposing to r.f.; (b) Ti element detected by EDAX on sample surface.

Figure 6 shows a SEM micrograph of a zirconia-50 vol% Ti specimen after exposure to r.f.. A large amount of porosity is observed. Grain boundaries cannot be perfectly distinguished even though black spots in the matrix have been identified as Ti. In the same figure it is shown the Ti surface distribution determined by EDAX (bright spots).

CONCLUSIONS

Electrical resistivity values of zirconia-Ti and zirconia-Nb composites decrease at room temperature as a function of metallic dispersoid volumetric concentration. This behavior has been predicated by the percolation theory and is in agreement with Landauer's model for volume fractions above 30%.

Composites with metallic dispersoids volume fraction above the percolation threshold show self-heating when exposed to radio frequency of an induction furnace. For high metallic dispersoid concentrations metal particle touching is observed in the grain boundary region.

The resistivity values at room temperature change drastically due to oxidation of metal particles. This is an indication that the space charge layers surrounding the metal particles are responsible for the electrical behavior of these composites.

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NOTES

p. 522:

*** Main impurities determined by flame espectroscopy: 160 µg/g Si, 200µg/g Mg, <40µg/g Fe, <30µg/g Na, <20µg/g Al, <40µg/g P.**

p. 523:

* Produced by Nuclear and Energy Research Institute, S.P. Brazil.
** From Carlo Erba, nominally pure P.A.
*** Model 5100, Micromeritics, U.S.A.
**** By using a turbula mixer.