Preparation and characterization of zirconia-yttria/zirconia-magnesia composites

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Abstract: ZrO_2: 3mol% Y_2O_3 powders were mixed in different proportions to ZrO_2: 8 mol% MgO, pressed and sintered at 1500°C for producing composites with oxygen ion conductivity better than that of ZrO_2: 8 mol% MgO and thermal shock resistance better than that of ZrO_2: 3 mol% Y_2O_3. The electrical conductivity was evaluated by the impedance spectroscopy technique at 600°C as a function of the partial pressure of oxygen using zirconia-based oxygen pump and sensor. The thermal shock resistance was studied by room temperature-1550°C dilatometry on sintered pellets. Moreover the composites were studied by X-ray diffraction and scanning electron microscopy. All composites are partially stabilized in the monoclinic-tetragonal phase and the apparent density is higher than 90% of the theoretical density. The thermal shock behavior of the composites is similar to that of ZrO_2:8 mol% MgO materials used in disposable high temperature oxygen sensors. The electrical response of the composites at high temperatures is better than the electrical response of ZrO_2:8 mol% MgO.

Introduction

There has been significant interest in ZrO_2-based solid electrolytes for several applications, for example, solid oxide fuel cells, oxygen pump and sensor. The monitoring of oxygen dissolved in molten steels can be done with disposable oxygen sensors with MgO-partially stabilized ZrO_2 [1-4]. These ceramics present high thermal shock resistance [5,6] to stand up to the temperature change without cracks during rapid inserting into molten steel at temperatures usually higher than 1500 °C.

The purpose of this work is the preparation and thermal and electrical characterization of ceramics composites, with ZrO_2: 8 mol% MgO and ZrO_2: 3 mol% Y_2O_3. The former presents higher resistance to thermal shock and the latter higher electrical conductivity. The main goal is to find oxygen sensors with enhanced performance for use in the steelmaking process, which requires high thermal shock resistance up to 1600 °C in harsh environments (molten steel) and high oxide ion conductivity for detecting oxygen at ppm levels.

Experimental

The starting materials were ZrO_2: 8 mol% MgO (Sales, USA) and ZrO_2: 3 mol% Y_2O_3 (Tosoh, Japan). Ceramic composites of (ZrO_2: 8 mol% MgO)$_x$ (ZrO_2: 3 mol% Y_2O_3)$_{1-x}$, x = 0,

0.2, 0.4, 0.5, 0.6, 0.8 and 1, were prepared by thoroughly mixing, uniaxial pressing (50 MPa) and sintering at 1500 °C for 1 h in air.

Apparent densities of sintering pellets were determined by the Archimedes method, and phase identification was performed by X-ray diffraction (Bruker-AXS D8 Advance), using CuKα radiation. The volume fraction of the monoclinic phase (Vm) of ZrO_2 was estimated by equation 1 [7]:

$$Vm = \frac{1{,}603 \times \mathrm{Im}(\bar{1}11)}{1{,}603 \times \mathrm{Im}(\bar{1}11) + Ic,t(111)} \quad (1)$$

Im and Ic,t are the intensities of monoclinic and cubic/tetragonal reflections.

The thermal shock resistance of the green and sintered pellets was studied by dilatometric techinique in air (Netzsch DIL 402 ES/3/E) from room temperature to 1550 °C with heating and cooling rates of 8 °C/min and 10 °C/min, respectively.

Ceramic composites morphology and grain morphology of fractured sample surfaces were observed by scanning electron microscopy (Oxford model LEO 4401).

The electrical behavior as a function of the partial pressure of oxygen (pO_2) of the ceramic composites, prepared in tubular form, was evaluated in the 5 Hz to 13 MHz frequency range at 600 °C using an impedance analyzer (Hewlett Pachard model 4192A) coupled to a system using zirconia-based oxygen pump and sensor that takes advantage of the electrochemical properties of the zirconia based solid electrolytes to produce and detect controlled pO_2. The ceramic tubes were prepared by solid state synthesis of the mixed starting materials by uniaxial pressing at 50 MPa, thermal treatment at 800 °C, drilling in a lathe and sintering at 1500 °C for 1 h in air. After sintering, each tube was painted inside and outside with platinum paste. The tube was filled with $Cr\text{-}Cr_2O_3$ reference electrode. Ni-Cr terminal leads were used. Finally, a high temperature cement was used to close the tube, as shown in Fig. 1.

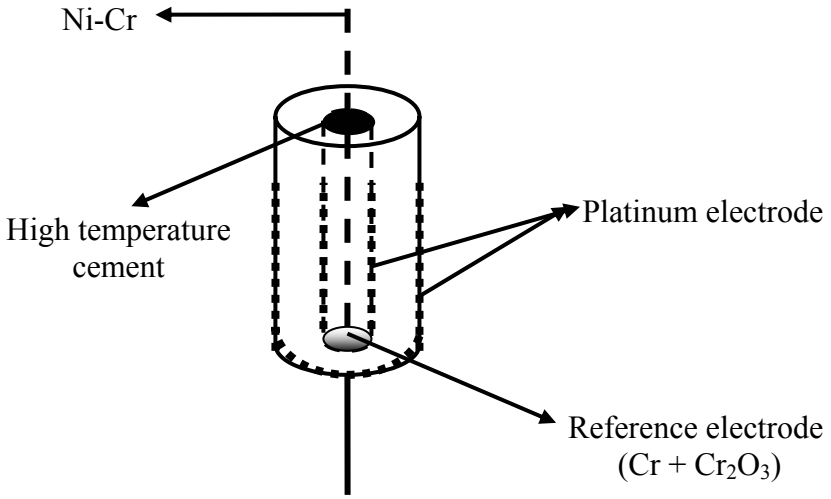

Fig. 1. Schematics of the set up of the composite electrolyte for electrical measurements.

Results and discussion

Fig. 2a shows X-ray diffraction patterns and Fig 2b the monoclinic-to-cubic/tetragonal phases of the $(ZrO_2$: 8 mol% $MgO)_x$ $(ZrO_2$: 3 mol% $Y_2O_3)_{1-x}$ composites. All

specimens show diffraction peaks corresponding to monoclinic (m) and cubic/tetragonal (c/t) phases (Fig 2a). The sintering at 1500 °C of the zirconia-magnesia/zirconia-yttria composite increases the volume fraction of monoclinic phase (% Vm), reaching a maximum value of 55% for the composition x=0.8 (Fig 2b). Is known that partially stabilized zirconia presents smaller coefficient of thermal expansion that fully stabilized zirconia, contributing to higher thermal shock resistance due to the large volume shrinkage associated with the phase transformation of MgO-PSZ from monoclinic to tetragonal during heating [8].

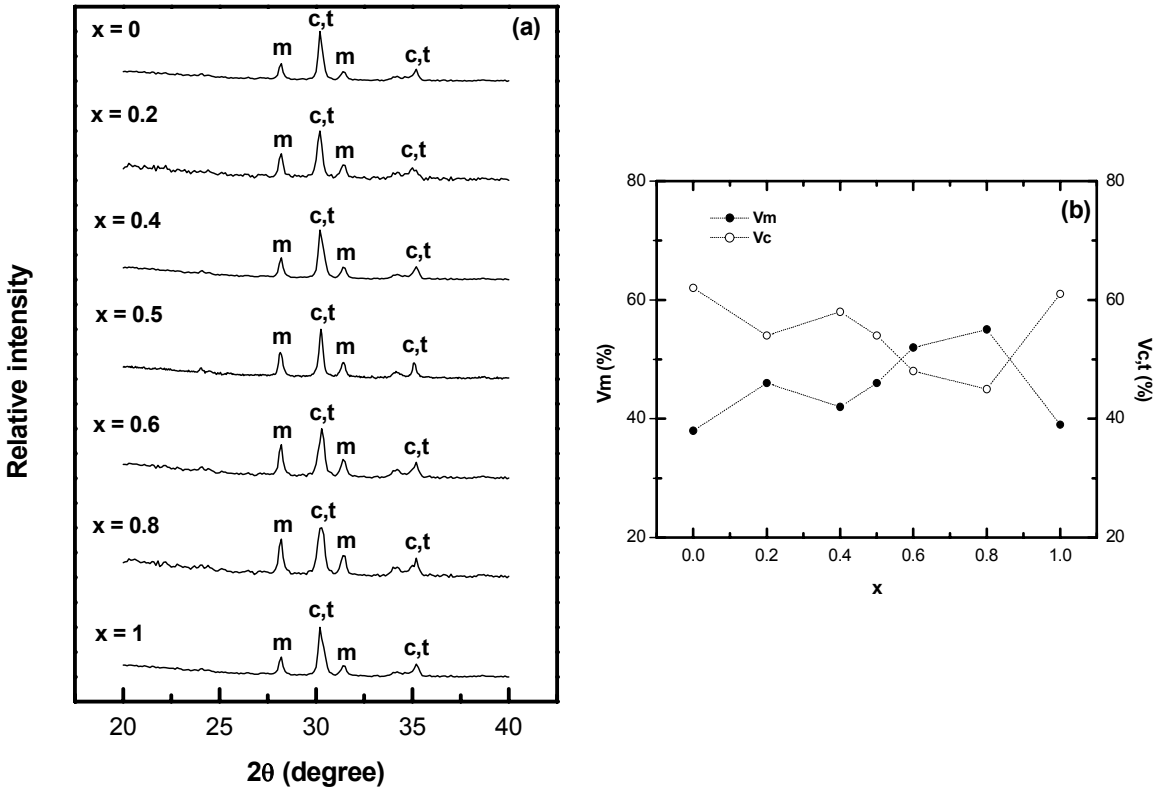

Fig. 2. (a) X-ray diffraction patterns and (b) volume fraction of monoclinic (Vm) and cubic/tetragonal (Vc,t) phases of $(ZrO_2$: 8 mol% $MgO)_x$ $(ZrO_2$: 3 mol% $Y_2O_3)_{1-x}$ for x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.

For dilatometric analysis were chosen the ceramic composites presenting intermediary values of monoclinic-to-cubic/tetragonal phases (Fig. 2b). The linear shrinkage of the pellets is shown in Fig. 3a. Total volume shrinkage values for the compositions with x = 0.2, 0.5 and 0.8 were 21, 19 e 19%, respectively. They are associated to the monoclinic-to-cubic/tetragonal phase transformation and also to sintering of the composites.

The thermal expansion coefficient of MgO-PSZ could be reduced by heat-treatment [8]. In this work the same pellets used previously were submitted to a new heating and cooling cycles as shown in Fig. 3b. The total shrinkage curve after heat-treatment presents a behavior similar to the described previously for the solid electrolyte of zirconia-magnesia used in disposable high-temperature oxygen sensors [8]. The shrinkage volume for all pellets occur at the temperature range 940-1030 °C, corresponding to the phase transformation from monoclinic to tetragonal. The x=0.2 composition shows a lower value of the volume shrinkage (0.1%). During cooling, a hysteresis is observed for all pellets, at temperatures related to the cubic/tetragonal to monoclinic phase transformation, due to the remaining fraction of zirconia that has not been stabilized during sintering.

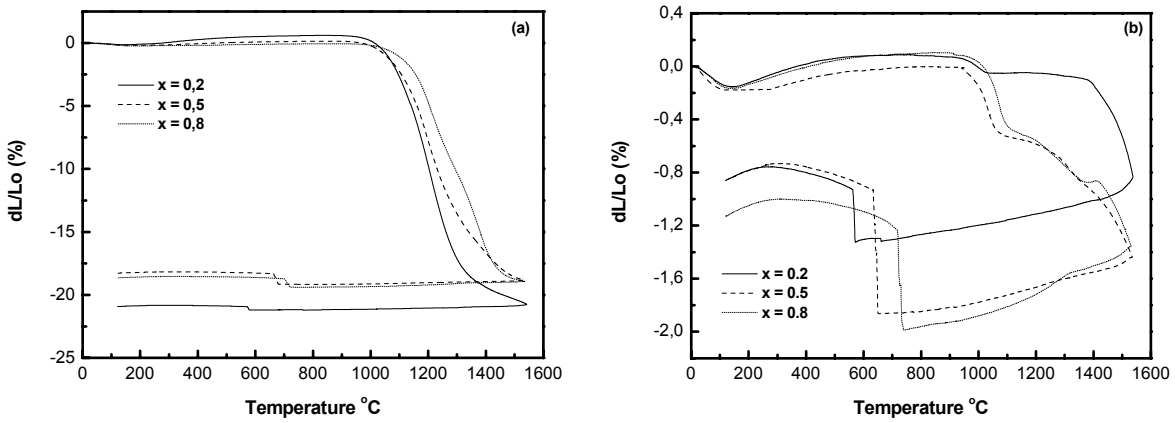

Fig. 3. Linear shrinkage behavior during heating and cooling (a) and after sintering (b) $(ZrO_2$: 8 mol% $MgO)_x$ $(ZrO_2$: 3 mol% $Y_2O_3)_{1-x}$ for x = 0.2, 0.5 and 0.8.

Fig. 4 shows typical micrographs of the fracture surface of sintered pellets. The main characteristic features are low-porosity, in agreement with the results obtained for apparent density determined by Archimedes method, where all ceramic composites show densities higher than 92% of the theoretical density (considered the limit for avoiding oxygen gas permeation for using as sensors for measuring oxygen activity in molten steels) and grains with uniform shape and similar average size. The specimens with x = 0.2 and 0.8 show fracture surface similar to the x = 0.5 specimen, an evidence that the zirconia-yttria content added to the zirconia-magnesia does not produce changes in the morphology as well as in the average grain size.

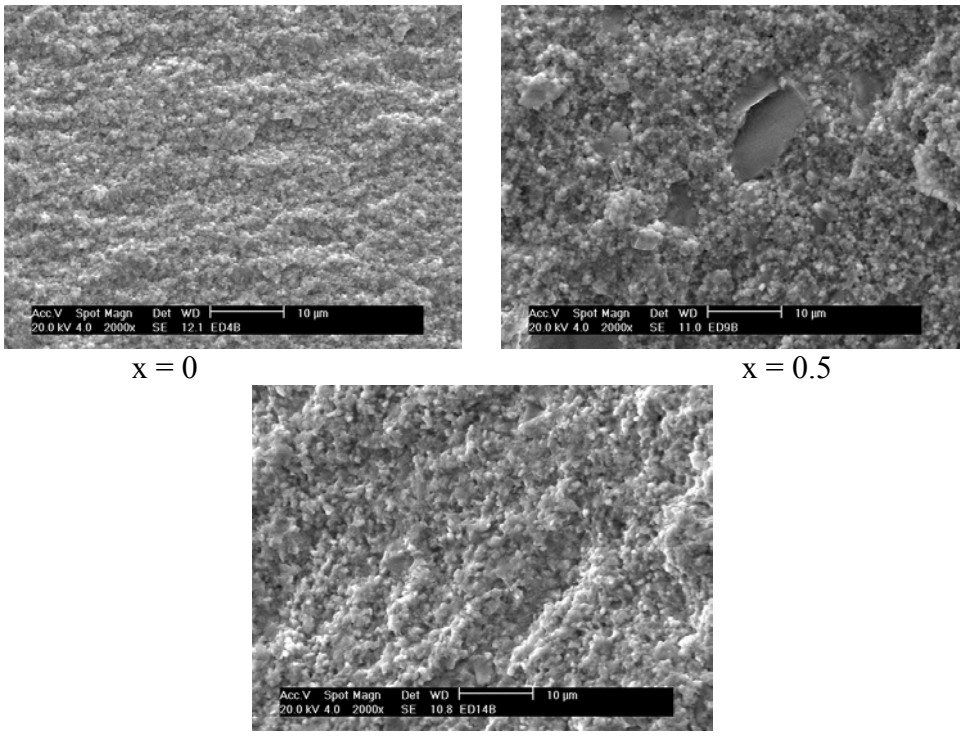

Fig. 4. Scanning electron micrograph of a fracture surface of $(ZrO_2$: 8 mol% $MgO)_x$ $(ZrO_2$: 3 mol% $Y_2O_3)_{1-x}$ for x = 0, 0.5 and 1 sintered pellets.

Fig. 5 shows impedance diagrams as a function of pO_2 measured at 600 °C. The numbers stand for the logarithm of the frequency (Hz) of the applied signal.

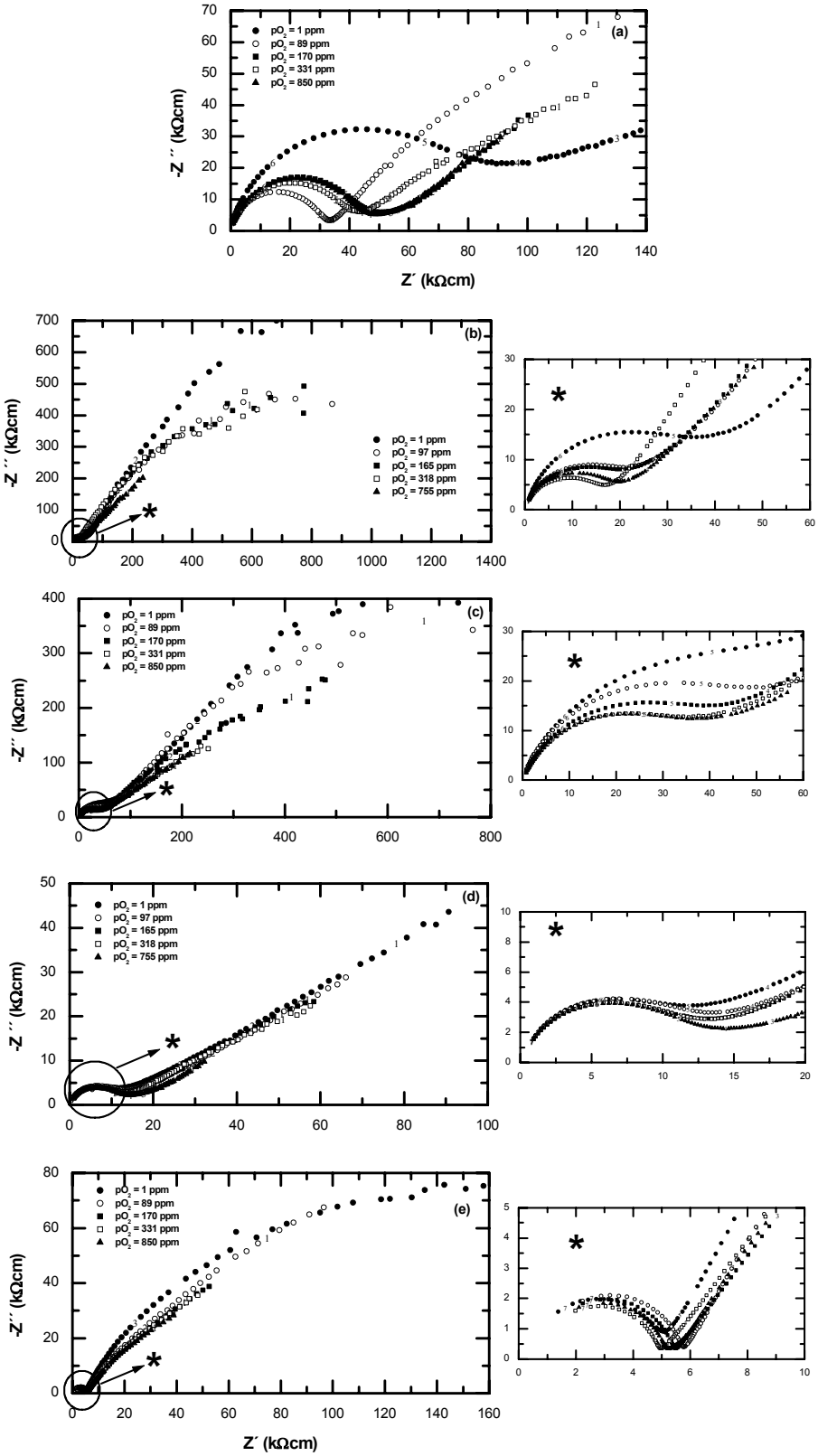

Fig. 5. Impedance diagrams of $(ZrO_2$: 8 mol% $MgO)_x$ $(ZrO_2$: 3 mol% $Y_2O_3)_{1-x}$ pellets, for x = 1 (a), 0.8 (b), 0.5 (c), 0.2 (d) and 0 (e) at 600 °C as a function of the partial pressure of oxygen from 1 to 850 ppm.

All compositions present a well defined semicircle at high frequency related to the intragranular (bulk) response. The low frequency response is related to the electrode response [9]. The addition of zirconia-yttria leads to a huge modification of the impedance diagram in the high frequency region. This is expected because it is well known that the zirconia-3mol%yttria solid electrolyte has an electrical conductivity larger than that of zirconia-magnesia solid electrolytes. This was one of the purposes of this work, to enhance the electrical conductivity by adding zirconia-yttria to zirconia-magnesia. The low frequency region, the electrode response region, also changes. This is due to the change in the kinetics of the electrode/electrolyte oxygen reaction ($1/2\ O_2 \leftrightarrow O^{2-} + 2e^-$), which depends on the amount of O_2 gaseous species in the electrode/electrolyte interfaces.

There are no changes in the intragranular resistivity of the x = 0 and x = 0.2 specimens, in agreement with the electrical response of pure ionic conductors [10]. In these temperature and pO_2 ranges the electrical resistivity of zirconia-yttria depends only on the free oxygen vacancy concentration, which is constant for fixed T and pO_2. The specimens with x = 0.5, 0.8 and 1 show similar behavior: the intragranular resistivity changes upon varying the partial pressure of oxygen. This might be due to the electronic contribution to the electrical conductivity of these solid electrolytes at these low partial pressures of oxygen.

CONCLUSIONS

In summary, we have prepared zirconia-magnesia/zirconia-yttria ceramic composites looking for a compromise for obtaining sintered ceramics with improved electrical conductivity due to zirconia-yttria and with good thermal shock resistance due to zirconia-magnesia. The composites are found to have thermal shock resistance similar to the zirconia-magnesia solid electrolytes used in commercial oxygen sensors for use in the steel making processes. Moreover, the electrical conductivity is improved with zirconia-yttria addition, showing that the ceramic composites may be a solution for designing oxygen sensors for use in high temperature harsh environments for the detection of low concentration of oxide ions.

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