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Effects of Mechanical Damage on the Electrical Properties of Zirconia Ceramics

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Abstract

The capability of impedance spectroscopy to characterize cracks in solids has been evaluated. Measurements were performed on yttria-stabilized zirconia. Cracks were induced by Vickers indentation with loads in the 0–625 N range. Two regimes have been observed. Under loads lower than approximately 200 N unexpected results indicate a predominant decrease of the specific resistivity of the material and of the blocking coefficient at the grain boundaries. At higher loads the anticipated observations were made: the blocking coefficient and the grain-boundary capacitive effect indicate an increase of the internal surface density with increasing loads. The transition between the two regimes is marked by a very high value of the grain-boundary blocking effect.

Es wurde untersucht, ob sich die Impedanzspektroskopie zum Nachweis von Rissen in Festkörpern eignet. Die Messungen wurden an Yttrium stabilisiertem ZrO_2 durchgeführt. Die Risse wurden durch einen Vickerseindruck im Lastbereich von 0–625 N eingebracht. Zwei Bereiche wurden beobachtet. Bei Lasten, die etwa 200 N nicht überschreiten, zeigte sich unerwartet vorwiegend eine Abnahme des spezifischen Widerstandes des Materials und des Widerstandes an den Korngrenzen. Bei höheren Belastungen ergaben sich die erwarteten Resultate: der Widerstand und die Kapazität an den Korngrenzen weisen mit wachsender Last auf eine Vergrößerung der internen Oberflächendichte hin. Der Übergangsbereich der beiden Bereiche ist durch einen sehr hohen Wert des Widerstandes an der Korngrenze gegeben.

On a évalué l'aptitude de la spectroscopie d'impédance à caractériser les fissures présentes dans les solides. Les mesures ont été réalisées sur de la zircone stabilisée à l'yttrium. Les fissures étaient induites par indentation Vickers avec des charges comprises entre 0 et 625 N. On a observé deux régimes. Pour les charges inférieures à environ 200 N les résultats indiquent, de manière inattendue, une diminution prédominante de la résistivité spécifique du matériau et du coefficient de blocage aux joints de grains. Pour des charges plus élevées, les observations suivantes, correspondant à ce que l'on avait prévu, ont été faites: le coefficient de blocage et l'effet capacitif des joint de grains indiquent une augmentation de la densité de surface interne avec des charges croissantes. La transition entre les deux régimes est marquée par une valeur très élevée de l'effet de blocage des joint de grains.

1 Introduction

A detailed investigation by impedance spectroscopy[1,2] of the grain-boundary effect in sintered yttria-stabilized zirconia (YSZ) has shown that the contacts between the grains are not perfectly permeable to the mobile oxide ions. This was confirmed by measurements on bicrystals[3] and a contact between sintered samples.[4] The simplest explanation which can be suggested is that the geometrical matching between the grains is not 'intimate' enough over all the surface of contact.

From the instrumental point of view it was also concluded that impedance spectroscopy is an accurate tool to measure the density of internal surfaces in ionically conducting solids.

A first application which can be developed from this conclusion is a continuous monitoring of the

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sintering process. First measurements[5] did confirm this interesting new capability of impedancemetry.

A second potential application[6] is a non-destructive measurement of crack density in ceramics. The term 'density' will certainly have to be more clearly defined. This paper reports on exploratory investigations of this new field. Measurements were performed on fully yttria-stabilized zirconia (YSZ). Cracks were induced at room temperature by Vickers indentation.

2 Sample Preparation

Samples of the system $(ZrO_2)_{1-x}(Y_2O_3)_x$ with $x = 0{\cdot}1$ (10 mol.%) were prepared by wet mixing of ZrO_2 (Merck, Lyon, France) and Y_2O_3 (Ampere, Serezin-du-Rhone, France) industrial powders without any sintering adjuvant to avoid any addition of chemicals which could increase the grain-boundary blocking effect. The purities of the ZrO_2 and Y_2O_3 powders were respectively 0·999 and 0·9999 with about 200 ppm of SiO_2 in ZrO_2 and 20 ppm in Y_2O_3. They were compacted under 200 MPa. Sintering was carried out at 1850°C for 2 h in air. The final density was around 95% of the theoretical value. The average grain size was about 13 μm. Pellets 3 mm thick and 7 mm in diameter were machined with diamond tools. Such a thickness was found sufficient to avoid a total fracture of the samples under loading. Their surfaces were polished to a microstructural observation quality with diamond abrasives[7] down to 6 μm. Cracks were generated by Vickers indentation. A Vickers diamond pyramid indenter (Model DIA-TESTOR 2n Wolpert, Amsler Otto Wolper-Werke GMBH, Ludwigshafen, Germany) was used at room temperature in the 0–625 N load range.

3 Measurements

Measurements were carried out by impedance spectroscopy. An impedance analyzer (Model 4192 A LF, Hewlett-Packard, US) coupled to a computer (Model 85 B, Hewlett-Packard, France) was used in the $5\text{–}1{\cdot}3 \times 10^7$ Hz frequency range. The investigated temperature domain was 350–700°C. All experiments were performed in air. The measurement cell is sketched in Fig. 1. The base surface was coated with a silver paste baked at 150°C. This coating was used as a counter electrode. The pin-shaped measuring electrode was used to allow local measurements (on an area of about 0·1 mm^2). In this

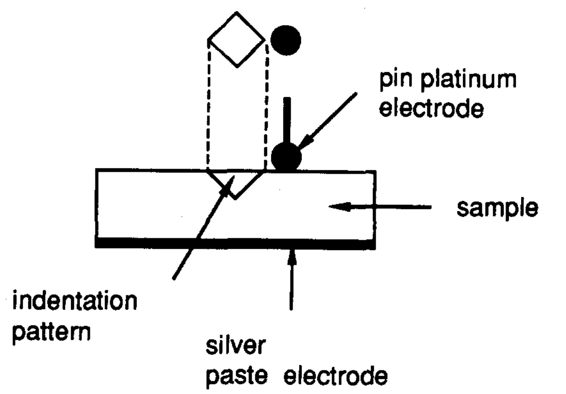

Fig. 1. Sketch of the impedance measurement cell.

series of measurements it was made of platinum and was positioned on a symmetry axis of the indentation at 0·25 mm away from an indentation corner (Fig. 1). This distance was fixed to within $\pm 0{\cdot}1$ mm.

4 Results and Discussion

A typical example of impedance diagram is given in Fig. 2. It shows a good separation between the bulk and the grain-boundary characteristics. The high-

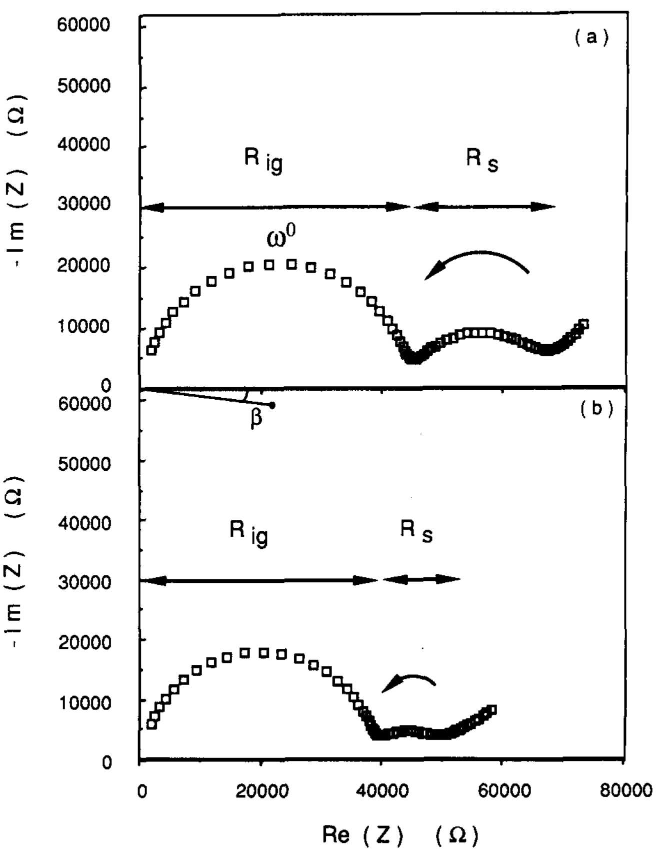

Fig. 2. Complex impedance diagrams showing the arcs corresponding to the intragrain behavior (ig) and the grain-boundary effect (s) for two samples: (a) Reference sample, at 475°C; (b) sample loaded under 98 N, at 475°C. The arrows indicate the direction of increasing frequency. Re(Z) and Im(Z) are respectively the real and the imaginary components of the sample impedance. ω^0, Relaxation frequency; β, depression angle.

Table 1. Activation energies of R_{ig}, R_S and R_t determined from the corresponding Arrhenius plots

Sample	*Indentation load (N)*	*Activation energy (eV)*		
		R_{ig} ($T > 500°C$)	R_S	R_t
1	0	1·03	1·12	1·14
2	29·4	0·99	1·05	1·07
3	49	0·93	0·95	0·99
4	98	0·97	0·89	0·97
5	153·12	0·99	0·98	1·01
6	198	0·95	1·03	1·01
7	294	0·98	1·02	1·04
8	392	1·07	1·04	1·07
9	490	1·03	1·05	1·06
10	612·5	0·89	0·91	0·92

frequency semicircle diameter which measures the intragrain resistance is R_{ig}. The low frequency one which corresponds to the additional internal surface resistance is R_S. The sum of these two resistances, R_t, which is the DC resistance of the material, is also used as a parameter to describe the results. For each indentation load the variations of these parameters with temperature were measured. The low indentation measurements were repeated three times and the others twice. The reproducibility of the measured parameters was around 15%. Some scatter was also due to a great sensitivity of the point contacts to vibrations. From the resistance Arrhenius plots the corresponding activation energies were determined. The results are compiled in Table 1.

Several marked trends can be noticed. A surprising result is a decrease of the total resistance R_t and the other resistance parameters for loads in the range 0–98 N (Fig. 3). At 475°C, the total resistance drop can reach 24%. This decrease is also accompanied by a slight decrease of the resistivity activation energy (Table 1). In electronic conductors a decrease of the electrical resistance under stress is frequently observed and is generally interpreted in terms of generated cracks acting as sources of electric carriers (the cracks being surrounded by space charges). In oxides Chang,[8] for instance, observed a similar decrease of the electrical resistivity in Al_2O_3 during transient creep. The extrapolation of this model to an ionic conductor such as YSZ would assume that cracks can act as sources of mobile ions. This is consistent with the existence of electrochemical double layers in the sub-surfaces of the solid ionic conductors. Along this line, Klein & Gager have suggested that oxygen vacancies could be generated in plastically deformed MgO.[9]

Another essential observation is the similarity between the variations of R_{ig} and R_S (Fig. 3). This is a rather general observation which has led Kleitz *et al.*[1] to conclude that there is no difference in the elementary conducting mechanisms in the bulk and through the grain boundaries. These boundaries will simply act as 'filters' which partly block a fraction of the mobile ions coming from the bulk. Ions would pass where the contact is intimate enough and would be blocked elsewhere.[1] For this reason it was decided that the significant parameter describing the blocking effect will be the blocking coefficient α_R defined as[2]

$$\alpha_R = \frac{R_S}{R_t}$$

Figure 4 shows the variation of this parameter, calculated at 475°C, as a function of the indentation load. This parameter, being a ratio of two resistances measured under the same conditions, is less sensitive than the others to experimental irreproducibilities, especially to the unavoidable small variations of the contact area of the point electrode. Its plot clearly indicates the existence of two distinct domains corresponding to low loads and high loads. In the low load domain, even more surprising is a decrease of the blocking factor. A detailed examination of the

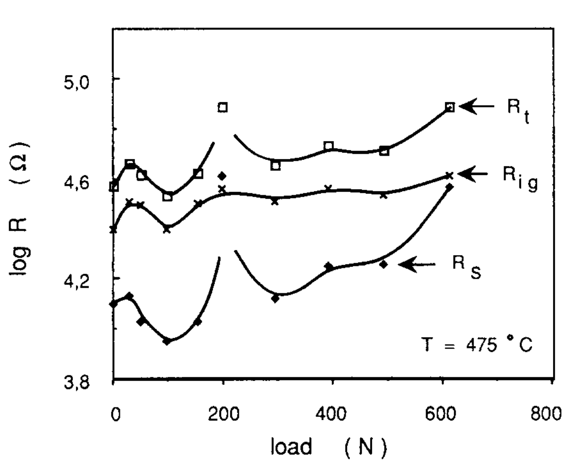

Fig. 3. Variations of the total resistance R_t, the intragrain resistance R_{ig} and the additional internal surface resistance R_S with load, measured at 475°C.

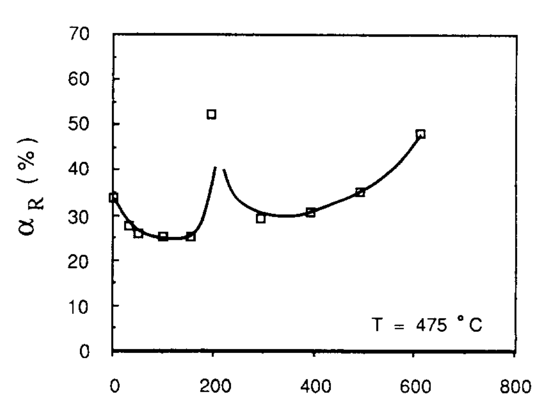

Fig. 4. Influence of the loading charge on the blocking coefficient α_R, at 475°C.

data shows that this is predominantly due to a more rapid decrease of the grain-boundary resistance. For instance, after an indentation under a load of 98 N the decreases of R_{ig} and R_S are respectively 14% and 44% of the initial values. In the high load domain the observed behavior is more consistent with expectation that the grain-boundary resistance and the blocking factor increase with the load, i.e. most probably with the density of cracks.

Another point to be underlined is the 'scattered' result obtained under 196 N of load. Whatever the parameter selected to represent the results, even α_R, this point appears markedly out of the average variation laws. Several sets of measurements were performed on different samples. The same result was obtained under 196 N. Here the reproducibilities of the experimental results were within 20%.

The evaluation of the relaxation frequency ω^0 at the top of each semicircle allows us to determine the average capacitive terms C_{ig} and C_S, by applying the following equation:

$$RC\omega^0 = 1$$

C_{ig} represents the average dielectric properties of the bulk and is directly related to the dielectric constant ε of the YSZ phase (ε was not calculated because of uncertainties on the geometrical factor of the measurement cell). C_{ig} is of the order of a few picofarads as expected from evaluations calculated with a dielectric constant of the order of 20. As shown in Fig. 5 this parameter varies a little with a minimum as a function of the indentation load. C_S describes the capacitive effect of the grain boundaries. A previous investigation[2] has shown that C_S is proportional to the surface of these boundaries. It is of the order of a few nanofarads as usually observed with a point electrode on YSZ. It varies significantly with the indentation load especially in the high load domain. Comparison of Figs 4 and 5 shows that under loads higher than 300 N the independent parameters α_R and C_S vary in very similar ways. This is the expected behavior which would characterize a geometrical mismatch along the internal surfaces. Under these conditions either of these two parameters can, in principle, provide a direct measurement of the density of internal surfaces and therefore of cracks. In regularly sintered samples both of them were previously found[2] proportional to the area of the internal surfaces.

Note also that the scattering of the 196 N load point is only faintly observable on the C_S' curve (Fig. 5).

Another set of information which can be extracted from the impedance diagram is the variation

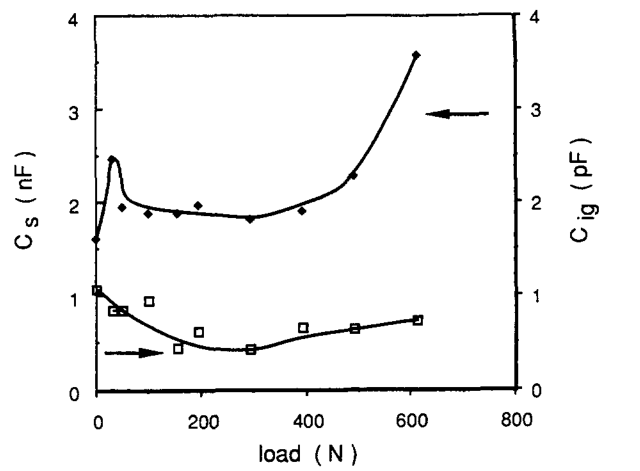

Fig. 5. Variations of the average capacitive terms C_S and C_{ig} with the indentation load, measured at 475°C (see text for further explanations).

of the 'depression' angles β of the semicircles. Many interpretations[1,10] have been put forward for such parameters. The most commonly admitted is in terms of heterogeneity. The depression angle is viewed as 'measuring' the dispersion of the local parameters around average values; the greater this angle, the higher the heterogeneity. Such a dispersion can in principle result from variations of the dielectric constant or the resistivity. This last parameter, being much more sensitive to composition heterogeneities, is generally viewed as being predominantly responsible for the dispersion. Figure 6 shows the variation of the bulk and grain-boundary dispersion angles, β_{ig} and β_S respectively. The first one remains small and almost unaffected by the indentation, indicating that bulk properties remain approximately homogeneous. On the other hand, the grain-boundary parameter β_S exhibits a large variation with a maximum for a load of about 400 N. At this stage, no sound explanation can be suggested except that real grain boundaries and cracks may contribute differently. Then a shift from the predominance of the grain boundaries under low

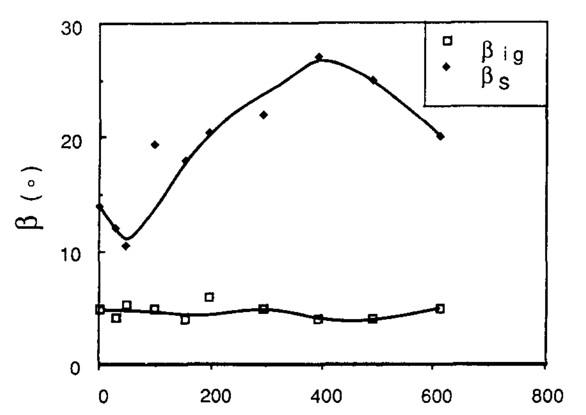

Fig. 6. Variations of the depression angles β_{ig} and β_S related to high and low frequencies semicircles.

loads to a predominance of the cracks under high loads could explain a variable heterogeneity.

5 Conclusions

The general conclusion which emerges from this exploratory investigation is that there are two distinct domains depending on the magnitude of the indentation load. The anticipated behavior appears observable only for loads higher than about 200 N. Under these conditions the dielectric and conductivity properties of the bulk of the grains are almost unaffected. Their homogeneity remains high. On the other hand, the blocking and the capacitive effects associated to internal surfaces increase with the crack density.

In the low load domain, an unexpected behavior is observed, dominated by a decrease of the specific resistivity of the material. A reduction of the blocking coefficient is also observed as if the contact between the grains were improved by the loading. It should be noted that a similar observation on the blocking coefficient has been made on quenched samples.[2,11,12]

Between the two domains a sort of 'accident' occurs, mostly due to an abrupt and localized increase of the internal surface resistance.

A large variation of the homogeneity coefficient, β_S, of the grain boundaries has also been observed.

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