Irreversible conductivity change of Ca $\beta''$-alumina at high temperature

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Polycrystalline Ca $\beta''$-alumina was produced in a relatively gentle way by increasing stepwise the Ca content of (Na, Ca) $\beta''$-alumina in suitable mixtures of molten salts (Ca(NO$_3$)$_2$ and CaCl$_2$). When determining the conductivity of Ca $\beta''$-alumina as a function of temperature by the four-probe technique, an irreversible decrease of the conductivity was observed in subsequent measurements if the temperature during the first conductivity measurement was extended beyond 600°C. Impedance measurements on such samples demonstrated that the conductivity decrease was due to an increase of the contribution of the grain boundary resistivity to the total specific resistivity.

1. Introduction

The conductivity data, reported [1-5] in the literature for Ca $\beta''$-alumina, differ greatly even for materials which were produced by ion exchange of Na $\beta''$-alumina in suitable molten salts. It was demonstrated [2-4] that the conduction is due to Ca$^{2+}$ and not to the small amount of Na$,^\ast$ left in samples with large extents of exchange (about 95%). Three factors have been considered responsible [4] for the differences in conductivity data:

(a) The type of starting material (MgO or Li$_2$O stabilized);
(b) the ion exchange process and the subsequent washing procedure;
(c) the conductivity determination (four-probe technique or impedance spectroscopy).
An additional cause, namely
(d) irreversible change of conductivity when extending the temperature range above 600°C, was discovered recently [6] and is described subsequently. It depends upon the experimental conditions to what extent the various factors (a) to (d) will influence the conductivity measurements.

2. Experimental

The polycrystalline samples of Ca $\beta''$-alumina were produced from Na $\beta''$-alumina of Ceramtec Inc. in the way described in ref. [4]. The extent of exchange was determined by INAA. As in the preceding work [4], it was found difficult to obtain a 100% exchange of Na by Ca. Instead, samples with exchanges above 95% were used here.

Four-probe measurements of the conductivity of (Na, Ca) $\beta''$-aluminas with Pt electrodes displayed [6] a considerable hysteresis between heating and cooling cycle when the temperature was increased above about 600°C. The conductivity, determined during a subsequent cycle, was smaller. To study this effect in more detail, impedance measurements were carried out as a function of time at a constant temperature on samples with exchanges above 95%.

Pt films with a thickness of about 200 nm were sputtered on the large surfaces of the samples for the impedance measurements. The set-up for the automated impedance measurements at constant temperature, the holder for the solid electrolyte and the program for the simulation of the frequency dependence of the cell metal/solid electrolyte/metal were described before [7]. Then impedance spectra were
taken at 522, 600 and 700°C in intervals of one hour to determine the time dependence.

3. Results and discussion

A plot of the negative value of the capacitive component of the impedance versus the ohmic component is shown for a 95% exchanged specimen at 522°C in fig. 1. The measurements, obtained by the impedance meter HP 4192A, are given by the solid line, those from the meter IMS-e by the dashed line. As previously found [7], the agreement between the two impedance meters is satisfactory. The plot in fig. 1 allows a graphical extrapolation of the curve to the abscissa at high frequencies if a higher resolution is used. This extrapolated value corresponds to the intragranular resistance of the β⁺-alumina. However, it is very difficult to determine by graphical extrapolation the total specific resistivity (sum of intragranular and intergranular resistivities).

The equivalent circuit in fig. 2 was employed for the latter purpose. By choosing appropriate values of the parameters in the equivalent circuit, it is feasible to simulate the frequency dependence of the impedance at constant temperature in a satisfactory fashion. $R_g$ designates the intragranular resistance (resistance inside the grain). The grain boundary impedance is approximated by the parallel circuit of $R_{gb}$ (grain boundary resistance) and a constant phase element $C_{gb}$. The frequency dependence of the interphases is difficult to simulate. A possible circuit is represented by the right hand elements in fig. 2. The best fit of the simulation was achieved by optimization of the parameters of the equivalent circuit in fig. 2 by the program FIRDAC [7,8].

An equivalent circuit, similar to that in fig. 2, had previously been successfully used [7] in the interpretation of the impedance data for the system Pt/Ag β⁺-alumina/Pt in a wide temperature range. The correctness of the simulation procedure was verified by comparing values of $(R_g + R_{gb})$ with values of the bulk resistance obtained by the four-probe technique for the same sample. The four-probe measurements were carried out before the impedance measurements and did not extend beyond 600°C to avoid changes with temperature and time. To reduce the influence of changes with time, the impedance data in fig. 3 represent the first measurement at a given temperature. The agreement of the curves for the total conductivity in the Arrhenius plot of fig. 3 is satisfactory. The curve, obtained from $R_g$, lies considerably higher. The intragranular resistance is much lower than the grain boundary resistance.

The dependence of the intragranular and intergranular resistances as a function of time at 522, 600 and 700°C is given in a normalized fashion in fig. 4. The resistances of the first measurement were used in the normalization procedure. It is evident from fig. 4 that the normalized intragranular resistance does not change much with time. In contrast, the intergranular resistance decreases somewhat with time at 522 and 600°C. It displays a large increase at 700°C. Heating of Ca β⁺-alumina to temperatures above 600°C leads to an increase of the grain boundary resistivity. The effect is time dependent.

An attempt to interpret the data, obtained for the interfacial behavior of the system from the simulation, was not undertaken. This is due to the difficulty of separating the contribution of the heterogeneous surface on the impedance from that of the electrochemical reactions. Additional assumptions, the va-
Fig. 3. Arrhenius plots of the total and the intragranular conductivity.

Fig. 4. Time dependence of normalized resistances at different temperatures.

...lidity of which cannot be checked, have to make for such an interpretation.

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