ELECTRICAL BEHAVIOUR OF THE CERAMIC γ-AlON

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ABSTRACT — In this paper some measurements on the impedance of aluminium oxynitride samples, using a Fourier technique, are presented and discussed.

1 – INTRODUCTION

A solid electrolyte is a real crystal showing defects like its surface, dislocations or point defects [1-3].

Usually, a solid electrolyte is presented as a material where the electrical conductivity is mainly assured by the ions [4]. In many solid electrolytes a single species is responsible for the electric current; among its most important features one might mention an electric conductivity lower than in metals or semiconductors, an exponential temperature dependence, no convection problems and a temperature-dependent defect concentration [5].

Ionic mobility may be derived from measured impedance spectra; in solid electrolytes this is more convenient than conventional electrochemical methods. Due to inhomogeneities, a solid electrolyte may show a frequency-dependent impedance behaviour with two main contributions: one corresponding to polarization effects inside the grain and the other to a conduction blocking effect at the grain junction. Care must be taken in the choice of the measuring technique in order to evaluate the different contributions involved (bulk and stray ones).

2 — EXPERIMENTAL METHOD AND RESULTS

2.1 — *Measurement technique*

The impedance spectrum $Z(\omega)$ is obtained by sweeping the frequency of the applied electrical potential; for solid electrolytes, one often uses the range 1-100 kHz.

Solid electrolytes appear mainly as compressed powders, ceramics, or solidified melts; their bulk conductivity can not be considered equivalent to a single resistor [6].

The measured current depends on the sample impedance but is also affected by a number of other contributions:

— the electrode/electrolyte interfacial impedances
— the measuring leads impedance
— the empty cell impedance

The electrical behaviour of the solid cell is due to the overall bulk (grain and intergrain) contribution of the sample and the interfacial sample/electrode contribution. This may be described using a series or parallel arrangement of different RC circuits [7-9].

A considerable number of electrical measuring techniques may be used for experimental characterization of the sample [10-12]. However, a Fourier technique allows a rapid analysis by means of the extended frequency spectrum of a d. c. pulsed regime as well as a better elimination of the noise from the measured signal.

In the Fourier technique, which we have employed, instead of scanning the impedance spectrum of a solid cell by using one frequency at a time, a square wave or a train of pulses is used. Pulsed measurements are performed either by imposing the current and measuring the potential difference across the sample (or vice versa) providing the same information with a better elimination of the noise. The data are collected by means of a transient recorder (see Fig. 1). This is a gated device, Solatron Model 1170; it generates an output signal with a frequency lying within the range 10^{-4} - 10^{6} Hz and measures the incoming voltage signal, the potential difference across the sample, during a triggering time Δt. The averaged values are analog/digital converted and stored in a microprocessor. By triggering at the start of each new pulse (or each new wave) and adding the signal response of a large number of wave periods, the noise effects are averaged out.

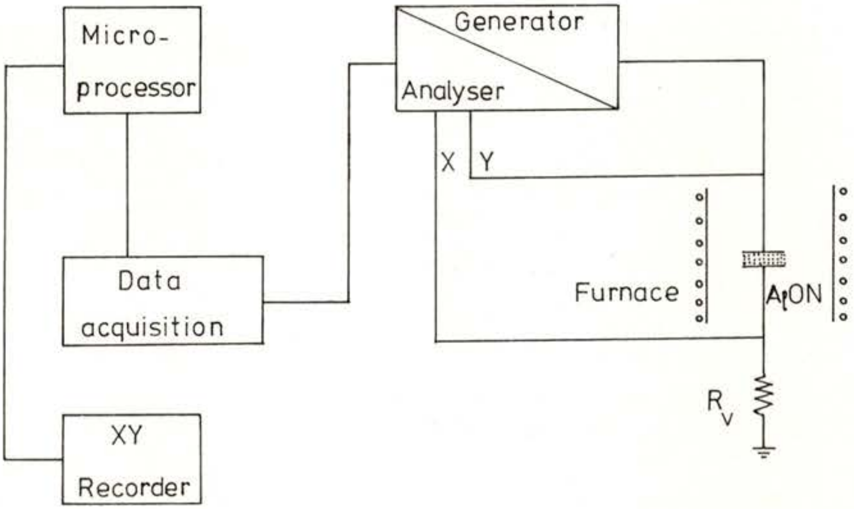

Fig. 1 — Measuring system

The system response is processed using the Fourier technique by an Hewlett Packard microprocessor H80. The results are presented in terms of X/Y ratio with $Z = (Y/X - 1)\ R_v$, where R_v is a calibrated resistance.

A tubular furnace, with two different thermocouples (one close to the heating elements and the other to the sample), is used. The samples are placed inside an aluminium oxyde chamber filled with N_2 gas. To prevent contamination, the chamber is previously pumped down to a vacuum better than 10^{-4} torr.

2.2 — *Experimental results*

2.2.1 — Sample preparation

The AlON used is obtained by alumina nitration in the presence of carbon (carbon black). The first step leads to the formation of aluminium nitride AlN

$$Al_2O_3 + N_2 + 3\ C \rightarrow 2\ AlN + 3\ CO\ ;$$

this, in a second step, reacts with the alumina excess and originates the AlON :

$$Al_2O_3 + AlN \rightarrow AlON$$

This reaction is non-stoichiometric and once the involved component ratios are deffined, the reaction will proceed until total decay of the alumina [13-14].

The powder of AlON obtained by the described process, with an average size of 6 μm, is then hot-pressed at 40 MPa for 4 hours at 1800°C; afterwards it is submitted to a grain growith thermal treatment in a N_2 atmosphere (24 hours, 1950°C).

2.2.2 — Impedance spectrum

The experimental results are shown in Fig. 2. We can see that the impedance spectrum includes a single contribution, in this case [7-9] the one due to the microstructure of the sample.

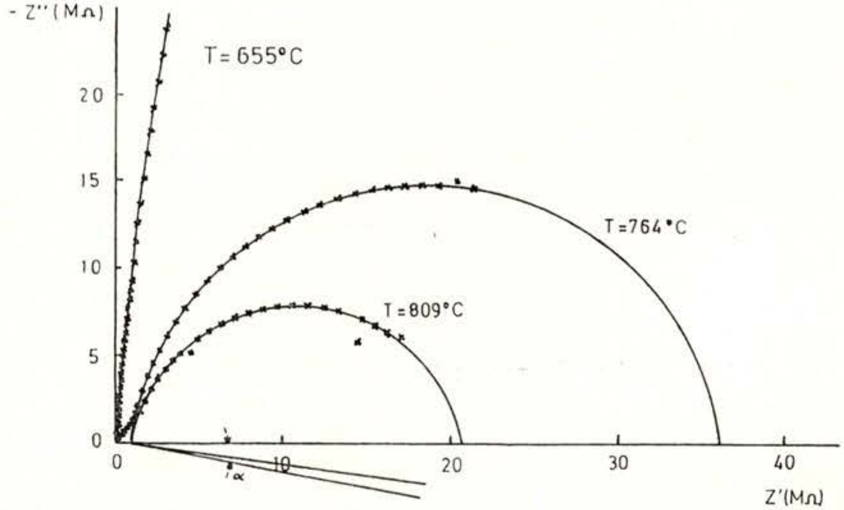

Fig. 2 — Experimental results obtained using the temperature as a parameter

The dielectric behaviour of the AlON sample, with a relative dielectric constant, ε_r, equal to 10-13 and a loss tangent, tgδ, in the range 0.01-0.03 can be obtained from an equivalent circuit like the one shown in Fig. 3. There the r C parallel arrangement (r = 20-40 MΩ represents the intergranular resistance and C = 20-35 pF represents a double layer capacitance corresponding to the polarization effects at the grain junction) characterizes the intergranular zone and R = 1 MΩ the bulk (grain) contribution.

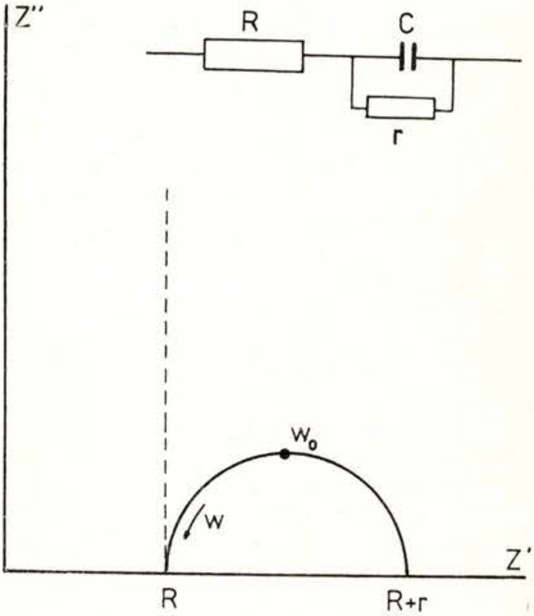

Fig. 3 — Simplified equivalent circuit for an AlON sample

2.2.3 – Activation energy

From the Arrhénius representation of Fig. 4 we infer that the sample shows a poor conductivity, even at high temperatures, which is confirmed by the large value of the activation energy. An activation energy, E_a, equal to 1.27 eV, was obtained and this value agrees well with other experimental values in the literature [15].

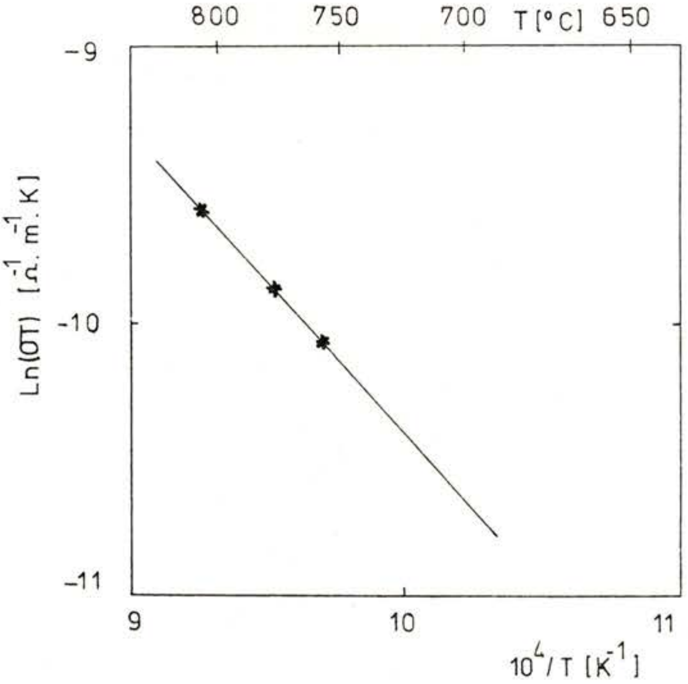

Fig. 4 — Arrhénius representation

3 – DISCUSSION

In this paper we present some experimental results obtained for the ceramic AlON using a Fourier technique. Usually in sintered electrolyte, the interface electrolyte/electrolyte near the grain junction and the non-homogeneous electric field zones originate an impedance spectrum with two main contributions. In this situation, one corresponds to the polarization efects inside the grain and the other to the conduction blocking efect at the grain junction. In our case this is not observed. The absence of the second contribution may be easily understood; it is due to the low porosity of well compact samples, like our own. In fact, similar behaviour has been found in other sintered materials with porosity ratios less than 10 %; there again the impedance spectra show a single contribution and the angle between the real axis and the half-circle diammeter is almost temperature-independent (in our case $\alpha \simeq 12^{\circ}$) [16]. Therefore the spectrum contribution may be correlated with the sample bulk properties; this represents a first step to the understanding of the electrical behaviour of this type of solid electrolytes.

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