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AC-Conductivity Measurements on γ-Aluminium Oxynitride

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Abstract

AC-conductivity measurements were performed on aluminium oxynitrides (Alons) because of their interesting defect structure. Although it became apparent that these Alons are not stable in the temperature range used, the electrical properties of the materials could be measured with impedance spectroscopy using a special procedure. The activation energy for charge transport in Alons with 67·5, 73 and 77·5 mol% Al_2O_3 at temperatures between 1173 and 1373 K was 2·78, 2·85 and 2·97 eV, respectively, while the pre-exponential factors increased with increasing number of aluminium vacancies. The conductivity shows a more-than-linear dependency on the amount of aluminium vacancies. Charge is transported via aluminium vacancies but the large amount of vacancies does not result in greatly changed mobilities: the interesting defect structure of Alon does not lead to extraordinary electrical properties.

1 Introduction

γ-Aluminium oxynitride (Alon) is a ceramic material with a spinel-type crystal structure.[1] The ideal composition for this system (Al_3O_3N) is outside the homogeneity region of Alon[2,3] and the actual Alon phase can be described with the constant anion model, in which all anion sites are occupied by oxygen or nitrogen and the cation sites are partly occupied by aluminium.[4] As about one aluminium atom is missing in each unit cell,[5] Alon is a highly defective material. Because it might be possible to have high ion mobilities in such a material and because the electrical properties of Alon were largely unknown, we decided to investigate these properties for three Alons with different compositions. During these investigations it became apparent, however, that Alon has only a limited stability, as is reported in detail elsewhere.[6] However, interesting Alon/Al_2O_3 and Alon/Al_2O_3/SiC composites can be obtained in spite of these restrictions[7,8]

The conductivity for ionic conductors is thermally activated and can be described by $\sigma = \sigma_0/T \times \exp(-\Delta H_m/kT)$, in which σ is the specific conductivity (S m^{-1}), σ_0 is a scaling constant (K S m^{-1}), T is the temperature (K), k is Boltzmann's constant, and ΔH_m is an activation enthalpy (J mol^{-1}). To determine ΔH_m, $\ln(\sigma T)$ is plotted against $1/T$ in an Arrhenius plot; the slope in this plot is equal to $\Delta H/k$, provided that the number of charge carriers is constant over the temperature range considered.[9]

2 Experimental

Details of the preparation of the Alons were reported earlier.[10] The Alons had compositions corresponding to 67·5, 73 and 77·5 mol% Al_2O_3 and will be designated 'L', 'M' and 'R', respectively, in this paper. Mechanical and optical properties of these materials were reported earlier.[11] Samples were flat discs, typically 8 mm in diameter and 0·5 to 1 mm thick. These were polished, cleaned in boiling nitric acid (60%), neutralized with ammonia, rinsed thoroughly with deionized water and dried. Platinum electrodes (diameter 5·5 mm, thickness ~3 μm) were deposited on the samples by sputtering and subsequent painting (Demetron 308 A paste). The electroded samples were annealed at 873 K for 2 h in air.

AC-measurements were performed with a set-up based on a Solartron 1174 Frequency Response Analyzer which was interfaced to a computer. The computer was also used to control a DC-driven tube furnace containing a spring-loaded alumina conductivity cell, comparable to that of Metselaar and Larsen.[12]

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The partial oxygen pressure was kept low because the oxidation of Alon to Al_2O_3 is faster than the decomposition of Alon into Al_2O_3 and AlN. Experiments were done in flowing nitrogen (pressure 10^5 Pa, purity 99·999%) which was led over graphite powder at a temperature of 1273 K before it entered the measurement set-up.

For each temperature a new sample was used which was heated to the desired measuring temperature (heating rate 344 K h^{-1}) and kept there for 20 min to stabilize. For composition M, stabilization times of 6 h were also used for comparison. After this stabilization the frequency response of the material was measured in the frequency range 1 MHz–0·1 Hz, which took about 30 min, the greater part of which was spent in measuring the lower frequencies. This cycle of stabilizing and measuring was repeated two times or more (typically three impedance diagrams were taken) and the resulting impedance diagrams were extrapolated linearly to t=0, which is the time at which the sample reaches the measuring temperature for the first time. The stabilization time was chosen in such a way that the impedance–time plot for any frequency was well approximated by a straight line. Temperatures used ranged from 1123 to 1373 K. Measurements were performed with a measuring voltage of 50 mV (voltages of 100 and 200 mV gave the same results).

No Nernst potential measurements were performed because the material degrades fairly rapidly. In our equipment specimens have to be mounted at high temperature to obtain a gas–tight seal before the measurements can take place. As a result of this, the material would already change considerably before any measurement could be performed.

3 Results

A number of typical complex impedance diagrams of Alon with composition M are stacked together in Figs 1(a) and 1(b). Both diagrams show several measurements on one specimen each and the extrapolation that was made to t=0. Measurements with a stabilization time of 20 min always showed one arc only. Measurements with a stabilization time of 6 h showed results similar to Fig. 1(b) at all temperatures, although the second and third arcs were not always as clearly visible as in this figure. At t=0 the complex impedance diagram consists of one depressed arc only. As the sample is held at the measuring temperature, the intersection of the arc with the real axis shifts to higher values. At still longer holding times, a second and a third arc appear in the diagram. Table 1 lists the results of the measurements with a stabilization time of 20 min on the three types of Alon. Each entry represents the value of the real part of the complex impedance at t=0.

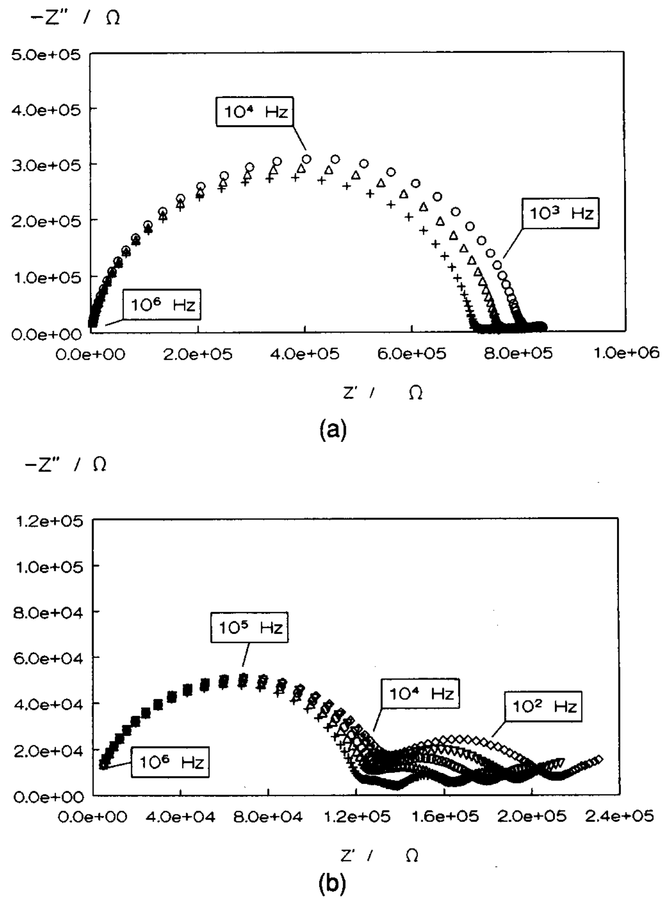

Fig. 1. Two typical sets of measurements on Alon with composition M together with extrapolations to t=0 (inner circle, +): (a) shows measurements at 1248 K with a stabilization time of 20 min); (b) measurements at 1348 K with a stabilization time of 6 h (Δ = first measurement, ○ = second measurement, ∇ = third measurement and ◇ = fourth measurement).

At temperatures above 1373 K no reliable extrapolation to t=0 could be made (degradation is too fast). Moreover, the characteristic frequency of the first arc was about 1 MHz and as this is the maximum measuring frequency, half of the arc

Table 1. Extrapolated values of the specific resistance at t=0 (the time at which the measuring temperature was reached for the first time) at various temperatures for L, M and R Alons. The stabilization time used for the measurements was 20 min.

Temperature (K)	*Specific resistance (Ω m)*		
	Composition L	*Composition M*	*Composition R*
1173	$2{\cdot}32 \times 10^5$	$1{\cdot}86 \times 10^5$	$1{\cdot}16 \times 10^5$
1198	$1{\cdot}25 \times 10^5$	$1{\cdot}00 \times 10^5$	$6{\cdot}63 \times 10^4$
1223	$8{\cdot}06 \times 10^4$	$6{\cdot}79 \times 10^4$	$3{\cdot}76 \times 10^4$
1248	$4{\cdot}29 \times 10^4$	$3{\cdot}58 \times 10^4$	$2{\cdot}34 \times 10^4$
1273	$2{\cdot}93 \times 10^4$	$2{\cdot}11 \times 10^4$	$1{\cdot}40 \times 10^4$
1298		$1{\cdot}34 \times 10^4$	$7{\cdot}65 \times 10^3$
1323		$9{\cdot}00 \times 10^3$	$4{\cdot}66 \times 10^3$
1348		$5{\cdot}74 \times 10^3$	
1373		$3{\cdot}35 \times 10^3$	

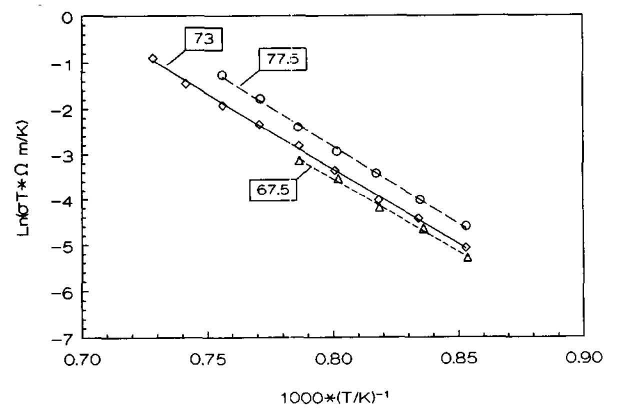

Fig. 2. Arrhenius plot for all measurements with a stabilization time of 20 min (Δ = L, ◇ = M and ○ = R).

could not be measured. Below 1123 K, the DC-resistance of the samples was > 10 MΩ. As it is not possible to measure these impedances accurately with the set-up used, no measurements were performed in this region. At temperatures below 1173 K equilibration was too slow and reliable extrapolation was not possible.

An Arrhenius plot containing all measurements is given in Fig. 2. Activation energies of 2·78, 2·85 and 2·97 eV were obtained for L, M and R, respectively. These values were determined with a linear least-squares fit of the data. Correlation coefficients were 0·998, 0·999 and 0·999, respectively.

Table 2 lists the results of the measurements on Alon with composition M with a stabilization time of 6 h. As can be seen in Fig. 3, the measurements at 1240 K give almost the same results as the measurements with the short stabilization time and the measurements at 1340–1350 K resulted in slightly higher conductivity values than the measurements with the short stabilization time.

X-ray diffraction (XRD) on specimens before and after testing showed that the lattice parameters had decreased slightly during the experiments. Unfortunately, the uncertainty of the XRD measurement is of the same magnitude. No other phases than Alon were observed with XRD. Alons of composition L and M were still translucent after testing but specimens of composition R were afterwards slightly more opaque than before.

Table 2. Extrapolated values of the specific resistance at t=0 of M Alon at several temperatures with a stabilization time of 6 h

Temperature (K)	*Specific resistance (Ω m)*
1241	$3{\cdot}80 \times 10^4$
1241	$3{\cdot}80 \times 10^4$
1242	$3{\cdot}70 \times 10^4$
1341	$4{\cdot}5 \times 10^3$
1344	$4{\cdot}8 \times 10^3$
1347	$4{\cdot}0 \times 10^3$

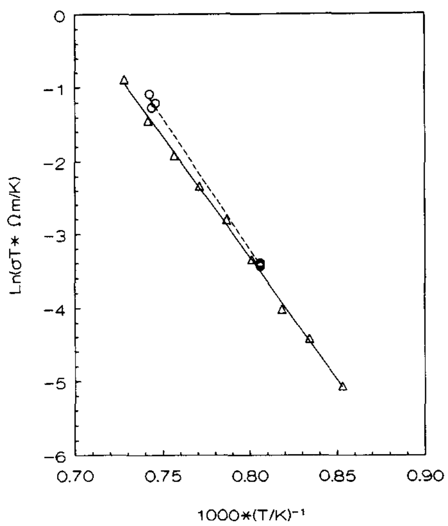

Fig. 3. Comparison between measurements on M Alon with short stabilization times (20 min, Δ) and those with long stabilization times (6 h, ○)

If Alon specimens were kept for some days at the measuring temperature, α-Al_2O_3 was found on the outer surface of the specimens.

4 Discussion

At first, there is only one arc in the impedance diagrams, corresponding to the bulk material, while after a certain period of time one or two additional arcs appear. The bulk material decomposes because of the instability of the material at the measuring temperature. The additional arcs can, for instance, be due to accumulation of oxygen on the grain boundaries (probably the first step in the oxidation of the material) or to electrode reactions. The slight decrease of the lattice parameters also indicates an increase in the oxygen content. The opaqueness of the R specimens can be due to the formation of Al_2O_3-rich regions in the material.

The results of the experiments with long stabilization times are only different from those with short stabilization times at high temperature. At high temperature, degradation does not proceed linearly with time when the time between observation is too long and reliable extrapolation is not possible.

If the amount of intrinsic aluminium vacancies is plotted against the specific conductivity for various temperatures, Fig. 4 is obtained. As can be seen, the conductivity is higher when the amount of vacancies increases, which is an indication that the migrating species are the aluminium vacancies.

The literature data on electrical properties of Alon are limited to one publication of Kim and Richards[13] who measured the AC-conductivity of Alon with compositions corresponding to 70 and 76·3 mol% Al_2O_3 at temperatures of 1573, 1673

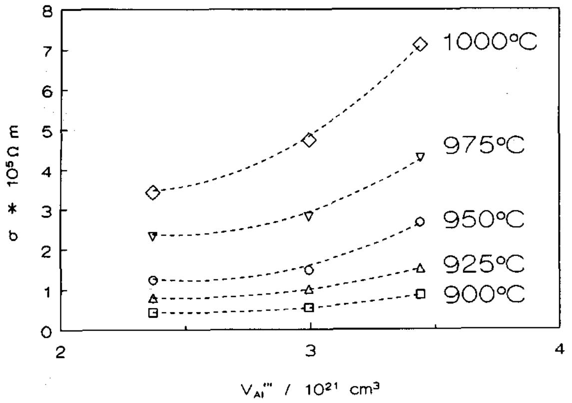

Fig. 4. Electrical conductivity of Alon as a function of concentration of aluminium vacancies at various temperatures.

and 1773 K in flowing nitrogen. They report an activation energy of 116 kJ mol^{-1}, which we were unable to reconstruct from their data. If their data are fitted with the equation for ionic conductors we obtain an activation energy of 329 kJ mol^{-1} (3·41 eV). The differences between their results and this investigation are probably due to faster degradation of the materials at the higher measuring temperatures used by Kim and Richards.

There are some data on the electrical behaviour of $MgAl_2O_4$, which has the same crystal structure as Alon. Sonder[14] showed that conduction in $MgAl_2O_4$ is almost purely ionic in character and argued that the transporting species most probably are cation vacancies. It was also shown that the conductivity between 700 and 2000 K is not greatly influenced by either ambient oxygen pressure (10^5–10^{11} Pa) or iron impurities up to 0·1%.[14,15] The activation energies ranged between 1·50 and 2·74 eV, dependent on the temperature range considered. Bates and Garnier[16] observed nearly the same range of activation energies with measurements on single crystal and polycrystalline $MgAl_2O_4$ at temperatures between 650 and 1260 K. Comparison between diffusion coefficients of magnesium, aluminium and oxygen in MgO, Al_2O_3 and $MgAl_2O_4$ show that the mobility of oxygen is several orders of magnitude lower than that of magnesium and aluminium.[17] From these literature data it can be concluded that the charge transport in $MgAl_2O_4$ takes place via cation vacancies. Because Alon has the same type of crystal structure as $MgAl_2O_4$ and nitrogen ions are even larger than oxygen ions, it seems plausible that the same situation exists in Alon. The influence of impurities on the amount of cation vacancies will also be limited in Alon because the intrinsic defect concentration is already quite high.

If we assume that aluminium vacancies are the transporting species, it is possible to calculate the diffusion coefficient of these vacancies from the Nernst–Einstein relation. If we take for instance the specific resistance of Alon with composition M at 1373 K, a diffusion coefficient of 8×10^{-15} m^2 s^{-1} can be calculated. This diffusion coefficient is of the same order of magnitude as the diffusion coefficient for Mg^{2+} in stoichiometric magnesium aluminate spinel.[17] However, the conductivity shows a more-than-linear dependency on the amount of aluminium vacancies (Fig. 3). A similar phenomenon was observed by Aggarwal and Dieckmann[18] in their investigation of non-stoichiometric cobaltous oxide, in which the mobility of the cationic defects also increased with increasing deviation from stoichiometry. They tentatively attribute this effect to a decrease in the lattice parameter and/or to changes in the type of defects, but at the moment the physics behind this phenomenon are not understood.

Let us assume for a moment that Alon is a semiconductor instead of an ionic conductor. In this case, energies of 2·64, 2·74 and 2·86 eV can be calculated for L, M and R, respectively, using $\sigma = \sigma_s \times \exp(-\Delta H_s/kT)$. The correlation factors remain unchanged. A possible mechanism could be extrinsic electron conduction due to silicon impurities (about 800 ppm) that can act as donors. If we assume complete ionization, the amount of free electrons (n) is equal to the amount of silicon atoms ($n = [Si_{\dot{A}l}] = 6{\cdot}3 \times 10^{25}$ m^{-3}) which gives a mobility (b) of 3×10^{-11} m^{-2} V^{-1} s^{-1} (from $\sigma = n \times e \times b$). Although low values for the electron mobility are known to exist in small polaron semiconductors, this value is so small that it makes electron conduction improbable. Also, the activation energy of 2·8 eV is high for the activation energy of a donor. In comparison, Lee and Kröger reported a value of about 1·7 eV for the activation energy of silicon donors in Al_2O_3.[19] If we take also Fig. 4 into account we conclude that electronic conductivity can be ruled out.

5 Conclusions

AC-conductivity measurements were performed on Alons because of their interesting defect structure. Although it became apparent that Alons are not stable in the temperature range used, the electrical properties of the materials could be measured with impedance spectroscopy using a special procedure. The activation energy for charge transport at temperatures between 1173 and 1373 K was shown to be 2·78, 2·85 and 2·97 eV for compositions L, M and R respectively, while the pre-exponential factors increased with increasing number of aluminium vacancies. The conductivity shows a more-than-linear dependency on the amount of aluminium vacancies. Charge is transported via aluminium vacancies but the large amount of vacancies does not result in greatly changed mobilities: the interesting defect structure of Alon does not lead to extraordinary electrical properties.

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