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Sintering of zirconia–yttria ceramics studied by impedance spectroscopy

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Abstract

Sintering of ZrO_2:Y_2O_3 ceramic compacts have been studied by impedance spectroscopy measurements at 400°C in the 5 Hz–13 MHz frequency range. Cold-pressed samples processed by a co-precipitation route were heat treated at 1350°C for different periods of time. The intragranular resistivity remains constant while the intergranular resistivity decreases for increasing sintering time. A correlation between sintering time and parameters related to pore density determined by impedance spectroscopy was found. The results show that details of the sintering process can be followed by impedance spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zirconia-based ceramics are widely used as electrochemical transducers in oxygen sensors [1]. Some of the requirements for using these ceramics in sensor devices are high density and reproducibility of the electrical properties. Hence the sintering process has to be well controlled in manufacturing the ceramic bodies. Sintering can be described briefly as the phenomenon that occurs during heating up green compacts leading to pore elimination associated to grain growth and providing well defined grain boundaries [2]. There is basically the conversion of a large number of small particles into a lower number of larger particles, that is, grain growth and solid–solid interfaces substitution for higher energy gas–solid interfaces. In most cases this is accompanied by densification. The geometric variation of the ceramic dimensions associated to sintering follows three stages: the initial stage with particles forming bonds at the particle contacts; the intermediate stage with the smoothing of the pore structure; and the final stage corresponding to closed spherical pores that shrink slowly by vacancy diffusion to grain boundaries [3,4]. Several processes are known to occur during sintering, the solid state sintering being the most important in zirconia ceramics manufactured for mechanical, electrical and optical applica-

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tions. In this case, the main sintering process involves no liquid phase formation, i.e., all constituents of the powder compacts stay in the solid state [5].

Almost 30 years ago the complex admittance technique was applied for the first time to a solid electrolyte, $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ [6].

The electrical conductivity of polycrystalline ceramics has two main components: bulk conductivity and internal surfaces conductivity. The former depends on the grain or intragranular mobility of charge carriers, while the latter on the blocking of charge carriers, mainly at grain boundaries. Grain boundary conductivity may be decreased by the blocking of charge carriers by other microstructure defects like pores or insulating second phase inclusions, these defects being called 'blockers' [7]. Mobile charge carriers can either permeate freely through grain boundaries or be blocked at certain grain boundary locations. Two blocking parameters have been proposed [8,9]: the resistance blocking factor α_R and the frequency ratio α_f. The resistance blocking factor, defined as the amount of charge carriers that are blocked at grain boundaries, is determined simply by dividing the grain boundary resistivity by the total resistivity, and these values are taken from the impedance diagrams. The resistance blocking factor α_R is a characteristic parameter related to the contact between grains and can be associated to grain boundary density. The grain boundary density is already known to be related to the specimen average grain size [9,10]. Here will be taken into account that α_R is proportional to the equivalent blocker area normal to the electric field. Or simply, in other words, α_R is proportional to the average surface between grains, i.e., the average pore surface. The other blocking parameter, the frequency factor, is defined as the ratio of the characteristic frequency of the grain boundary resistivity to that of the grain resistivity. The characteristic frequencies are the apex frequencies in the semicircles in the impedance diagrams. Kleitz et al. have shown that α_f is proportional to the average blocker thickness or to the average intergranular distance, i.e, to the average pore thickness. The product of both resistance blocking factor and frequency factor ($\alpha_R.\alpha_f$) is then proportional to the volume between grains, i.e. to the pore volume.

The main idea behind this investigation is the modifications that might occur in the impedance spectroscopy of ceramics during sintering. In zirconia–yttria solid electrolytes oxygen ion vacancies could be used as local probes in the microstructural evolution of the polycrystalline specimens. Starting with a green pellet full of pores and internal surfaces and ending in a fully dense specimen, electrical measurements using impedance spectroscopy should give enough details for sintering studies. Results on impedance spectroscopy of zirconia ceramics as a function of sintering parameters have been reported [2,9–14]. Conductivity measurements with current of variable frequency taken in zirconia–yttria solid electrolytes with different average grain sizes showed that the bulk (grain) conductivity does not depend on grain size while the grain boundary conductivity does [12,14]. Specimens with different grain sizes were obtained by firing hot-pressed samples at different temperatures up to 2000°C. The effect of microstructure on yttria–zirconia conductivity, using the impedance spectroscopy technique has been reported, showing that the higher is the average grain size, the lower is the grain boundary resistivity, the bulk resistivity remaining constant [15,16]. Recently, the densification process of barium titanate has been studied by impedance spectroscopy [17]. A correlation has been found between the activation energies of grain and grain boundary conductivities and the density after sintering.

Usually sintering is monitored by density or shrinkage measurements. In this paper, impedance spectroscopy is used to determine parameters for studying sintering in zirconia ceramics.

2. Experimental

ZrO_2:8% mol Y_2O_3 powders were prepared by the coprecipitation technique using $>99\%$ pure Y_2O_3 and ZrO_2 produced at the Zirconium Pilot Plant at this Institute. The powders were fired at 900°C for 2 hours in air. Phase analysis were evaluated by X-ray diffraction with a Bruker AXS D8 Advance and a Philips PW3710 diffractometers. Powder suspensions were prepared for observation in a JEOL JEM200C transmission electron microscope for determination of average particle size and particle agglomeration.

Linear retraction measurements upon heating were carried out in a Netzsch DIL402E/7 dilatometer. Sample pellets 10 mm diameter and 4 mm thickness were prepared by uniaxially followed by isostatically pressing at 200 MPa. The planar opposite surfaces of the pellets were painted with Demetron A308 Pt paste and fired at 800°C. The samples were inserted into an alumina sample chamber and positioned inside a tubular furnace. Platinum electrodes connected the painted surfaces of the specimen to an HP4192A LF Impedance analyzer controlled by a model 362 Hewlett Packard Controller for collecting, storing and processing ($-Z'' \times Z'$) data in the 5 Hz–13 MHz frequency range. The applied voltage signal amplitude was 100 mV. A S-type thermocouple with its tip located close to the sample was used to temperature monitoring. The temperature cycling was the following: 10°C/min up to the measuring temperature $T_m = 400°C$, data collection, 10°C/min up to the sintering temperature $T_s = 1350°C$ for t_s between 0 and 3.7 h, cooling down to T_m for data collection.

3. Results and discussion

In Fig. 1 the dilatometric curve of a ZrO_2:8% mol Y_2O_3 green pellet is shown. The well known three stages for these solid electrolytes are identified: from room temperature to approximately 900°C, where re-adjustment of particles without shrinkage occurs, from 900°C to 1350°C with large linear retraction and high shrinkage rate, and from 1350°C upwards with grain growth and pore elimination. The maximum retraction temperature of 1350°C, with about 23% linear retraction, has been chosen for sintering for different periods of time.

Impedance diagrams of ZrO_2:8% mol Y_2O_3 as a function of sintering time at 1350°C are shown in Fig. 2. All measurements have been done at 400°C Two semicircles are easily resolved: one at high frequencies due to the contribution of the ceramic grains to the electrical resistivity and the other due to the contribution of grain boundaries to the electrical resistivity [2,11]. The data at frequencies below approximately 10 Hz belong to the electrode polarization. The most striking feature of these results is that the larger is the sintering time at 1350°C, the smaller is the diameter of the semicircle due to the grain boundaries, no variation being detected in the diameter of the semicircle due to oxygen ion vacancy

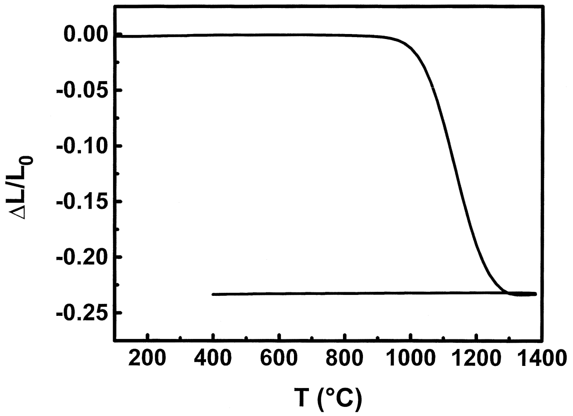

Fig. 1. Linear retraction of cold-pressed ZrO_2:8% mol Y_2O_3 as a function of temperature.

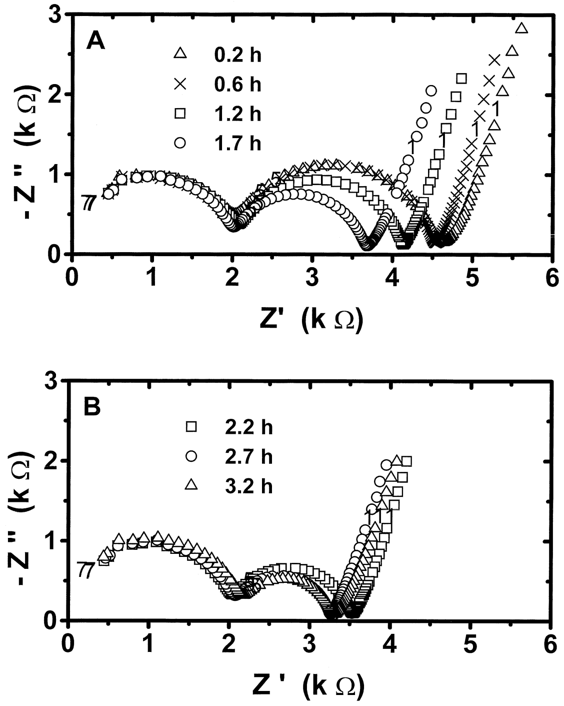

Fig. 2. Impedance diagrams of ZrO_2:8% mol Y_2O_3 sintered at 1350°C for (A) 0.2h, 0.6 h, 1.2 h and 1.7 h; (B) 2.2 h, 2.7 h, 3.2 h and 3.7 h. Numbers 1, 5 and 7 replace points measured at 10, 10^5 and 10^7 Hz, respectively.

transport inside the grains. That means that the impedance diagrams show the increase of the average grain size as a function of the isothermal sintering time.

The semicircle arcs in the impedance diagrams due to grains (intragranular contribution) do not change for different sintering times at 1350°C. The semicircle arc due to grain boundary contributions, on the other hand, decreases for increasing sintering times. These results, after data deconvolution, are plotted in Fig. 3.

The dependence of the grain resistivity R_g and the grain boundary resistivity R_{gb} on the sintering time at isothermal conditions are an evidence that the kinetics of grain growth may be followed by impedance spectroscopy. The higher is the average grain size, the lower is the grain boundary density and consequently the lower is the grain boundary resistivity. The limit situation is that of a single crystal with an impedance diagram with only one semicircle due the bulk contribution to the conductivity.

From the impedance diagrams of the ZrO_2:8% mol Y_2O_3 ceramics sintered at 1350°C for different times, α_R and α_f were determined. In Fig. 4 the product $\alpha_R.\alpha_f$ is plotted as a function of sintering time. The decrease of that product points to pore elimination, as expected. The higher is the sintering time, the higher is the average grain size at the expenses of pore elimination.

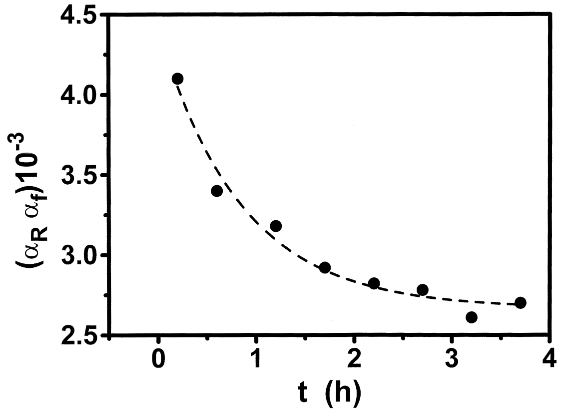

Fig. 4. Dependence of ($\alpha_R.\alpha_f$) on the sintering time of ZrO_2:8% mol Y_2O_3. α_R: resistance blocking factor, α_f: frequency factor (*see text for details*).

An effort has been made to find a correlation between the relative pore content, as determined by impedance spectroscopy diagrams (calculating the $\alpha_R.\alpha_f$ product) and sintering time. Previous reported models of pore density as a function of sintering time show that the following equation holds: $\varepsilon^{3/2} = C + B.t^{-1/3}$ [ref. 3, p. 165]. In Fig. 5 the relative pore density (expressed by the $\alpha_R.\alpha_f$ product) to the power 3/2 is plotted as a function of the sintering time to the power (−1/3). A good correlation is found. That means that $\alpha_R.\alpha_f$ product does behave as the relative pore density. Moreover, the impedance spectroscopy technique may be used to follow pore elimination during ceramic sintering.

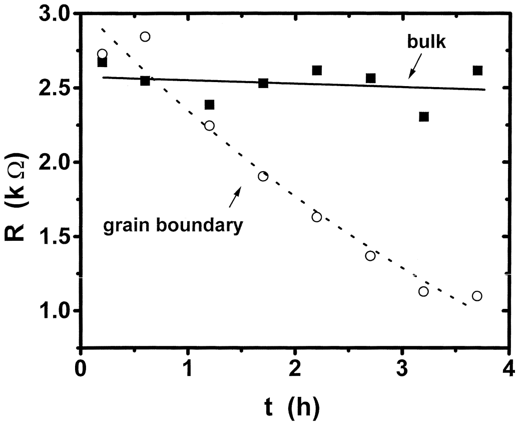

Fig. 3. Intragranular (bulk) and intergranular (grain boundary) resistances of ZrO_2:8% mol Y_2O_3 as a function of sintering time at 1350°C.

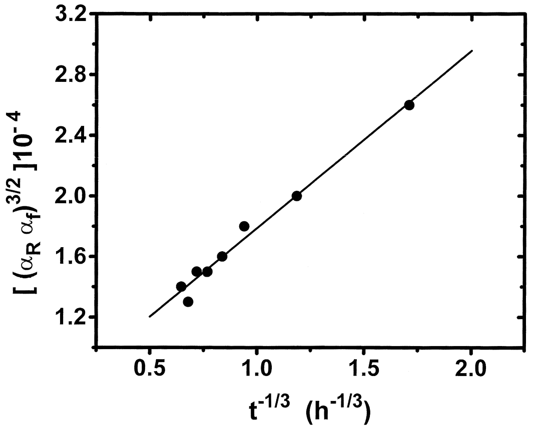

Fig. 5. Linear correlation between $(\alpha_R.\alpha_f)^{1.5}$ and $t^{-1/3}$. The $\alpha_R.\alpha_f$ product describes the relative pore density and t stands for sintering time under isothermal conditions (*see text for details*).

4. Conclusion

Grain growth in zirconia–yttria solid electrolytes can be studied by impedance spectroscopy by following the dependence of grain and grain boundary resistivities upon sintering time in isothermal conditions. The increase in the average grain size can be accurately determined in the impedance diagrams allowing for the study of its kinetics. Impedance spectroscopy measurements during sintering on a series of well studied ceramics are under way to evaluate the contribution of the technique to the study of sintering mechanisms.

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