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Effect of Oxygen Content on the Corrosion of AlN Powder in Diluted Acid Solution

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Abstract

Corrosion exposures at room temperature in different diluted acid media (0·025N and 0·05N HCl) were performed on two aluminum nitride powders with different oxygen contents: 0·6 wt% and 1 wt%. The process was monitored, measuring the amount of Al^{3+} *leached and the solution pH. The results show that the corrosion kinetics are dependent on the acid concentration, and that the amount of oxygen present in the powder in solid solution is the factor that controls the length of the low rate attack step of the corrosion process.*

Zwei Aluminiumnitridpulver mit unterschiedlichem Sauerstoffgehalt (0·6 und 1 Gew%) wurden bei Raumtemperatur verschiedenen, verdünnten Säurelösungen (0·025N und 0·05N HCl) ausgesetzt und die Al^{3+} *Konzentration sowie der pH-Wert während des Prozesses gemessen. Die Ergebnisse zeigen, daß die Korrosionskinetiken abhängig von der Säurekonzentration sind, und daß der im Pulver gelöste Sauerstoff derjenige Parameter ist, der die Dauer des langsamsten Schrittes während der Korrosion bestimmt.*

Nous avons soumis deux poudres de nitrure d'aluminium, contenant 0·6% pd. et 1% pd. d'oxygène, à de la corrosion dans deux solutions acides (0·025N et 0·05N HCl) à température ambiante. Nous avons suivi l'évolution de la réaction en mesurant la quantité d'Al^{3+} *libérée et le pH de la solution. Les résultats montrent que la cinétique de corrosion est dépendante de la concentration de l'acide, et que c'est la quantité d'oxygène en solution solide dans la poudre qui contrôle la durée de l'étape d'attaque lente dans le processus de corrosion.*

1 Introduction

Aluminum nitride ceramics have attracted much interest in the last few years mainly in the electronics industry because of the need for smaller and more reliable integrated circuits and the need for higher voltage devices for power applications.[1–3] In this sense the evolution of the chemical stability of AlN in different environments is considered nowadays as a key technological objective. Some reports have been published on the degradation of AlN in aqueous media at high temperature (900–1400°C)[4–6] and at room temperature;[7] however, no data have been reported in the literature at room temperature under dilute acid conditions.

In the present work a study has been carried out on AlN degradation in diluted acid solution at room temperature. The acid medium was chosen in order to speed up the degradation process of the powder. At the same time this acid medium tries to reproduce the working conditions of electronics equipment used outdoors.[3]

2 Experimental Procedure

2.1 Starting materials

Two different AlN powders supplied by Isman (Chernogolovka, Russia) obtained by self-propagating high-temperature synthesis (SHS),[8] labeled AlN-115 and AlN-116 have been used in this study.

The impurities were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), the specific surface area by the BET method, the particle size distribution by laser scattering, the oxygen content by elemental analyzer

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(EF-400 LECO Co., St Joseph, MI, USA) and the morphology of both AlN powders by scanning electron microscopy (SEM).

2.2 Corrosion test

Corrosion tests were carried out at room temperature for times ranging from 30 to 180 min in the following acid media: (a) 0·05N HCl and (b) 0·025N HCl.

The powders (2 g) were stirred with a PTFE-covered magnetic bar on top of a magnetic plate in a 100 cc glass beaker containing 20 cc of one of the mentioned solutions. After each attack, the contents of the beakers were filtered. In the attack solutions, the pH was determined, and the Al^{3+} concentration was analyzed by ICP-AES, using the Al I 396·152 nm signal as the analytical line.

3 Results and Discussion

In Table 1 the physical and chemical characteristics of both of the studied powders are reported. Figure 1 shows SEM micrographs of the two different powders. As can be observed both powders are composed of hard agglomerates of smaller particles (1–5 μm) with very similar characteristics and morphology.

Figure 2 shows the concentration of leached Al^{3+} content in the solutions versus time. From this figure the following can be stated:

(i) Both powders present a similar attack behavior: an initial low rate stage followed by a high rate stage. The rate of each stage depends on the HCl acid concentration.
(ii) The duration of the initial low rate stage is significantly shorter (≈50%) in the AlN-116 powder than in the AlN-115 one.

A similar trend is observed in the pH versus time plot presented in Fig. 3.

The overall reaction process can be expressed by the following chemical reaction:

$$AlN + H_2O + 3H^+ \rightarrow NH_4OH + Al^{3+} \quad (1)$$

From this reaction it can be deduced that the higher

Table 1. Physical and chemical characteristics of AlN powders

	AlN-115	*AlN-116*
S_{BET} (m^2/g)	0·7 ± 0·1	0·8 ± 0·1
d_{50} (μm)	16 ± 1	17 ± 1
Impurities (wt%)		
(Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Ti, Zn, Zr)	<0·1	<0·1
Si	0·10 ± 0·05	0·08 ± 0·05
Oxygen content (wt%)	1·0 ± 0·1	0·6 ± 0·1

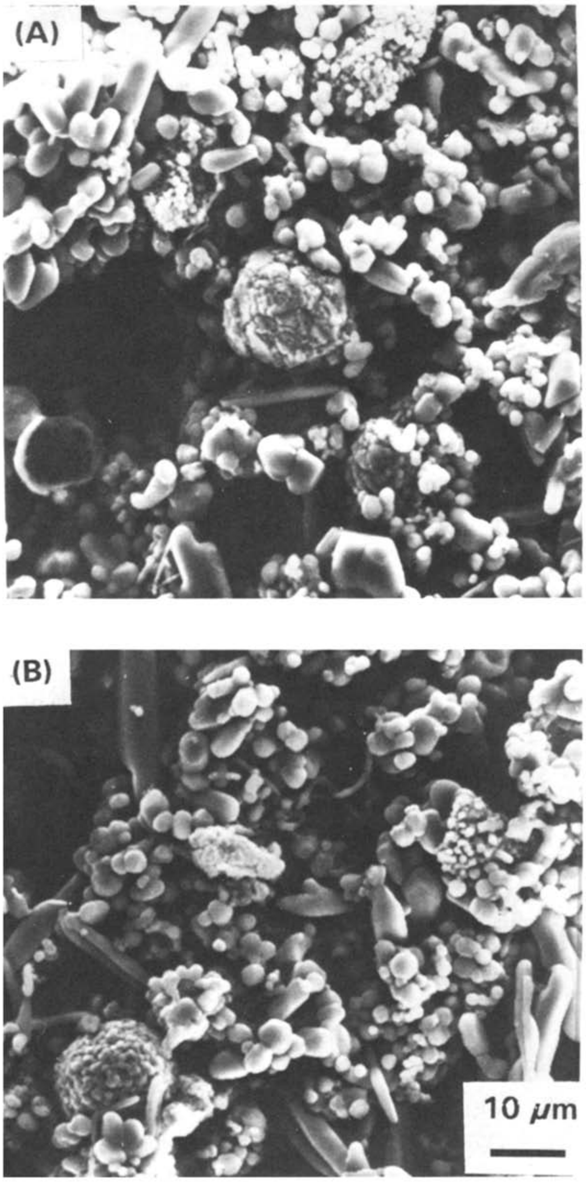

Fig. 1. SEM micrographs corresponding to: (A) AlN-115 powder, (B) AlN-116 powder.

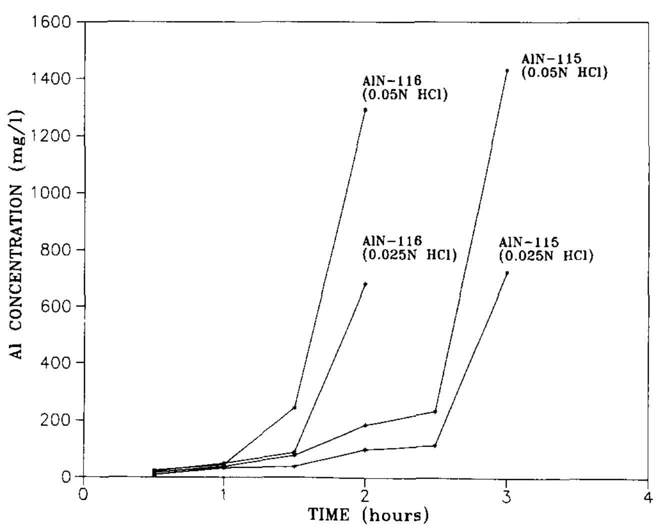

Fig. 2. Al^{3+} concentration in the solution versus time.

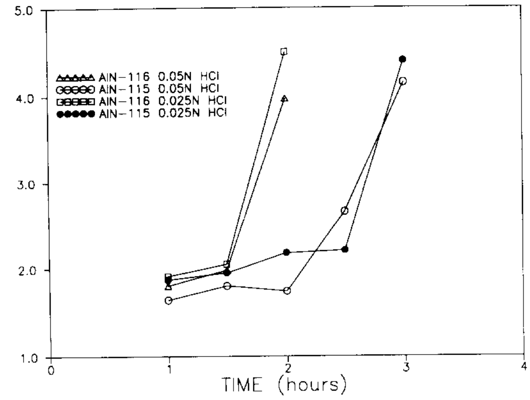

Fig. 3. Evolution of the pH of the solution versus attack time.

the concentration of Al^{3+} in solution, the higher will be the pH of the medium. This fact has been experimentally detected (Figs 2 and 3).

It is worth mentioning that the only significant difference between both AlN powders consists in their oxygen content (Fig. 1 and Table 1).

According to Bühr *et al.*,[9] the solubility limit of oxygen in AlN at 2000°C was found to be 1·6 wt%. Consequently, the amount of oxygen detected in both powders, obtained at $T > 2000$°C by the SHS process,[10] can be assumed to be in solid solution.

Slack[11] reports that the incorporation of oxygen in the AlN lattice occurs by the dissolution of Al_2O_3 according to the following reaction:

$$Al_2O_3 \rightarrow 2Al_{Al} + 3O_N + V_{Al}$$

where V_{Al} denotes an aluminum vacant site.

On the other hand, Dutta & Mitta,[12] through a TEM study, report that the oxidation kinetics are faster at the AlN basal planes containing Al. That is, as the corrosion attack proceeds by leaching of Al from the AlN lattice (reaction (1)), the overall kinetics of the process is dependent upon the Al concentration of the exposed AlN surface.

On the basis of the previous statements the results obtained in the present investigation may be explained by considering that in the starting AlN powders only the surface layer of the particles is completely oxidized, containing a higher concentration of Al vacancies than the bulk of the particle (Fig. 4).

Then, as both powders have almost the same specific surface area with a very similar morphology (Table 1 and Fig. 1), the higher the content of oxygen, the higher will be the thickness of the oxidized surface layer of the AlN particle.

This fact may justify the attack behavior observed in Fig. 2 where the length of the initial stage corresponding to the low oxygen content AlN powder (AlN-116) is ≈50% smaller than the one corresponding to the higher oxygen content (AlN-115).

The results obtained in the present investigation using coarse powder as a model to study the AlN corrosion in diluted acid conditions can be used as a basis to understand weathering problems of AlN substrates used in devices working in outdoor conditions such as, for instance, those pertaining to high-speed trains.

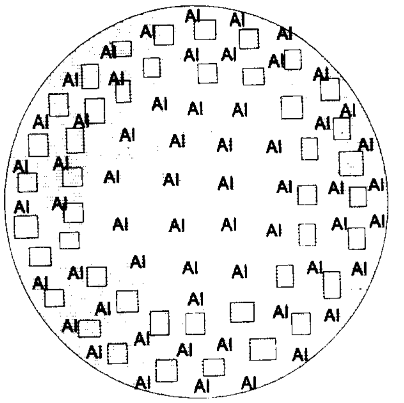

Fig. 4. Aluminium sublattice scheme of AlN-SHS particle showing the Al vacancies created by the oxygen solid solution.

4 Conclusions

The following conclusions can be drawn from the present work:

(1) The kinetics of AlN corrosion by HCl dilute solutions is related to the acid concentration in the media.
(2) The length of the initial low rate stage of the AlN corrosion attack has been found to be dependent upon the oxygen content of the starting powders. The higher the content of oxygen, the higher will be the length of the initial stage. This fact has been explained by assuming that a higher fraction of the oxygen is dissolved in the surface layer of the AlN particles.

Acknowledgements

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