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Oxidation of aluminium nitride

E. W. OSBORNE*, M. G. NORTON‡
School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA
E-mail: norton@mme.wsu.edu

The oxidation kinetics of polycrystalline aluminium nitride substrates in air at temperatures in the range 1150 to 1750 °C have been studied by measuring the weight increase in the oxidized samples. At the lowest temperature, the oxide layer was not continuous on the AlN surface and the oxidation kinetics followed a linear rate law with an activation energy of 175 kJ mol^{-1}. At all the higher temperatures, the growth kinetics followed a parabolic rate law with an activation energy of 395 kJ mol^{-1}. Samples oxidized at these higher temperatures were covered with a dense oxide layer having a fine-grained microstructure.

1. Introduction

Aluminium nitride (AlN) substrates are of interest for applications in electronic packaging because of several advantageous properties they possess. Aluminium nitride has a high theoretical thermal conductivity, a high electrical resistivity, and a comparable coefficient of thermal expansion to silicon. Some of the physical properties of AlN together with those of aluminium oxide (Al_2O_3) – the most widely used ceramic for electronic packaging – are listed in Table I. In order to exploit the full potential of AlN as a packaging material it is necessary that a compatible metallization system is available [e.g. 1, 2]. Metallization is needed for interconnection of circuit components and, in some cases, for package sealing. Because most conventional metallization systems have been developed for use with oxide ceramics, in particular Al_2O_3, they are often not suitable for use with AlN [3]. However, oxidation of AlN substrates has been shown to lead to improvements in the adhesion of deposited metal layers [4].

Following oxidation of AlN substrates at high temperatures (>900 °C) in air or oxygen the primary oxidation product is α-Al_2O_3 [5] according to the following reaction

$$2AlN + \tfrac{3}{2}O_2 \rightarrow Al_2O_3 + N_2$$

Oxidation at lower temperatures may result in the formation of oxynitride phases [6]. The structure and composition of such phases, if they are indeed formed, has not been determined.

Several groups have studied the oxidation behaviour of AlN, both in powder form and as consolidated substrates [5–12]. Among those studies which examined the kinetics of the oxidation process [6–9, 12] there is some disagreement about the type of rate law which governs the process. For example, Robinson and Dieckmann found that in the temperature range 1000–1300 °C the oxidation process of AlN substrates, sintered using an yttrium oxide phase, follows a linear rate law [8]. This implies that the rate-controlling step is an interfacial reaction; most likely the reaction occurring at the AlN surface. The observation of a linear rate law also implies that the oxide layer formed on the AlN surface is not protective. Bellosi and coworkers [9] reported that the oxidation kinetics of sintered AlN substrates depends on the type of sintering aid that is used in substrate fabrication. Using Y_2O_3 as the sintering aid it was reported that in the temperature range 1100–1400 °C the oxidation kinetics follow a linear rate law. However, oxidation of AlN substrates prepared using CaC_2 as the sintering aid was found to follow a linear rate law in the temperature range 1100–1200 °C and then a parabolic rate law at temperatures above 1250 °C. Sato and coworkers [7] found that at a temperature of 1250 °C the oxidation kinetics of hot-pressed AlN, without additives, also follow a parabolic rate law. This implies that the rate-controlling step in the oxidation of AlN is the diffusion of the oxidizing species through a protective oxide layer.

One of the problems encountered when comparing studies performed using different AlN substrates is that the chemistry and microstructure of the substrates are often very different. These differences arise, in part, because different sintering aids (and different amounts of sintering aid) are used in an effort to obtain a fully dense substrate material. Furthermore, different fabrication routes are often followed. In many cases these processes are of a proprietary nature and therefore it is difficult to obtain specific details about the process.

The calculated activation energies also vary from study to study. For AlN substrates sintered using a second phase the values of the activation energy for a linear oxidation process are typically around

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* *Present address*: Advanced Silicon Materials, Inc., Butte, MT 59701-3466, USA.
‡ Corresponding author: norton@mme.wsu.edu.

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TABLE I Comparison of some of the properties of AlN and Al_2O_3

	Density ($g\,cm^{-3}$)	Modulus of elasticity (GPa)	Resistivity (Ω-cm)	Thermal conductivity (W (m-K))	Coefficient of thermal expansion ($(^\circ C)^{-1}$)	Melting point (°C)
Al_2O_3	3.97	393	$> 10^{14}$	30	8.8×10^6	2050
AlN	3.10	300	10^{11}–10^{13}	320	4.5×10^6	2150

350 kJ mol^{-1} [8, 9]. When the AlN is densified without additives, the activation energy for a linear oxidation process has been determined to be about 250 kJ mol^{-1} [7, 9]. For powders, activation energies for a linear oxidation process are approximately 170 kJ mol^{-1} [6, 12]. For a linear rate law the chemical reaction occurring at the AlN surface is the rate-controlling step and it would be expected that this reaction should be independent of the form of the AlN, i.e. whether it is a consolidated substrate or a powder. The activation energy should depend only on the type of oxidizing species and on the surface of the AlN grains, for example the surface orientation and whether there is any contamination on the surface. The variation in the values given above probably reflects variations in the purity of the AlN (all the cited studies used air as the oxidizing environment). The AlN powders used by Katnani and Papathomas had a reported impurity concentration of <250 p.p.m. For AlN substrates densified with the use of sintering aids the impurity concentrations will be significantly higher. For example, the sintered AlN substrates used by Bellosi and co-workers contained at least 2 wt % of intentionally introduced impurities. If a large amount of these impurities are on the surface of the substrates then they would be expected to affect the oxidation kinetics.

When the growth of the oxide layer follows a parabolic rate law the reported activation energies from studies using powders agree very well; Suryanarayana [12] reports a value of 297 kJ mol^{-1} and Katnani and Papathomas [6] report a value of 234 kJ mol^{-1}. In the case of the oxidation of a consolidated ceramic substrate via a parabolic growth process, Bellosi and co-workers report a value for the activation energy of only 160 kJ mol^{-1}. (This value appears to be inconsistent with the other data in their paper. For example, they reported that the activation energy for the linear rate process is higher than that for the parabolic case.) When the oxidation process follows a parabolic rate law the rate-controlling step is diffusion of the oxidizing species through the oxide layer (sometimes called a protective oxide) to the reacting surface. For this type of process, values of the activation energy would be expected to vary from study to study because the diffusion rate depends on the microstructure of the oxide layer. Defects in the oxide layer such as grain boundaries, pores, and impurities will all affect the diffusion rate.

In this present study, the oxidation of sintered AlN substrates in air has been examined and the reaction kinetics determined. The substrates have a purity, as reported by the vendor, of $>99.5\%$. Earlier, the major impurities were determined, by X-ray diffraction, to be the yttrium aluminium oxide phases $Al_5Y_3O_{12}$ and $AlYO_3$ which are formed during the liquid-phase sintering process [5]. These phases are located primarily at triple points in the AlN microstructure [13].

2. Experimental procedure

The AlN substrates used in this study were obtained from Tokuyama Soda Co., Ltd. in Japan and have the trade name "Shapal". The stock substrates were in the form of sheets with dimensions $5 \times 5 \times 0.1$ cm. The sheets were diced, simply by scribing with a diamond-tipped scriber and snapping, into smaller pieces having approximate dimensions $1.2 \times 1.2 \times 0.1$ cm.

Oxidation was performed in air in a box furnace at temperatures between 1150 and 1750 °C for times up to 10 h. The times reported in this paper refer to the dwell time at peak temperature. Each AlN sample was weighed, prior to oxidation, using an analytical balance. The samples were reweighed after oxidation and the change in weight calculated.

Some of the samples were examined, after oxidation, using a Jeol JSM 6400 scanning electron microscope (SEM) operated at 25 kV. Sputter-coating of the insulating ceramic pieces with a thin layer of Pt–Au was necessary prior to examination in the SEM to avoid charging under the electron beam.

3. Results and discussion

Fig. 1 is a plot of the normalized weight change, W, of the substrate versus time, t, for AlN substrates oxidized for time up to 4 h. The weight change was divided by the surface area of the sample because the samples were not all of an equivalent size and this normalization takes into account any variations in the surface area from sample to sample.

At the lowest temperature investigated in this study, 1150 °C, the rate of the weight increase was linear with time. At temperatures $\geqslant 1350$ °C the normalized weight increase was no longer linear with time. At these higher temperatures the rate of weight increase was initially rapid then with increasing times the rate of increase became less. At 1750 °C this trend is very apparent with no measurable increase in weight occurring between samples oxidized for 2 and 4 h. In order to determine the reproducibility of the weight gain measurements several samples were run through equivalent heating cycles. The uncertainty in the measurements caused by errors associated with the balance and fluctuations in the heating cycle of the furnace was estimated to be $\pm 12\%$.

Because the results obtained at the higher temperatures suggest that the oxidation kinetics follow a parabolic rate law the square of the normalized weight change, W^2, was plotted against time as shown in Fig. 2. From Fig. 2 it can be seen clearly that for oxidation at temperatures 1350 and 1500 °C the plot of W^2 versus t is linear; confirming a parabolic rate law. At the highest temperature used in this study, 1750 °C, the plot of W^2 versus t is linear for times $\leqslant 2$ h but becomes non-linear for times > 2 h. A similar type of behaviour was observed by Katnani and Papathomas during oxidation of AlN powders [6]. It was suggested that as the oxide layer thickens the change in the surface area of the sample becomes significant and thus the weight gain becomes a non-linear function of thickness and consequently of time. Such an explanation may also be applicable to the results obtained in this present study.

The morphology of the oxide layer was examined using an SEM. The as-received substrates consisted of well-defined highly faceted grains having an average diameter of about 3 μm as shown in Fig. 3. Following oxidation at 1150 °C for 10 h the appearance of the substrate surface has changed as shown in Fig. 4(a). The AlN grains are partially covered with a thin oxide layer. The oxide coating does not appear to be continuous under these oxidation conditions and the underlying AlN grain structure is still clearly evident.

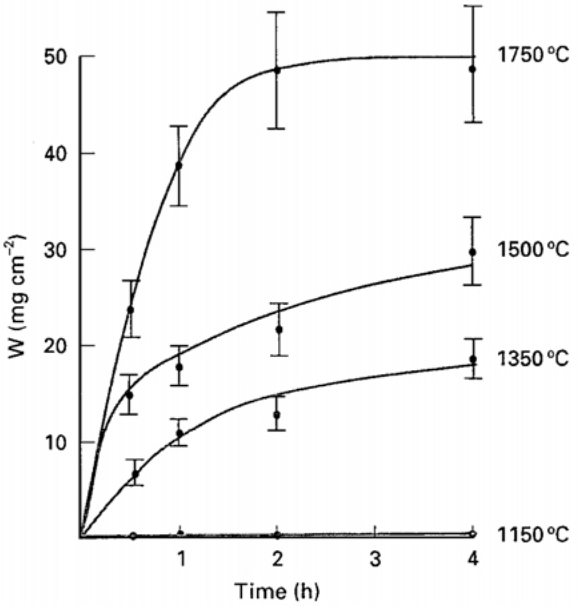

Figure 1 Comparison of normalized weight increase, W, as a function of time, t, for samples oxidized at 1150, 1350, 1500, and 1750 °C.

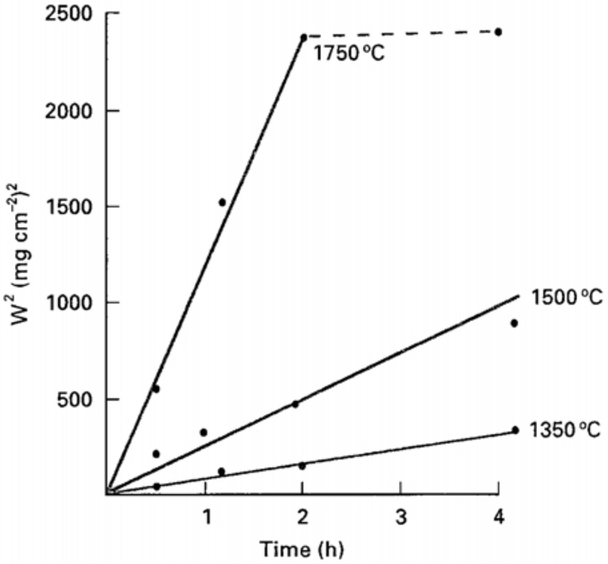

Figure 2 Square of the normalized weight increase, W^2, as a function of time, t, for samples oxidized at 1150, 1350, 1500, and 1750 °C.

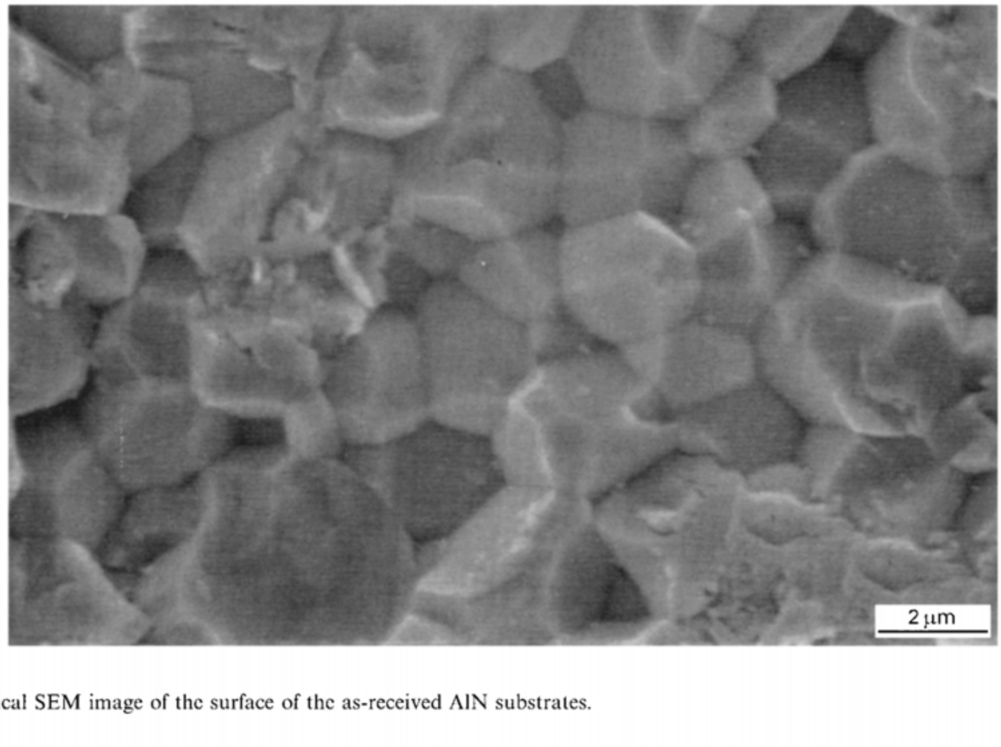

Figure 3 Typical SEM image of the surface of the as-received AlN substrates.

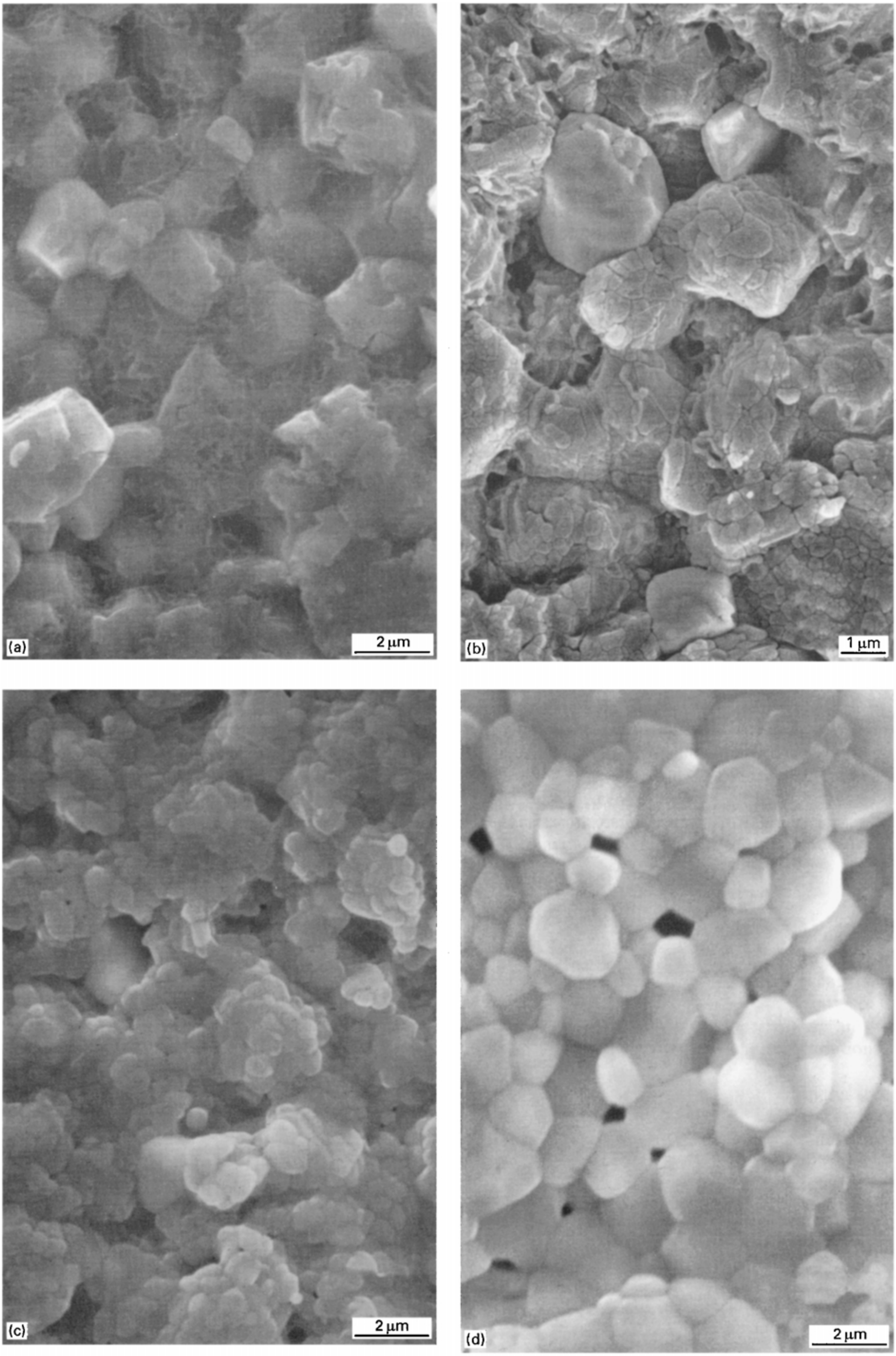

Figure 4 Montage of SEM images showing the change in the surface morphology of AlN substrates oxidized at different temperatures: (a) 1150 °C, (b) 1350 °C, (c) 1500 °C, and (d) 1750 °C.

This observation would be consistent with the linear rate law suggested by the results shown in Fig. 1. The oxidizing species can react directly with the AlN surface and this reaction is the rate-controlling step.

Oxidation at 1350 °C for 10 h produces a much more continuous coating over each of the AlN grains as shown in Fig. 4(b). The morphology of the underlying AlN grain structure is still apparent even though the grains themselves cannot be seen. The grain size of the oxide coating is $\leqslant 0.5\ \mu m$ – considerably smaller than the size of the AlN grains. As the oxide layer thickens it is necessary for the oxidizing species to diffuse through this layer prior to reacting with the nitride surface. Diffusion through the oxide layer now becomes the rate-controlling step and the oxidation kinetics follow a parabolic rate law as suggested by the results in Fig. 2.

Following oxidation of the sintered AlN samples at 1500 °C the underlying AlN is not discernible at all and a fine-grained oxide layer with a considerably uneven surface was obtained as shown in Fig. 4(c) for a sample oxidized for 3 h. Despite some degree of coarsening the majority of the oxide grains are still submicron in size. The oxide layer formed on samples oxidized at 1750 °C shows considerable evidence of coarsening with grains having diameters between 1 and 2 μm as shown in Fig. 4(d). The oxide layer appears fairly compact although there is still some porosity evident in the layer.

Very little evidence was found for cracking of the oxide layer. Some of the samples which were oxidized at the higher temperatures used in this study cracked parallel to the substrate surface. Cracking may well have occurred because of the large differences in coefficient thermal expansion of the two materials (Table I). Examination of the fracture surfaces, shown in Fig. 5(a) and (b), indicate that intergranular fracture occurred within the AlN substrate and failure did not occur at the oxide/nitride interface. This observation would suggest that the bonding at this interface is quite strong.

Fig. 6(a) shows an SEM image of the interface between the oxide layer and the AlN substrate. The region between the fine-grained oxide and the relatively coarse-grained substrate is readily discernible. At higher magnification, Fig. 6(b), the fine grains in the oxide layer and the tortuous arrangement of grain boundaries can be seen more clearly. From this image it is possible to imagine why fracture occurs preferentially within the AlN and not at the oxide/nitride interface. A crack propagated at this interface would have to transverse a much longer distance to produce failure of the sample than an intergranular crack in the coarse-grained AlN.

From the data presented in Figs 1 and 2 it is possible to calculate the activation energies for the two types of oxidation behaviour. For a linear oxidation process the change in thickness, x,

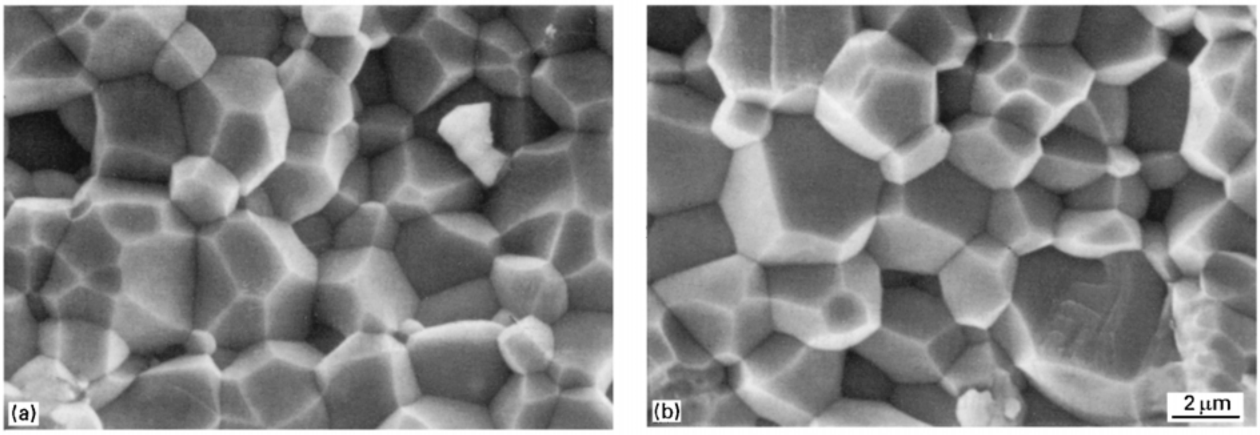

Figure 5 Fracture surfaces (a) top and (b) bottom of an oxidized AlN substrate.

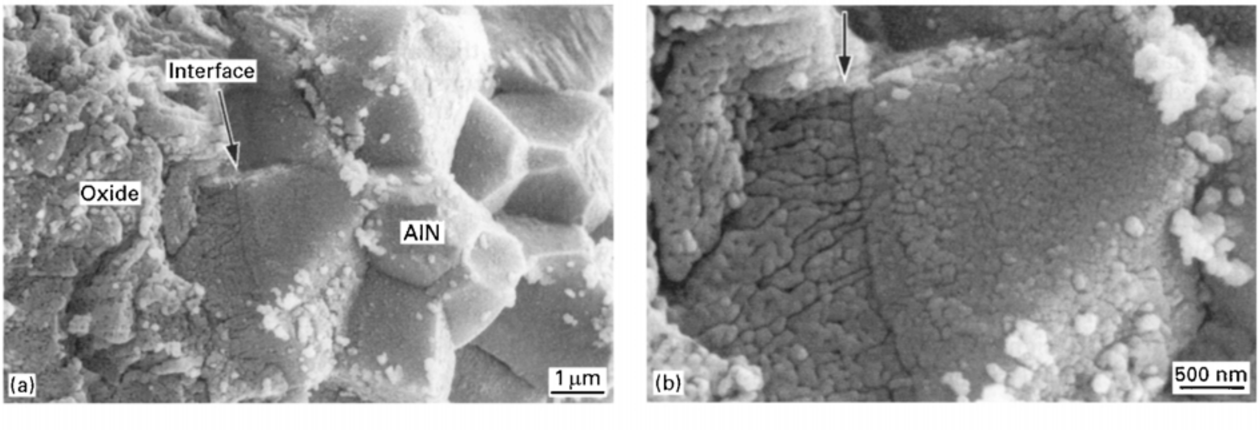

Figure 6 (a) Cross-section SEM image showing the interface between the AlN and the oxide layer. (b) A higher magnification image of the interface region; the arrow represents the position of the interface with the oxide layer on the left-hand side of the image.

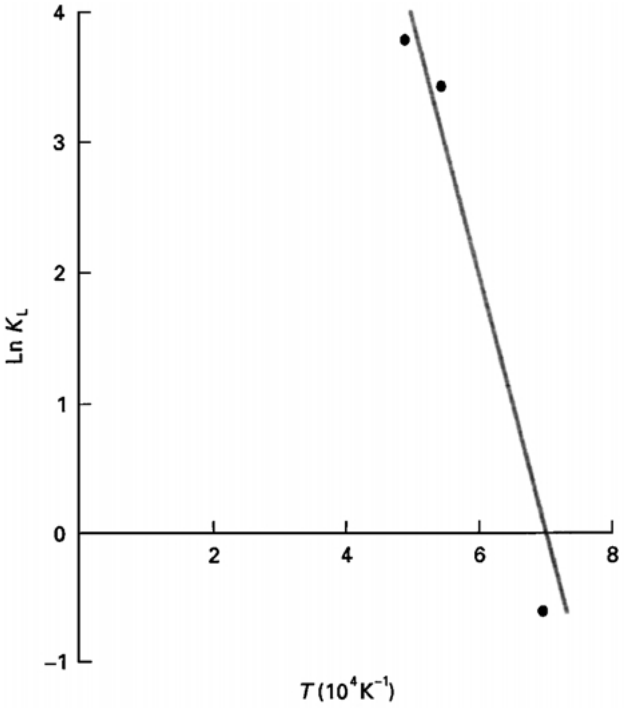

Figure 7 Arrhenius plot used to determine the activation energy for the linear rate law.

which is proportional, in this case, to the normalized change in weight, W, is given by

$$W \propto x = k_L t \tag{1}$$

where k_L is the linear rate constant. The oxidation rate follows Arrhenius's law, thus k_L increases exponentially with temperature

$$k_L = C \exp\left(\frac{-E_L}{RT}\right) \tag{2}$$

where C is a temperature-independent constant, R is the gas constant, and E_L is the activation energy. So a plot of $\ln k_L$ versus $1/T$ will give a straight line of slope $-E_L/R$. Fig. 7 shows an Arrhenius plot for the linear regions of the oxidation curves in Fig. 1. From the slope of the plot in Fig. 7 the activation energy for the linear rate law was calculated to be 175 kJ mol^{-1}. This result agrees well with those reported for the oxidation of AlN powders by Katnani and Papathomas [6] and Suryanarayana [12], but is somewhat lower than that reported in other studies using consolidated AlN. Once again comparisons are difficult because the exact nature of the substrate preparation is often not known. However, the substrates used in this present study are extremely pure and the second phase is located almost exclusively at triple points and so would not be expected to influence the oxidation kinetics to any appreciable extent. The substrates used by Bellosi and co-workers, for example, may well have had a significant amount of impurities, caused by the added sintering aids, on the surface which could account for the much higher activation energy that they reported for the linear oxidation process [9].

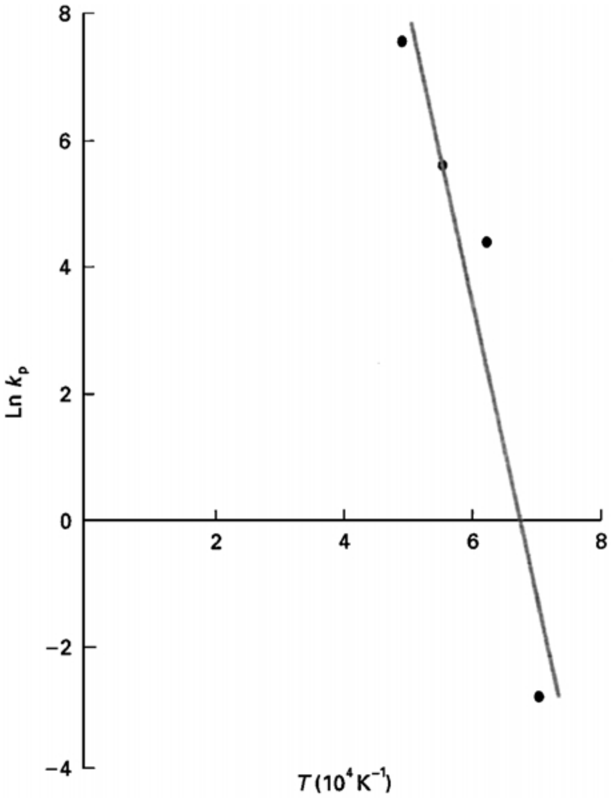

Figure 8 Arrhenius plot used to determine the activation energy for the parabolic rate law.

When the growth kinetics follow a parabolic rate law the oxidizing species have to diffuse through an ever thickening oxide layer. The flux, J, of diffusing species is given by Fick's first law

$$J = -D\frac{dc}{dx} \tag{3}$$

where D is the diffusion coefficient and dc/dx is the concetration gradient of the oxidizing species. The flux is proportional to the rate of growth of the oxide layer, dx/dt, which it will be assumed is equal to the rate of the weight increase dW/dt

$$\frac{dW}{dt} \propto D\left(\frac{c}{x}\right) \tag{4}$$

Integrating Equation 4 with respect to time gives

$$W^2 = k_p t \tag{5}$$

where k_p is the parabolic rate constant which, like the linear rate constant, varies exponentially with temperature

$$k_p = C' \exp\left(\frac{-E_p}{RT}\right) \tag{6}$$

where C' is a temperature-independent constant and E_p is the activation energy. A plot of ln k_p versus $1/T$ for the linear portion of the data plotted in Fig. 2 is shown in Fig. 8. From the slope of this line the activation energy for the parabolic rate law was calculated to be 395 kJ mol^{-1}.

The value reported in this paper for the activation energy for the parabolic growth process is higher than corresponding values reported for the oxidation of AlN powders; where values of 234 kJ mol^{-1} [6] and 297 kJ mol^{-1} [12] have been obtained. The differences may well be a result of differences in the microstructure (density, grain size, etc.) of the oxide layer. In the results reported in this present study the oxide layer appears to be dense with a very fine grain size. In the two cited studies using AlN powders the microstructure of the oxide layer was not reported. The observed activation energy of 395 kJ mol^{-1} is within the range of values reported for oxygen diffusion in polycrystalline Al_2O_3 [14–16]. The range of values reflect the fact that the measurements are influenced by extrinsic parameters such as the presence of impurities and grain boundary diffusion, which is also the situation for the present oxidation investigation.

4. Conclusions

The oxidation of polycrystalline AlN substrates at high temperatures follows two types of rate processes. At the lowest temperature investigated in this study, 1150 °C, the oxidation was found to follow a linear rate law with an activation energy of 175 kJ mol^{-1}. This value is consistent with similar data for the oxidation of high-purity AlN powders. At higher temperatures, when the oxide layer thickens, the growth kinetics follow a parabolic rate law with an activation energy of 395 kJ mol^{-1}. This value agrees very well with the activation energy calculated for oxygen diffusion in polycrystalline Al_2O_3.

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