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Oxidation of an Al_2O_3–γAlON ceramic composite

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The oxidation of dispersed aluminium oxynitride particles in an alumina matrix has been studied. The kinetics law of this reaction is linear and the activation energy is 420 ± 40 kJ mol^{-1} (100 ± 10 kcal mol^{-1}). A γ'-alumina layer is formed and leads to α-alumina above 1200° C. The γ'-alumina formation produces surface compressive stresses, and thus the mechanical properties (σ_f, HV) are improved. We have proved that the formation of γ'-alumina in the Al_2O_3–AlON composite can lead to the best properties for this ceramic. A γ'-alumina layer has a very interesting effect on the wear resistance of this material.

1. Introduction

The dispersion of γ-aluminium oxynitride (γ-AlON) particles in an alumina matrix leads to a new material with interesting properties [1–3]. Its behaviour at high temperature is better than that of alumina. Our purpose is to determine its oxidation mechanism up to 1550° C.

The AlON oxidation follows very specific phenomena [4–7]. In an oxygen atmosphere, above 1200°C, AlON is oxidized into α-alumina. Under this temperature, AlON is completely oxidized but some nitrogen is trapped in the spinel structure; this new phase is called γ'-alumina and is made of two phases: γ-alumina and γ-alumina containing atomic nitrogen [6].

In this study we examine the consequences of the γ'-alumina formation on both the kinetics of oxidation and the mechanical behaviour of alumina–aluminium oxynitride ceramics.

2. Experiments

The samples were prepared by hot-pressing Al_2O_3–AlN mixtures (Al_2O_3 A6Z Criceram, France; AlN, S. Starck, West Germany). Reaction sintering (T = 1800° C) produces an alumina ceramic composite containing 15, 20 and 30 vol % AlON with a porosity smaller than 1%. The specimens were cut into cubes in order to use the cubic symmetry for the kinetics study. All the samples were polished down to 3 μm diamond paste. Their microstructures are presented in Fig. 1.

The oxidation kinetics has been followed by thermogravimetric analysis (NETZSCH STA 429) in a pure oxygen atmosphere in the temperature range 1000 to 1550° C. The pellets were maintained in an argon atmosphere up to the chosen soaking temperature. After treatment, X-ray analysis and ceramographies (SEM) were performed.

The influence of oxidation on mechanical properties was investigated by three-point bending tests on specimens (18 × 4 × 3 mm^3) machined from hot-pressed samples. All the tests were performed with a cross-head speed of 0.1 mm min^{-1}. Hardness was measured on both sample surfaces and on cut and polished samples.

3. Results of thermogravimetric analysis

3.1. Determination of AlON contents

The complete oxidation (T = 1500° C) of a ground Al_2O_3–30 vol % AlON composite into α-Al_2O_3 allows the determination of the γ-AlON formula; $Al_{2.81}O_{3.55}N_{0.45}$.

3.2. X-ray diffraction analysis

The results are similar to those obtained with γ-AlON powder [4–6]. Below 1150° C, oxidation leads to the γ'-alumina spinel phase the parameters of which are very similar to that of AlON; in the temperature range 1150 to 1250° C, the θ- and δ-alumina phases appear, while α-alumina is observed above 1200° C.

3.3. Surface aspect

The aspect of the sample surfaces depends on the oxidation temperature: at 1050° C, the cubes loose their brightness. At 1130° C they are covered by a very thin white film and are completely white above 1250° C. Some cracks appear on some sample edges after oxidation.

3.4. Thermogravimetric analysis

Temperatures of 1050, 1130 and 1250° C were investigated initially. The mass variations were very low for 1050 and 1130° C and not uniform for 1250° C, so no model was considered.

Reaction kinetics were studied in the temperature range 1365 to 1550° C by measuring samples weight increase (Δm): Δm was used to determine the degree of reaction (α), by using $\alpha = \Delta m/\Delta m_\infty$, for the reaction γ-AlON + oxygen → α-alumina + nitrogen (Fig. 2).

3.5. Kinetics mechanisms

We have applied different kinetics laws using cubic symmetry. Oxidation can be represented by the classic linear equation

$$G(\alpha) = 1 - (1 - \alpha)^{1/3}$$
$$= kt \qquad \text{(up to } \alpha \approx 0.3)$$

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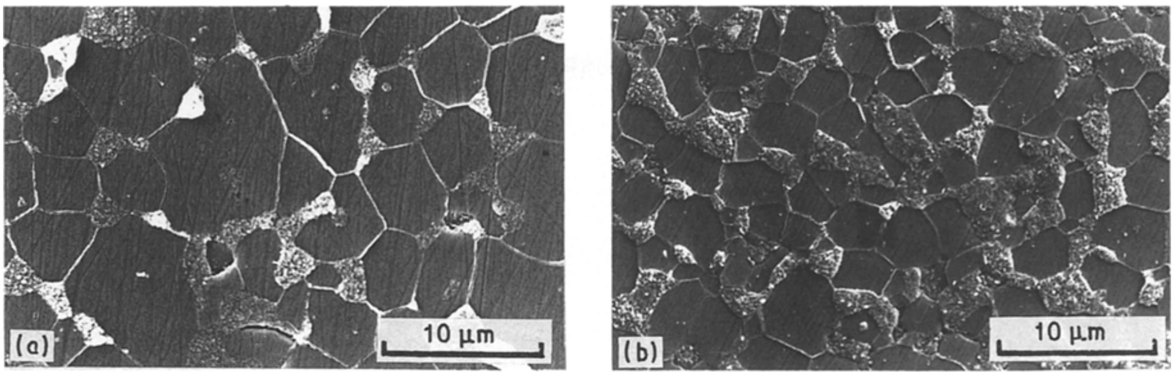


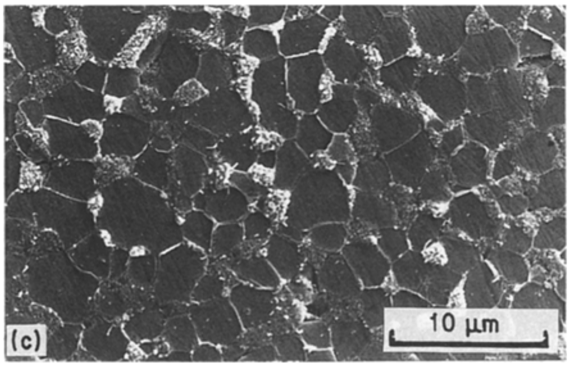


Figure 1 Microstructures (SEM) of the studied composites. (a) Al_2O_3–15 vol % AlON; (b) Al_2O_3–20 vol % AlON; (c) Al_2O_3–30 vol % AlON.

The curves $G(\alpha)$ against time plotted in Fig. 3 are linear for small reaction degrees. For each composition, the linear constant k obeys the Arrhenius law and the calculated values of the activation energies are, respectively (Fig. 4),

$$E_{15\%\,\text{AlON}} = 440 \pm 55\,\text{kJ}\,\text{mol}^{-1}$$
$$(105 \pm 13\,\text{kcal}\,\text{mol}^{-1})$$
$$E_{20\%\,\text{AlON}} = 460 \pm 40\,\text{kJ}\,\text{mol}^{-1}$$
$$(110 \pm 10\,\text{kcal}\,\text{mol}^{-1})$$
$$E_{30\%\,\text{AlON}} = 420 \pm 80\,\text{kJ}\,\text{mol}^{-1}$$
$$(101 \pm 20\,\text{kcal}\,\text{mol}^{-1})$$

In the third case, the standard-deviation is twice as large as for 15 or 20 vol % AlON. So the γ' alumina content is more important and we have a multilayer system which explains the non-linear plot of the Arrhenius law in the case of 30% AlON (Fig. 4).

The activation energy is different from that of the Al–N bond ($230\,\text{kJ}\,\text{mol}^{-1}$) [8] but can be compared with that of γ'-alumina decomposition ($420\,\text{kJ}\,\text{mol}^{-1}$) [6]. Under these conditions the oxidation should progress in the matrix by an intermediate layer of

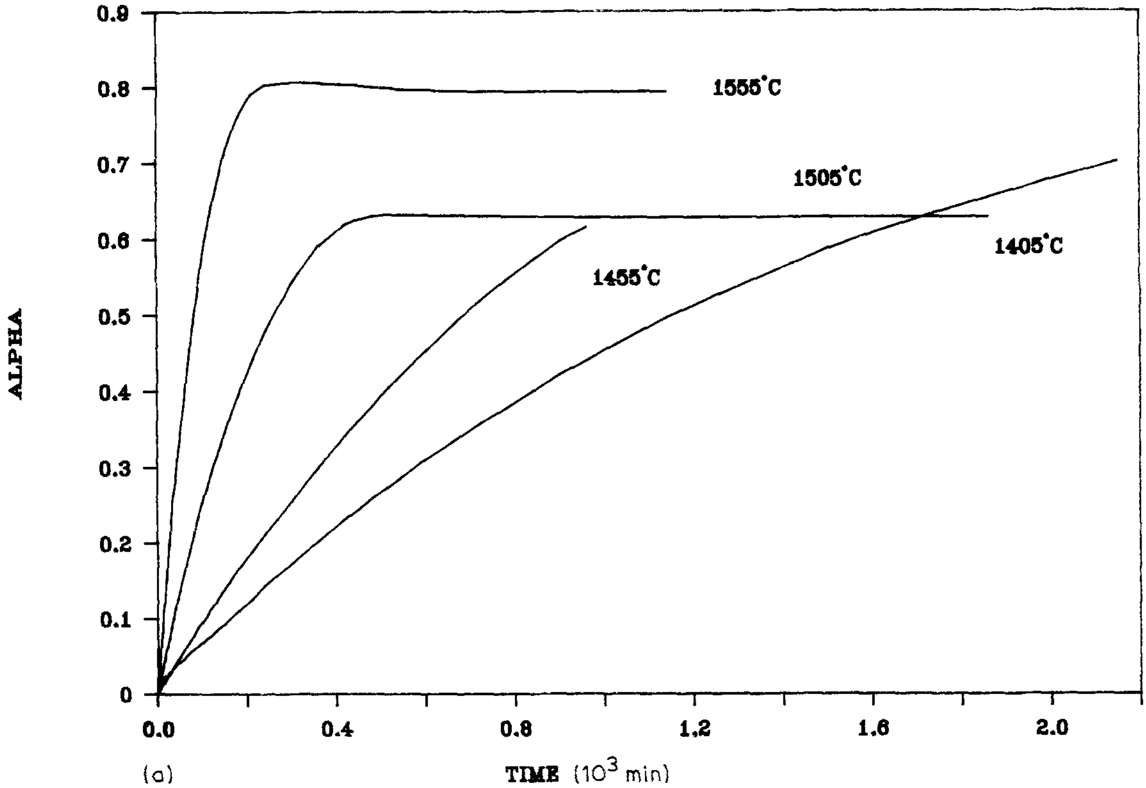
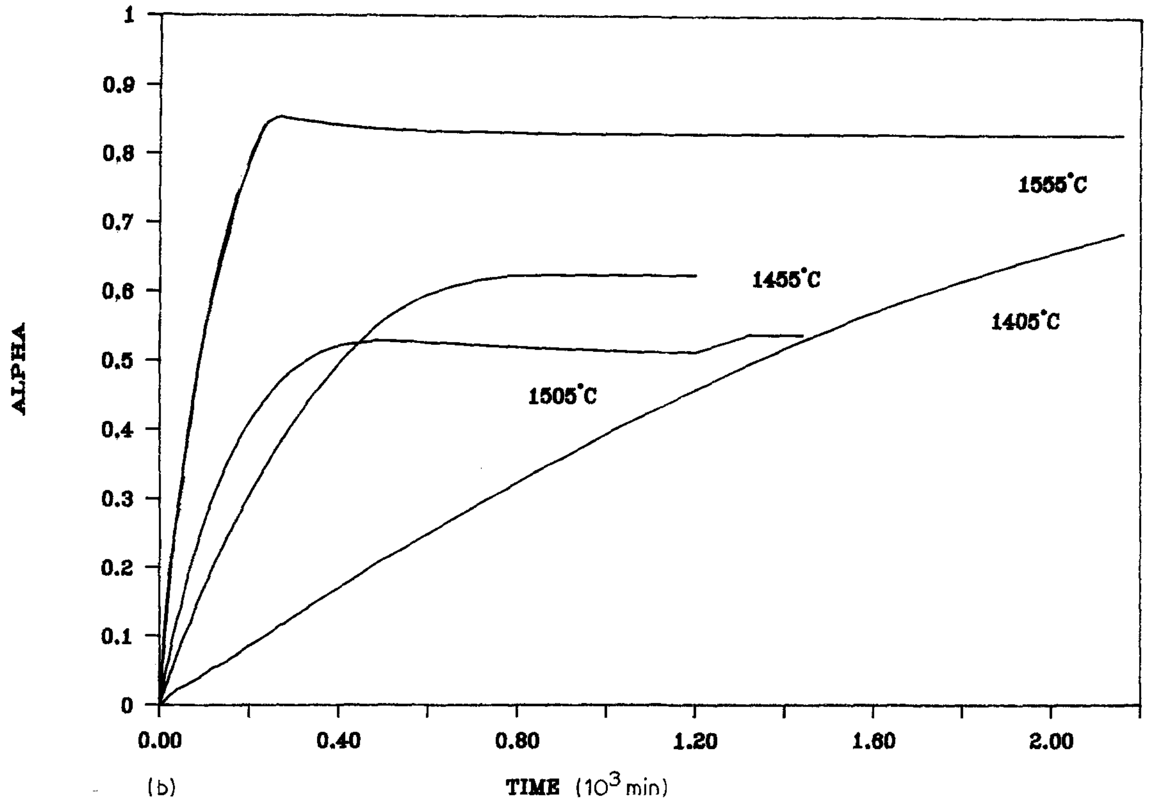


Figure 2 Reaction degree plotted against time for (a) Al_2O_3–15 vol % AlON, (b) Al_2O_3–20 vol % AlON, (c) Al_2O_3–30 vol % AlON.



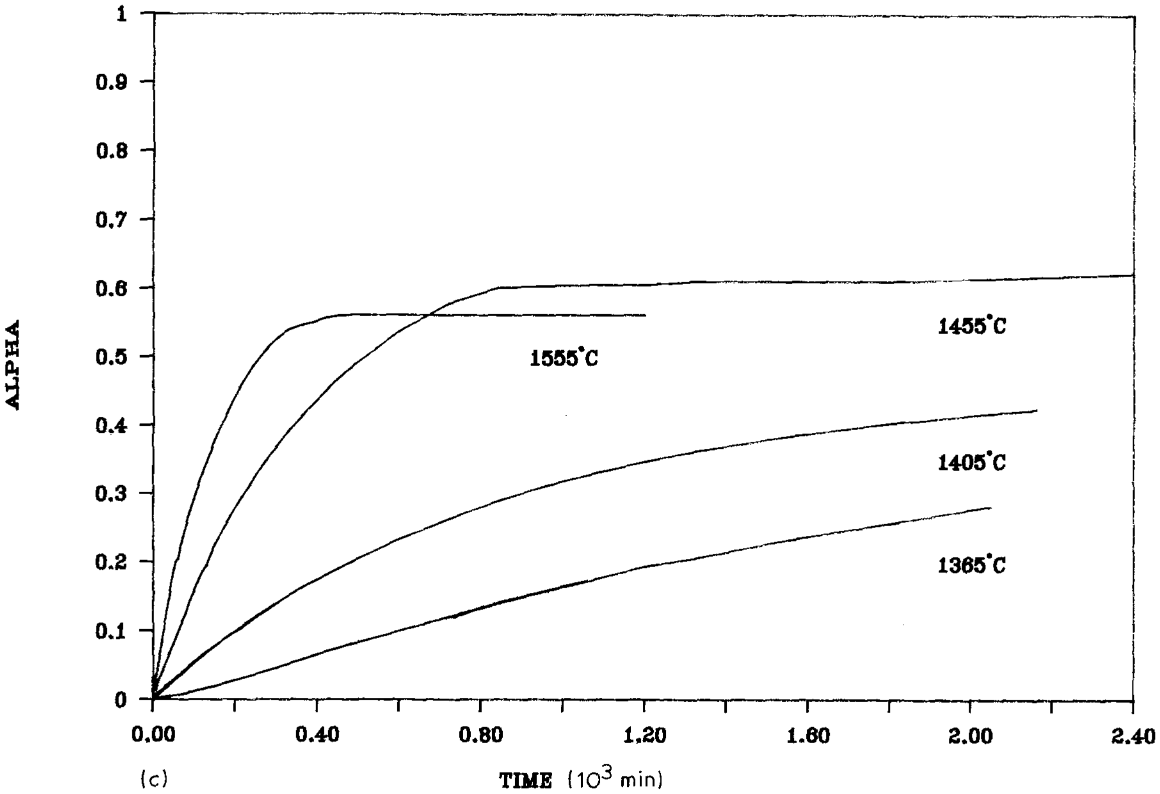


Figure 2 Continued

γ'-alumina. After the Al–N bond is broken, oxygen should not occupy all the anionic positions and some atomic nitrogen could stay in a spinel structure that changes into α-alumina above 1200° C. So the linear kinetics law should follow a macroscopic linear rule. It is necessary to work with a plane symmetry in order to avoid crack formation at the cube edges. For this reason plates were machined as thin as possible ($15 \times 8 \times 1\,\mathrm{mm}^3$) from Al_2O_3–30 vol % AlON samples; we consider they are a good approximation for the plane symmetry.

The curves of α (degree of reaction) against time plotted in Fig. 5 are linear only up to $\alpha = 0.35$, due to the sample thickness. The linear constant, k, obeys the Arrhenius law and the calculated value of activation energy is $380 \pm 50\,\mathrm{kJ\,mol^{-1}}$ ($90 \pm 12\,\mathrm{kcal\,mol^{-1}}$) (Fig. 6).

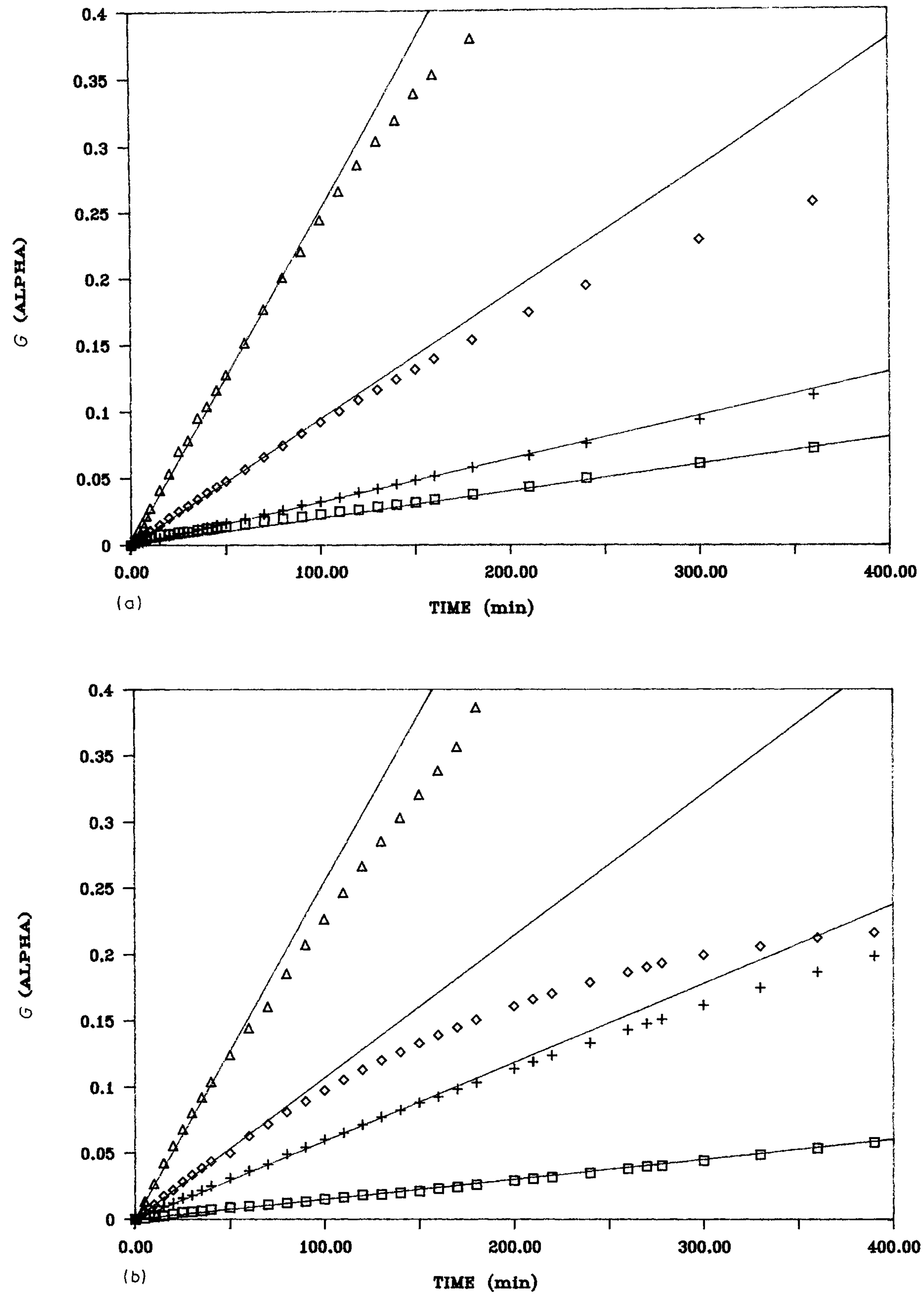


Figure 3 Transformed curves (cubic symmetry) showing the reaction kinetics for (a) Al_2O_3–15 vol % AlON, (b) Al_2O_3–20 vol % AlON, (c) Al_2O_3–30 vol % AlON at (□) 1405° C, (+) 1455° C, (◇) 1505° C, (△) 1555° C.

4. Discussion

In our system the evolution of the weight with time for different temperatures was followed; thus all the phenomena due to the interaction of γ-AlON and oxygen were studied. The degree of reaction is the result of all the reactions (the final product is α-alumina).

For powders, the lifetime of γ'-alumina is very short in the studied range of temperatures and does not affect the weight variation in a first approximation. In the case of Al_2O_3–γ-AlON composite, the γ'-alumina is a transitory phase more stable than in powders (we can offer no explanation for this).

For both plane or cubic symmetries we observe a kinetics law of reaction with an activation energy of about $420\,kJ\,mol^{-1}$ up to $\alpha = 0.3$. This energy

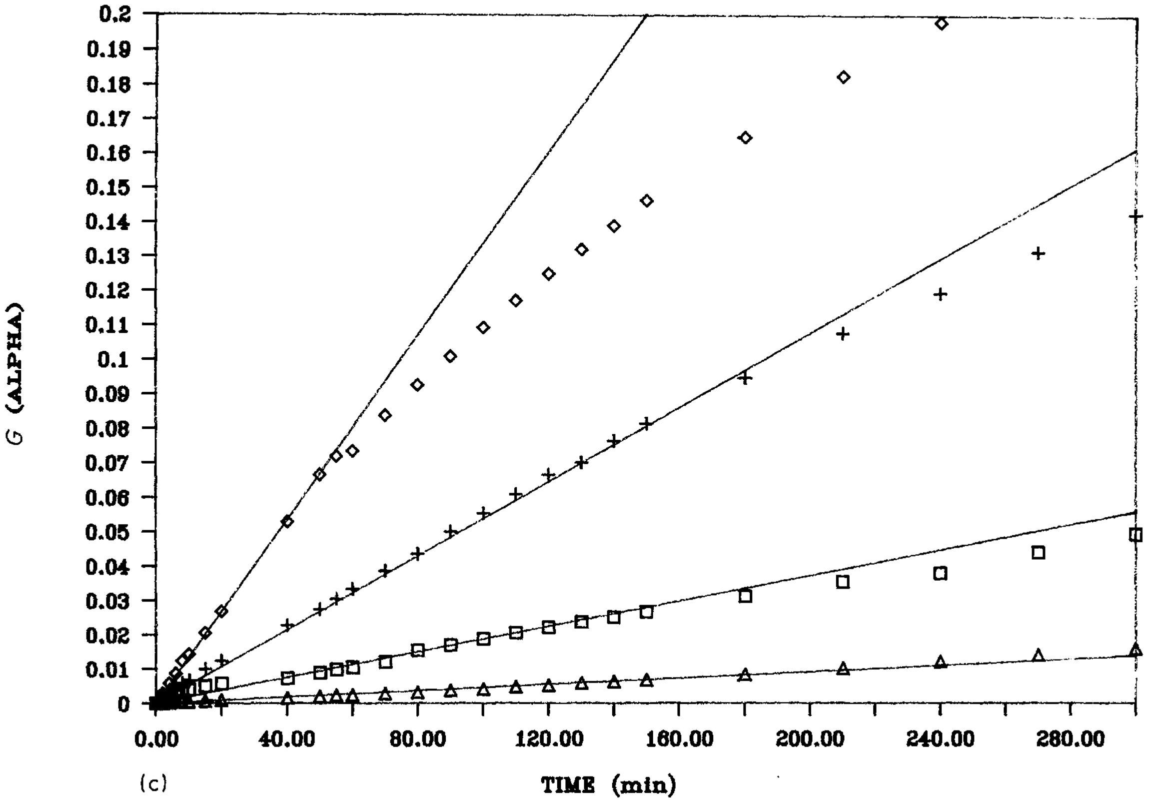


Figure 3 Continued

corresponds to the γ'-alumina decomposition. Under these conditions, oxygen progresses rapidly into the matrix (γ'-Al_2O_3/γ-AlON interface), while the advance of the γ'-Al_2O_3/α-Al_2O_3 interface is the limiting-step phenomenon. A microstructural study shows that the α-alumina upper layer is porous; this agrees with the expansion coefficient value ($\Delta < 1$) and then the reaction kinetics law is observed.

It can be noticed that the γ-AlON phase is metastable in the temperature range 1500 to 1600° C. However, its decomposition in Al_2O_3 + AlN is negligible during the initial steps of the reaction, for which kinetics laws were determined.

5. Mechanical properties of oxidized samples

Two ranges of temperatures, where the oxidation gave two different phases, were determined. Under 1200° C the γ'-alumina phase is stable and the expansion coefficient is greater than one; above 1200° C the γ'-alumina phase is not stable and changes into α-alumina with an expansion coefficient lower than one. On the one hand, it is expected that compressive stresses could increase the mechanical properties of the Al_2O_3–AlON composite oxidized within the temperature range 1050 to 1200° C. On the other hand, the porosity in the material oxidized above 1200° C should lead to a poor mechanical behaviour.

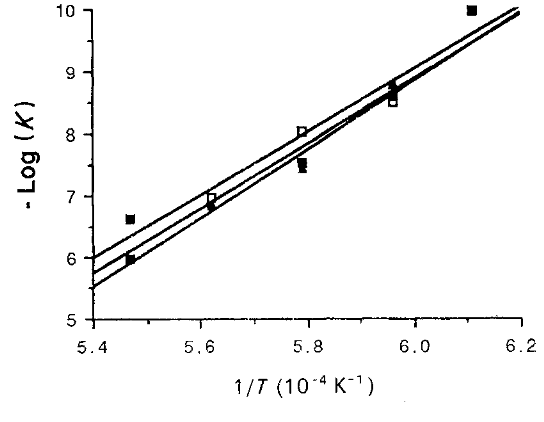


Figure 4 Determination of activation energy (cubic symmetry); (□) 15% AlON, (▲) 20% AlON, (■) 30% AlON.

Vickers hardness (50 N) and flexural strength (three-point) have been measured for an α-alumina–30 vol % AlON composite oxidized for 3 d at different temperatures (Fig. 7).

At 1050° C we observed a strengthening (+40%) effect due to the γ'-alumina formation. At 1130° C, the evolution of the γ part of the γ'-alumina to δ and θ aluminas ($\Delta V < 0$) compensates the compressive stresses due to γ'-alumina; so mechanical properties are similar to the non-oxidized material. Above 1200° C, α-alumina is formed which is porous (Fig. 8), then the mechanical properties decrease. A treatment at 1050° C for just 1 day has no effect on the composite resistance; but 3 days are necessary to observe the strengthening (Fig. 9).

To determine the reasons for this improvement in mechanical behaviour several samples were oxidized at 1050° C for 6 days. Then half of them were treated in an argon atmosphere at 1350° C. Oxidized and non-treated samples attained a bending strength of 760 ± 60 MPa, while the treated samples attained only 550 ± 50 MPa. During the post-treatment, γ'-alumina changed into the α-alumina phase without modification of the oxidized layer thickness. Thus compressive stresses are due to the γ'-alumina formation.

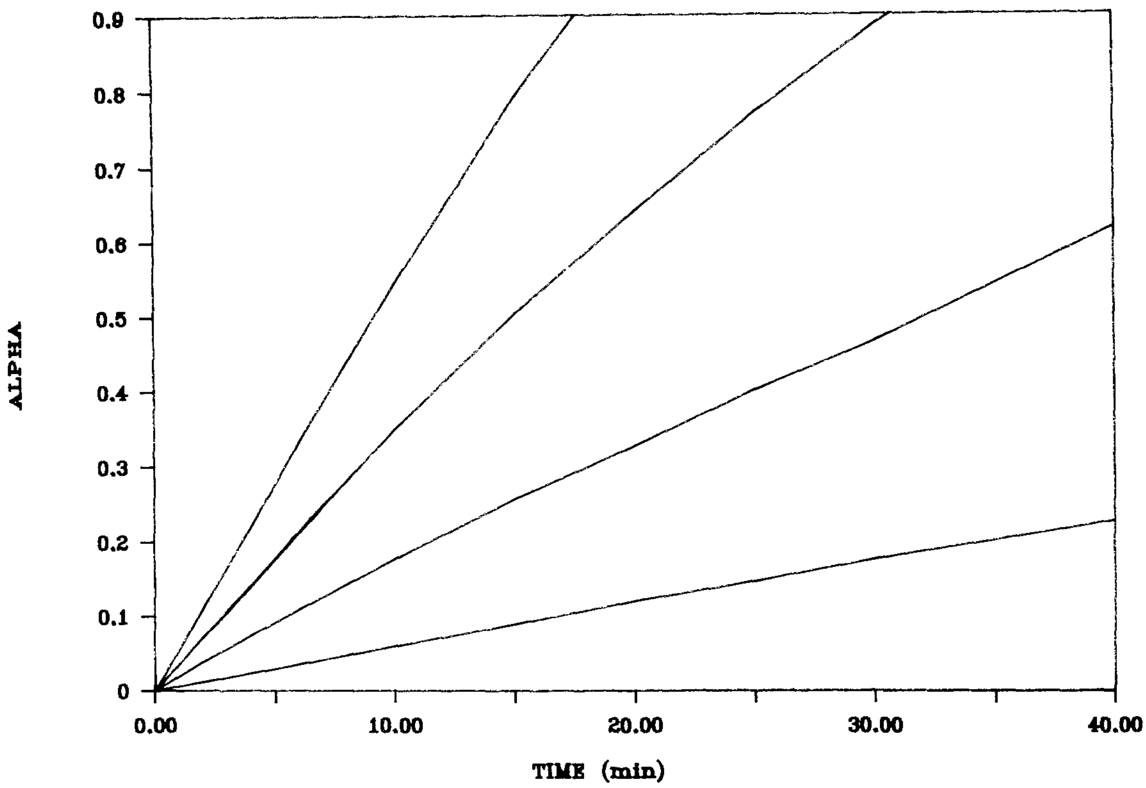


Figure 5 Reaction degree plotted against time (plane symmetry) for the Al_2O_3-30 vol % AlON composite.

6. Wear resistance

The wear resistance of the samples oxidized at 1050° C for 3 days has been investigated. The roughness (R_a) which was 0.03 μm, increases to 0.14 μm after oxidation. Some frictional experiments were run in water on a tribometer consisting of a cylinder rotating against a fixed plane. The cylindrical ring (diameter 35 mm) in 100.C6 steel quenched and annealed (64 HRC) was rubbed off before each experiment against a pure alumina reference. A 700 N load had to be applied to detect some wear. The sliding speed was about 0.36 m sec^{-1} for 30 to 120 min. During each test, the frictional stress was recorded. After the run, the wear traces were examined by optical and scanning electron microscopies; wear volume was calculated from the wear zone depth.

As shown in Fig. 10 a higher wear resistance was observed for the oxidized samples. This behaviour

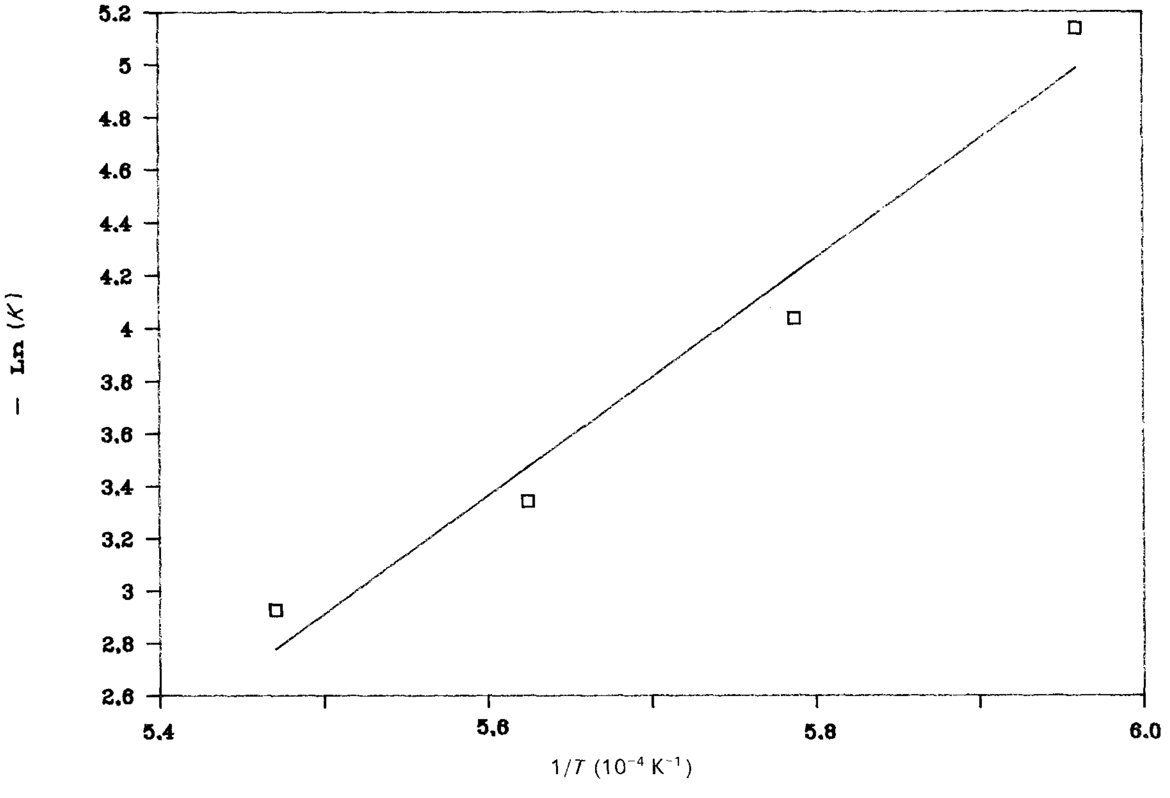


Figure 6 Determination of the activation energy (plane symmetry) for the Al_2O_3-30 vol % AlON.

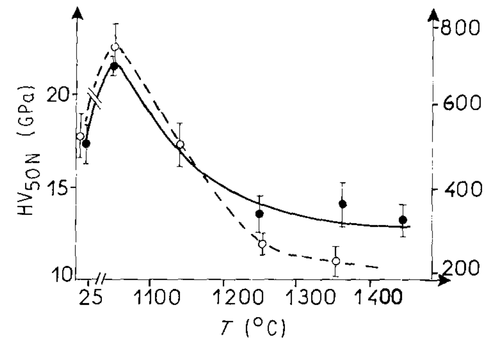


Figure 7 (○) Flexural strength (σ_f) and (●) Vickers hardness (HV) of Al_2O_3–30 vol % AlON oxidized for 3 days at 1050° C.

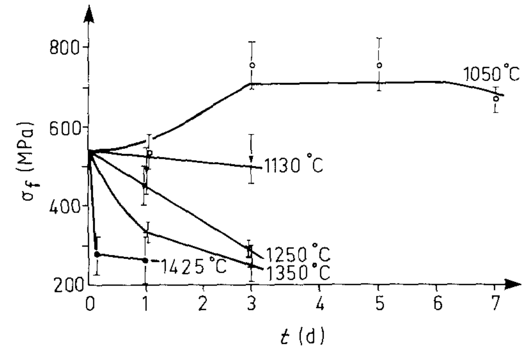


Figure 9 Flexural strength (σ_f) plotted against time for different oxidation temperatures.

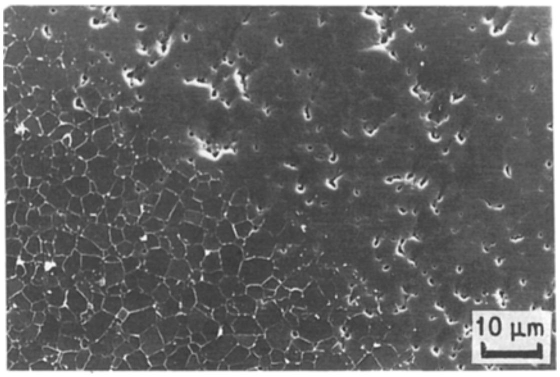


Figure 8 The interface of the oxidized layer–matrix.

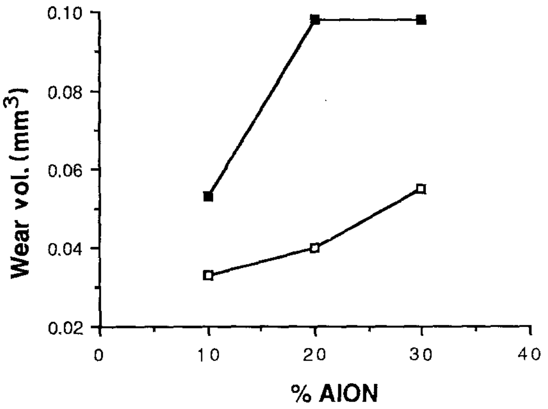


Figure 10 Wear resistance of (□) oxidized and (■) non-oxidized composites.

can result: (i) from improvement in the mechanical properties due to the compressive surface stresses; (ii) from the specific rheology of the transfer that so mears the friction surface. The transfer is constituted by a microcrystallized phase, the γ'-alumina, which traps metallic elements on contact and fills up the porosity. The same effect has been observed for the friction of microcrystallized $CoAl_2O_4$ [9].

7. Conclusions

The oxidation of Al_2O_3–γ-AlON composites leads to the γ'-alumina formation for the range of temperatures studied (1050 to 1550° C). After oxidation treatments up to 1200° C, the γ'-alumina phase is stable and induces compressive stresses at the composite surface. Thus its mechanical (σ_f, HV_{10N}) and tribological properties are enhanced. Above 1200° C, the γ'-alumina constitutes an intermediate layer. This phase changes into the α-alumina phase with a volume decrease. So a porous α-alumina layer is present at the composite surface, that leads to a decrease of mechanical properties.

For treatments above 1200° C, a kinetics study shows that the γ'-Al_2O_3/α-Al_2O_3 interface advance is the phenomenon-limiting step. The activation energy for both plane and cubic symmetries is $420\,kJ\,mol^{-1}$.

The good behaviour of the Al_2O_3–γ-AlON composite in air, in the temperature range 1000 to 1200° C offers the possibility of using this material for many applications: e.g. cutting tools, dies, etc.

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