

IMPEDANCE SPECTROSCOPY STUDIES OF ZIRCONIA-YTTRIA CERAMICS DURING SINTERING

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1. INTRODUCTION

Zirconium oxide (ZrO_2) ceramics are widely used in devices for detecting gaseous species. Some of the requirements for these ceramics are high degree of densification and reproducibility of the electrical properties. Consequently the sintering process has to be well controlled. It is known that porosity, grain growth, etc., which occur during sintering, are directly related to the processing of the solid electrolyte, i.e., to the sintering process itself. The sintering process can be simply described as the elimination of the porosity of compact powders, with associated grain growth and formation of well defined grain boundaries [1]. Although many of the ceramic materials produced by sintering have been developed for electrical purposes, electrical testing methods are very seldom used for following up the sintering process [2]. As the blocking of charge carriers at interfaces in solid ionic conductors can be studied by impedance spectroscopy measurements [3, 4], and the blocking effects are dependent on the sintering conditions, impedance spectroscopy is here used to the study of the evolution of microstructural parameters during sintering of $ZrO_2:8$ mol% Y_2O_3 ceramic specimens. The blocking parameters α_R and α_F , relating bulk and grain boundary resistivities, are dependent on the microstructural parameters like intergranular average distances, average pore size, etc.. In this work these parameters have also been determined to study their correlation to sintering behavior.

2. EXPERIMENTAL

$ZrO_2:8$ mol% Y_2O_3 ceramic powders have been prepared by the coprecipitation technique using >99% pure Y_2O_3 , and ZrO_2 produced at the Zirconium Plant at IPEN-Brazil; the powder was fired at 900 °C for 2 h in air and uniaxially pressed to 10 mm diameter and approximately 4 mm thickness pellets, followed by isostatic pressing at 200 MPa. The planar opposite surfaces of the pellet were painted with Demetron 308A Pt paste and fired at 800 °C. The sample was inserted in a spring-loaded sample chamber with Pt electrodes and leads. The sample temperature was monitored with a type S thermocouple connected to a Fluke 8050A digital multimeter. The sintering cycles were the following: the specimen was heated at 10 °C/min up to 400 °C, kept at that temperature for 12 min, and the impedance measurements were performed; the cell was then heated, at the same rate, up to 1350 °C for selected sintering times (t_s) from 0.2 up to 3.7 h. Impedance spectroscopy measurements were carried out, during sintering cycles, at approximately 400 °C, in the 5 Hz-13 MHz frequency range with 100 mV ac input signal with a Hewlett Packard 4192A impedance analyzer connected via HPIB to a 362 HP controller.

3. RESULTS AND DISCUSSION

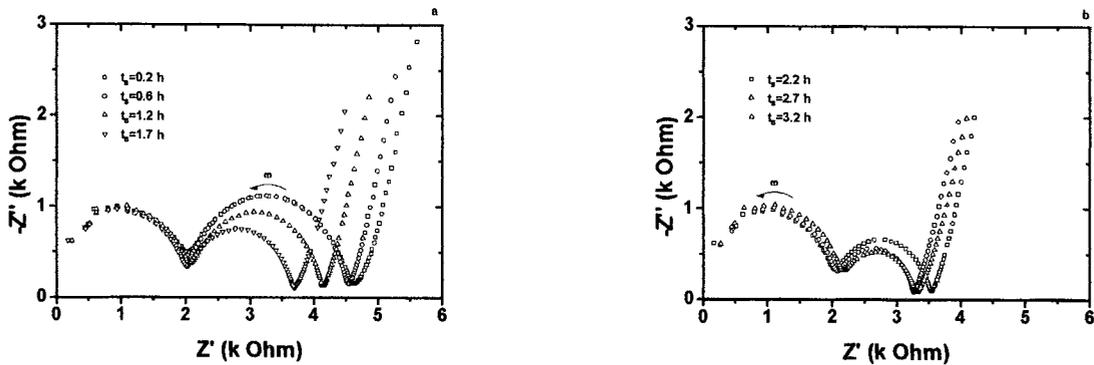


Fig. 1: Impedance Spectroscopy diagrams in the 5 Hz - 13 MHz frequency range of $ZrO_2:8\%mol Y_2O_3$ ceramic specimens sintered at 1350 °C at different times: 0.2 h, 0.6 h 1.2 h and 1.7 h (1a); 2.2 h, 2.7 h and 3.2 h (1b). Temperature of measurement: 400 °C.

Figure 1 shows impedance diagrams of $ZrO_2:8\%mol Y_2O_3$ samples measured at approximately 400 °C as a function of sintering time at 1350 °C. Two semicircles due to bulk (higher frequency region) and grain boundary resistivities are easily resolved. The intragranular (bulk) resistivity remains constant while the intergranular (grain boundary) one decreases for increasing sintering time, in agreement with reported results obtained during sintering at different temperatures (>1300 °C) [1, 5-10].

Figure 2 shows the variation of bulk and grain boundary resistance with sintering time. Isothermal annealing leads to pore elimination and consequently the evolution of grain boundary resistance is due to modification of the contact area between grains.

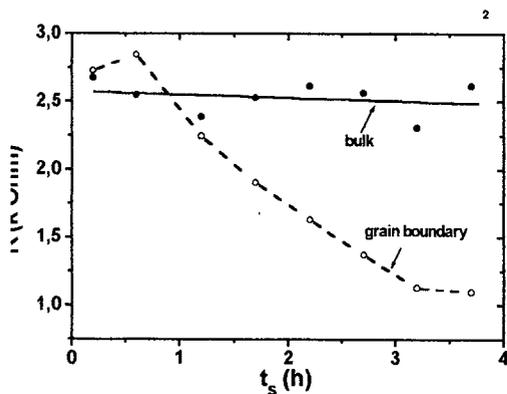


Fig. 2: Dependence of the bulk (intra-granular) and grain boundary (inter-granular) resistance on the sintering time. Sintering temperature: 1350 °C.

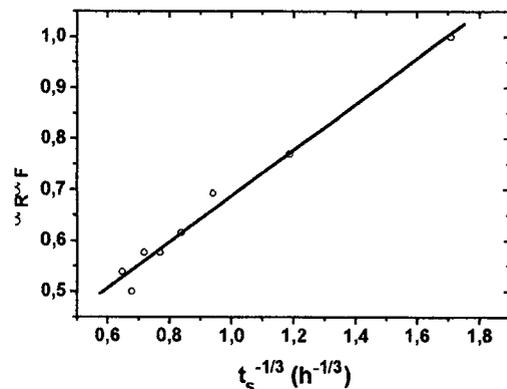


Fig. 3: Dependence of $\alpha_R \cdot \alpha_f$ on the sintering time (see text for details).

It has already been shown that grain boundary diffusion controls the densification rate according to $\varepsilon^{3/2} \propto (\text{time})^{-1/3}$, ε being the porosity [2]. Figure 3 shows the dependence of the product $\alpha_R \alpha_f$ on the sintering time. If one considers that the $\alpha_R \alpha_f$ product is directly related to the porosity ε of the ceramic specimen [10], the study of pore elimination could be followed simply by determining these blocking factors after the impedance spectroscopy diagrams.

4. CONCLUSIONS

The impedance spectroscopy technique showed to be an useful tool for the study of sintering mechanisms in ceramic solid electrolytes. The impedance diagrams measured in ceramic specimens during sintering allows for the determination of sintering parameters in $ZrO_2 \cdot 8\% \text{ mol } Y_2O_3$ solid electrolytes.

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