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Corrosion of aluminium nitride substrates in acid, alkaline solutions and water

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Aluminium nitride substrates were immersed in acid, basic solutions and deionized water for 1–120 h at room temperature. The corrosion rates are higher in basic solutions (NaOH and KOH) than those in acid solutions (CH_3COOH, HCOOH, HNO_3, HCl and H_2SO_4) and deionized water. The weight loss of AlN corroded in alkali aqueous reaches 70% and results in an increase in surface roughness ranging from 10 nm to 7 μm after 3 days corrosion. However, the weight loss in acid solution is only 1/700 of the alkali case. Violent chemical reactions between AlN and basic solutions were observed. Na_2O, or $Na_2Al_2O_4 \cdot 6H_2O$, is the intermediate product, and NaOH is a catalytic agent of the reaction. The surface morphology of the AlN etched by alkaline solutions is coral-like in microscopic view and appears like hills. In contrast, only several atomic layers of AlN surface are etched off in acid solutions and in deionized water. The lightly etched surface is mirror-like and flat, and the shapes of the grains are visible under the microscope, as the corrosion rate of each AlN grain varies with different crystal orientations. Consequently, after etching in acid solutions, the resulting microscopic surface morphology looks like a map of a jigsaw puzzle.

1. Introduction

In current microelectronic packages, ceramics are widely used for electronic substrates on which the circuitry is placed and devices mounted. Because of further miniaturization of electronic circuitry in high-performance electronic devices, such as high-speed VLSIs, logic VLSIs and high-power transistors, a greater amount of heat per unit area is generated. In order to dissipate the heat and guarantee higher reliability for such devices, a newer substrate material (AlN ceramic) with higher thermal conductivity (150–220 $W m^{-1} K^{-1}$ with theoretical value reaching 320 $W m^{-1} K^{-1}$) are considered to be the better option. In addition, AlN ceramics have excellent flexural strength around 5000 $kg cm^{-3}$, high electrical resistivity (10^{11}–10^{14} Ω cm), low dielectric constant (8.8 at 10 MHz), no toxicity and the coefficient of thermal expansion (4.5 p.p.m. $°C^{-1}$) is close to that of silicon (4 p.p.m. $°C^{-1}$). These merits make AlN a potential substitute for Al_2O_3 in an electronic package.

In the real application of AlN in the electronic industry, two problems must be resolved. The first one is the metallization. Surface metallization of AlN ceramic substrates is necessary for joining metals and ceramics for electronic circuit applications. One of the methods is to roughen the surface of the substrate to produce a good adhesion of metal on it because the mechanical interlocking is created in the interface between them. In addition to the influence of the surface roughness, a different surface morphology but with the same surface roughness would exhibit different adhesive strengths [1]. Moreover, careful control of the surface properties not only increases the adhesive strength but also avoids the problems of short circuiting when the width of the conductors and the size of the electronic devices tend to miniaturization in the microelectronic design.

The second problem to be resolved is the reliability of AlN in service. The moisture and corrosion environments will degrade the electrical and mechanical properties of AlN [2, 3], especially in the strong basic solutions. Therefore, it is important to realize the corrosion resistance of AlN to the chemical species. In the literature, it was reported that AlN ceramic reacted with water and produced aluminium hydroxide $Al(OH)_3$ and β-$Al_2O_3 \cdot 3H_2O$ [4]. The former was also identified through X-ray diffraction (XRD) analysis by Kurihara *et al.* [5] on the AlN ceramic which was immersed in warm water (80 °C). Accompanying these two phases, a large needle-shape matter was present on the AlN surface. Chanchani [6], who used electron spectroscopy for chemical analysis (ESCA), Fourier transform–infrared spectroscopy (FT–IR), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) to analyse the AlN, found that an amorphous hydrated alumina phase existed as a porous film formed over AlN after treatment in deionized (DI) water for 1 h at 100 °C. However, no other phases and reaction were found under the same conditions as the temperature of immersion was decreased to 70 °C. By measuring the *d*-spacing of an unidentified phase obtained from the reflection high-energy electron diffraction (RHEED), Abid *et al.* [7] argued that γ-AlOOH was formed when AlN was treated with water at 100 °C. In addition, in the Al(N, O, B) thin film, the conversion of AlN to Al_2O_3 in 100 °C hot water was also reported and detected by Rutherford backscattering spectroscopy (RBS) [8].

In spite of various kinds of the reaction products, the corrosion rate of AlN in the acid is low, even at boiling temperature. It was only around several hundred thousandths of an inch per year [9]. Srivastava *et al.* exposed the hot-pressed AlN to the vapour of a 1 N solution of HCOOH and CH_3COOH at room temperature for more than 1 day [2, 3]. The increase in both the dielectric constant and dissipation factor indicated that the porosity played an important role. A slight increase in mass was also found. Long and Foster [10] investigated the finely ground AlN powders that dissolved completely as immersed in 50% boiling H_2SO_4 solution for 4 days. It was concluded that the specific surface area must be as low as possible to reduce the corrosion rate in the deteriorated environments.

In the process of metallization in the microelectronic industry, the NaOH solution was used as the etchant for surface etching and cleaning to obtain a high adhesive strength between metal film and AlN substrate. Osaka *et al.* [11] thought that the chemical etching of AlN substrate was performed in two stages. The first was selective etching on both the triple points and grain boundaries, and the second was homogeneous etching on all parts of the substrate, including the AlN grains. It was also observed that $NaAl(OH)_4$ formed after etching [1].

Except for the acid, basic solution and water, AlN is very stable in contact with other materials at high temperature, such as aluminium, gallium and B_2O_3 liquid in argon, carbon monoxide and vacuum atmospheres [10] and molten carbonate melt (Na_2Co_3–K_2CO_3–Li_2CO_3) in a carbon dioxide atmosphere [12]. A summary of selected investigations is represented in Table I [1–15].

Although many kinds of reaction products have been proposed, because the AlN ceramic was immersed in the solution with $pH \leqslant 7$ at different temperature levels as described before, few investigations have been made of the relationship between the surface roughness, morphology and etching solutions, which are very important in the development of the current microelectronic industry. In addition, details of the kinetics and mechanism for the violent reaction taking place between the AlN substrate and basic solutions are not yet known. Furthermore, the increased resistance to corrosion of the AlN substrate when doped with elemental yttrium as the sintering aid, has not been fully investigated. In this study, AlN ceramics were corroded in various acid, base and neutral solutions. The relationship between the corrosion rate, surface roughness, surface morphology and reaction products was closely investigated. In addition, the reaction mechanisms when AlN reacts with the bases, are also discussed and proposed.

2. Experimental procedure

Commercial AlN substrates (SH-15, Tokuyama Soda Co. Ltd, Japan) with a small amount of added Y_2O_3 as sintering aid, were used in this study. The specifica-

TABLE I The chemical properties of various types of AlN samples under the different corrosive environments.

Sample		Chemical properties					Results		Ref.
Type	Composition	Method	Time	T (°C)	Environment (s)	Corrosion	Phase(s)	Summary	
Substrate	99.5% AlN	HTH	–	80	Air (RH 90%)	None	None		[5]
	0.5% CaO	PCT		121	H_2O (g), 2 atm	Mass ↑	–	Small needle-shape	
					H_2O (l)	Mass ↑	β-$Al_2O_3 \cdot 3H_2O$,	Large needle-shape	
				80			$Al(OH)_3$	SEM, XRD	
Oxidized AlN					H_2O (l)	None	None		
Single crystal	86% AlN		~Month	RT	H_2O (l)	None	None		[9]
(particles)	14%Al_2OC			b.p.	50% HCl	170 (mil/year)	–		
Cut HP-bar	Pressed	I	72 h	100	H_2O (600 ml)	14			
	powders:			72	Conc. HCl	320			
	96.0% AlN			110	50% HCl	570			
	2.1% Al_2O_3			305	Conc. H_2SO_4	180			
	1.9% others			145	50% H_2SO_4	550			
				120	Conc. HNO_3	150			
				111	50% HNO_3	200			
				57	Conc HF	160			
				57	50% HF	215			

TABLE I (Contd.)

Powder	92%–94% AlN	I		100	50% H_2SO_4	100 (mg/month)	–		[10]
				> RT	NaOH (aq)	Dissolve	NH_3 (g)	Collected in dil. H_2SO_4 (aq)	
		ball mill	72 h	RT	Methanol (moisture)	Corrode	57.5% AlN		
Finely ground powder	6%–8% Al_2O_3	I	4 days	b.p.	50% H_2SO_4	Dissolve completely	–		
				700	Wet air	None	None		
Bar (1 cm^3)		HTH		1000	Wet air	Oxidation, mass ↑	0.8% Al_2O_3		
					CO (g), Al, Ga and B_2O_3 (l)	None	None		
Powder (p.s. 50 μm)	99% AlN	I	24 h	100	H_2O	Corrode	γ-AlOOH	$AlN + 2H_2O = AlOOH + NH_3$ (probable reaction), HREED	[4]
–	–	–	–	–	H_2O	Corrode	$Al(OH)_3$	$AlN + 3H_2O = NH_3 + Al(OH)_3$	
Thin film ($\leqslant$ 150 nm)	Al(N, O, B) $AlB_x(NH_y)_z$ Al_2O_3	I	1 h	b.p.	H_2O	Corrode	Al_2O_3	20% Ni + 80% AlN = $AlNi_3$ RBS	[8]
Bulk	99% AlN 1% Ni			RT	1glycerol + 1HNO_3 + 1HF	Etching	–	Ni or (Ni, Al) phase 20% NI + 80% AlN = $AlNi_3$	[14]
–	–		–	–	Molten carbonate (Na_2CO_3–K_2CO_3–Li_2CO_3	None	None		[12]
Substrate (NEC)	99.5% AlN 0.5% CaC_2			RT	1 M NaOH	Etching	–	$AlN + NaOH + 4H_2O = NH_4OH + NaAl(OH)_4$	[1]
Substrate (NEC)	CaC_2-doped AlN				0.1 M NaOH	2 stage etching			[11]
HP-disc (porosity 0.2%)	99% AlN	V	> 1 day	RT	1 N HCl (g), HNO_3 (g)	Dielectric const. (ε) ↑, Dissipation factor $(\tan\delta)$ ↑ and mass ↑ (0.1–0.2%)			[2]
					1 N HCOOH (g), CH_3COOH (g)	ε ↑, $\tan\delta$ ↑ and mass ↑ (0.3%–0.4%)			[3]
Tape-case substrate	99.6% AlN (< 0.15% O)	I	1 h	RT	DI water	None	None		[6]
				70					
			> 20 min	100		Porous film	Amorphous hydrated alumina	ESCA, FT-IR, TGA, XRD AlOOH (suggested in [7])	
			1 h	100	pH = 3.0 and 8.2	None	None		
					pH range 4.4–5.5	Decomposition	–		
			500 h	85	air (RH 85%)	None			
HP-disc	AlN + 0.5% CaO $(Ca(NO_3)_2$		1 h	95	85% phosphoric acid	None	None	2nd phase is very small (suggested) SEM	[15]

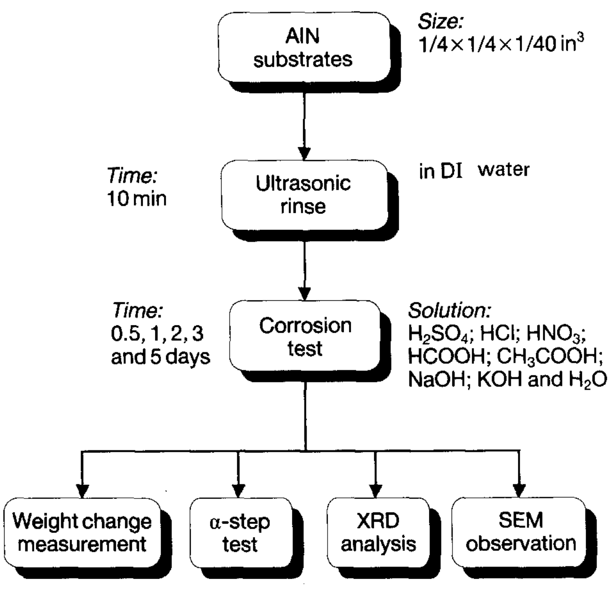

Figure 1 Flowchart of the experimental procedures.

tion of these samples is as follows: size $1 \times 1 \times 0.025$ in^3 ($\sim 2.5 \times 2.5 \times 0.06$ cm^3); surface roughness 0.3–0.8 μm; and flatness $\leqslant 0.05/25.4$ mm. After SiC grinding, diamond polishing and final SiO_2 polishing, the AlN substrates with a surface roughness around 10 nm were cut into pieces of dimensions $0.25 \times 0.25 \times 0.025$ in^3 ($\sim 0.6 \times 0.6 \times 0.06$ cm^3) for the corrosion test.

The samples were immersed in solutions of various analytical grade acids and bases. The concentrations and the pH ranges are shown in Table II. The corrosion time ranged from 0.5–5 days, and then the surfaces were washed and ultrasonically cleaned with deionized (DI) water for 10 min. The surface morphologies were examined by scanning electron microscopy (SEM, Camscan, UK), the surface roughness was measured by α-step (Alpha-Step 250, Tencor, USA) and the phases of the reaction products were detected by X-ray diffraction (XRD) (DMAX-B, Rigaku, Japan). The weight change was evaluated with a microbalance. The flow chart of the experimental procedure is presented in Fig. 1.

3. Results and discussion

In general, the corrosion resistance of AlN to the chemical species is worse than that of Al_2O_3 because the surface-oxided AlN substrate exhibits a higher corrosion resistance to water immersion [5]. If the high thermal conductivity characteristic of AlN is to be put in a microelectronic package, the relationship between AlN and its environments in service, especially, in the environments of humidity, acids and bases, must be understood. Owing to the fact that AlN is easily etched in basic solutions, the adhesive strength of the thick metal film on the AlN ceramic after metallization will be increased by the surface treatments of the ceramic itself.

On the basis of the differences in the corrosion environments, the results in this study are divided into two categories: one is in the neutral and acid solutions ($pH \leqslant 7$); and the other is in the basic solutions ($pH > 7$). The changes in weight, surface roughness and morphology of AlN with time of immersion in various solutions and the phases of the reaction products will be intensively studied.

TABLE II The concentration and pH values of the chemical solutions used for etching the AlN substrates at room temperature.

Components	Concentration	pH values	Increasing rate of R_a (nm day^{-1})
H_2SO_4:H_2O	1:1	< 0	1.19
HCl:H_2O	1:1	< 0	0.46
HNO_3:H_2O	1:1	< 0	1.02
HCOOH:H_2O	1:1	~ 1	1.51
CH_3COOH:H_2O	1:1	~ 2	1.46
H_2O (l)	Pure DI water	7	1.00
KOH (aq)	20 wt %	> 14	1.93 (μm day^{-1})
NaOH (aq)	20 wt %	> 14	–

3.1. pH ⩾ 7

The AlN pieces were immersed in H_2O, CH_3COOH, HCOOH, HNO_3, HCl and H_2SO_4. After 5 days corrosion, the surface roughness, R_a, of the AlN pieces corroded in different acids increased slightly with corrosion time. For examples, the surface roughness increased from 9 ± 2 nm to 16 ± 4 nm after the AlN pieces were immersed in the HNO_3 solution for up to 5 days at room temperature, as shown in Fig. 2. The rate of increase of R_a is about 0.95 nm day^{-1}. This value is rather small and it implies that only several atomic layers are etched out per day. The increasing rates of R_a in different solutions are summarized in Table II. Inspite of the different etching species, it is observed that the total trend of variation of R_a ranges from 11 ± 2 nm to 14 ± 4 nm after an etching time of 1–120 h, as indicated in Fig. 3. The area between the upper and lower lines in Fig. 3 represents the average distribution of R_a increases with corrosion time in water and acid solutions. Although the differences of the changes of R_a with the corrosion time are not appreciable under these etching conditions, the CH_3COOH and HCOOH solutions exhibit a higher etching rate of AlN, compared with the others. On the other hand, the AlN substrates are more resistant to the H_2O and aqueous HCl. Taylor and Lenie [9] proposed that hot-pressed AlN (96% AlN, 2.1% Al_2O_3 and 1.9% other impurities) with a lower theoretical density (< 99.1%) was corroded by several acids at their boiling temperatures. Their corrosion rates are around several hundred mil* per year, as shown in Table I. In addition, the acid solutions with 50% concentration have higher corrosion rates than the concentrated ones. This is in agreement with the results of the study that weak acids, such as CH_3COOH and HCOOH, are more etchable than the strong ones, such as HNO_3, HCl and H_2SO_4. Furthermore, the weight loss calculated from Table I is around 20–50 wt % after 5 days corrosion in boiling acids. At room temperature, there is no significant weight

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* 1 mil = 10^{-3} in = 2.54×10^{-3} cm.

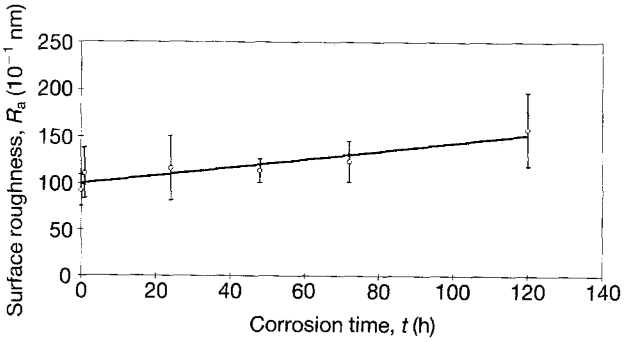

Figure 2 Effect of corrosion time on the surface roughness, R_a, of AlN immersed in HNO_3 acid solution.

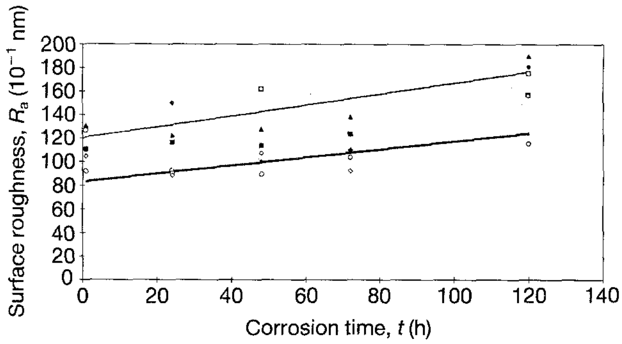

Figure 3 Effects of corrosion time on the surface roughness, R_a, of AlN immersed in deionized water and various acid solutions, such as (▲) CH_3COOH, (□) HCOOH, (■) HNO_3, (○) HCl, (◇) H_2O and (◆) H_2SO_4. The average trend of changes of R_a with time in various solutions is indicated between the upper and lower lines.

change measured using a balance, as shown in Fig. 4. It is argued that only very thin surface areas were attacked by acids at room temperature. This produces an increase in the surface roughness R_a, but no appreciable weight change is ever observed. In fact, the corrosion rates of the samples are related to their specific surface areas. Long and Foster [10] reported that the AlN powders were dissolved in 50% H_2SO_4 more quickly as the powders were ground more finely. It is reasonable, for densely sintered AlN bulks, as in this study (with a density of 3.375 $g\,cm^{-3}$ on average), that the corrosion rates are much lower than in porous bodies and loose powders.

Compared with the as-received AlN (Fig. 5a), the as-polished AlN (Fig. 5b) is mirror-like and flat even under the SEM. The dark area shown in Fig. 5b is constituted by the AlN grains. The white grains within the dark area are the Al–Y–O compounds, and the distributions of the elemental yttrium and aluminium can be clearly identified by EDX. The compounds identified by XRD are the $AlYO_3$ and $Al_5Y_3O_{12}$ garnet phases, as shown in Fig. 6, that were also reported elsewhere [16]. The shapes of AlN grains are developed more clearly after immersion in acid and neutral solutions, as indicated in Figs 7–12, which show the morphologies of AlN after corroding in H_2O, CH_3COOH, HCOOH, HNO_3, HCl and H_2SO_4 solutions, respectively. There are two types of etching morphology observed on the AlN-free surfaces after the corrosion tests. One is that the substrates without grain-boundary second phases are attacked by etchants on the grains themselves and the etching rate varies from grain to grain. The microscopic surface morphology looks like a map of a jigsaw puzzle. It is argued that the chemical etching resistance of the AlN crystals to the neutral and acid solutions is anisotropic. This anisotropic nature of the crystals also results in the variation of the hardness values with respect to the orientation of the crystals [9]. The second etching morphology is the pitting holes. Most of the pitting holes are distributed at the grain boundaries or at triple-point sites, yet only a few are in the grains. The hole size ($\leqslant$ 1 μm) is smaller than the AlN grain size (around 3–5 μm). Generally, the Al–Y–O compounds are more resistant to chemical etching than AlN grains because the white grains of Al–Y–O compounds are more protrusive than the dark ones of

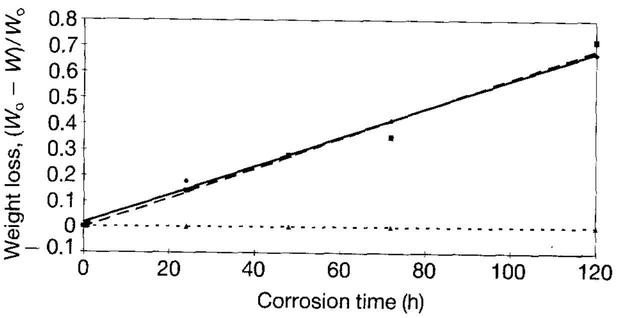

Figure 4 The change of weight loss with corrosion time for AlN immersed in deionized water, and various acid and base solutions. (--■--) NaOH, (—●—) KOH, (--▲--) H_2O, HCl, HNO_3, H_2SO_4, HCOOH, CH_3COOH.

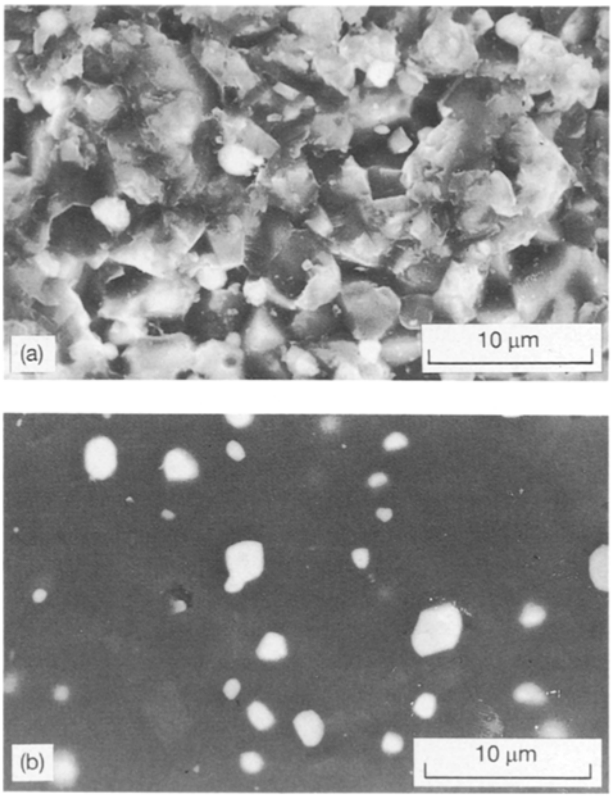

Figure 5 Surface morphologies of (a) as-received AlN substrate, and (b) as-polished AlN substrate. The white round grains in the AlN matrix are Al–Y–O compounds.

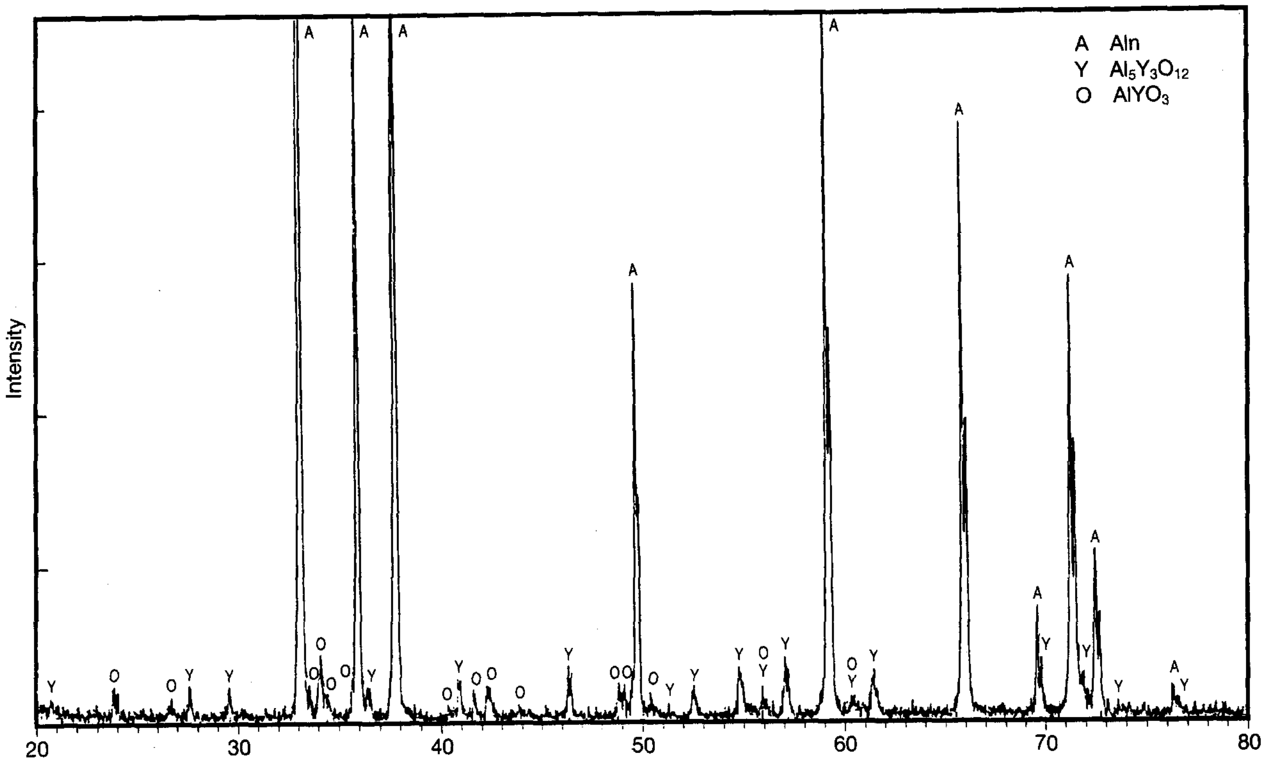

Figure 6 X-ray diffraction pattern of as-received AlN substrate.

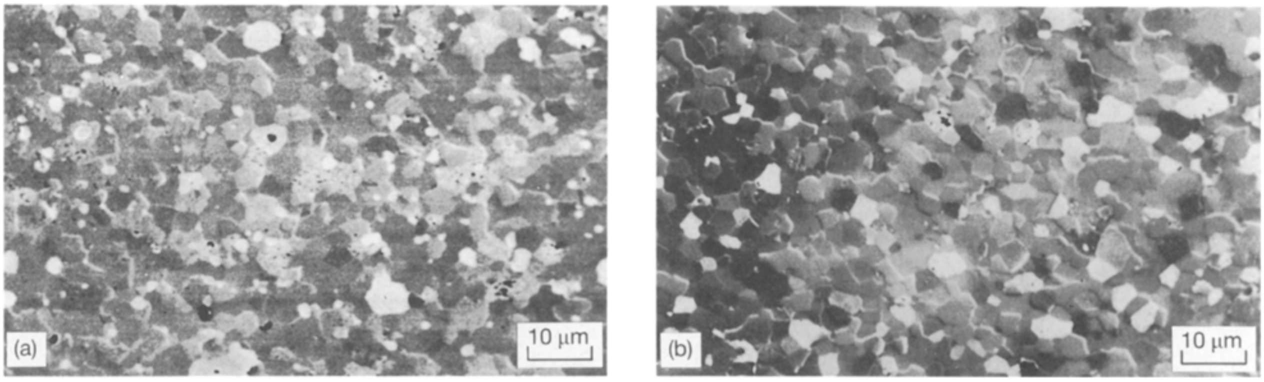

Figure 7 Surface morphologies of corroded AlN after immersion in H_2O for (a) 12, and (b) 120 h.

AlN (see Figs 7–12). The smaller pitting holes appear to be distributed densely on the Al–Y–O grains that result in a rougher surface morphology.

3.2. pH > 7

The surface morphology of the AlN etched by NaOH and KOH are shown in Figs 13 and 14. It is different from those etched by solution of pH $\leqslant$ 7. The irregular attack of the basic solution on the AlN substrate surface results in a blurred grain-shape morphology where the random sharp edges show up. This causes some difficulty in distinguishing grains between the AlN and Al–Y–O compounds. The morphology is coral-like in appearance.

In comparison with the pH $\leqslant$ 7 solutions, the AlN substrate can lose up to 70% of its weight after 5 days immersion in KOH and NaOH solutions, as indicated in Fig. 4. The surface roughness increases from ~ 10 nm to ~ 7 μm after 3 days corrosion, which is almost 700 times higher than that of the acid-etched AlN substrate (Fig. 15). From the microscopic view, it seems that there is no appreciable variation in the surface morphologies of the samples etched for 1–120 h. It is argued that the increase in R_a is attributable to the rough surface morphology on a macroscopic scale. The differences in the macroscopic surface morphologies of AlN corroded by NaOH solution for 12 and 72 h can be observed in Fig. 16a and b, respectively. It is interesting to note that the etched surface of AlN after 72-h immersion has a hill-like appearance. The cross-sectional view of AlN after 120 h, corrosion in NaOH solution, as shown in Fig. 17a, indicates a very rough surface with a peninsula structure. The corresponding backscattered electron image (BEI) (Fig. 17b) indicates that the white

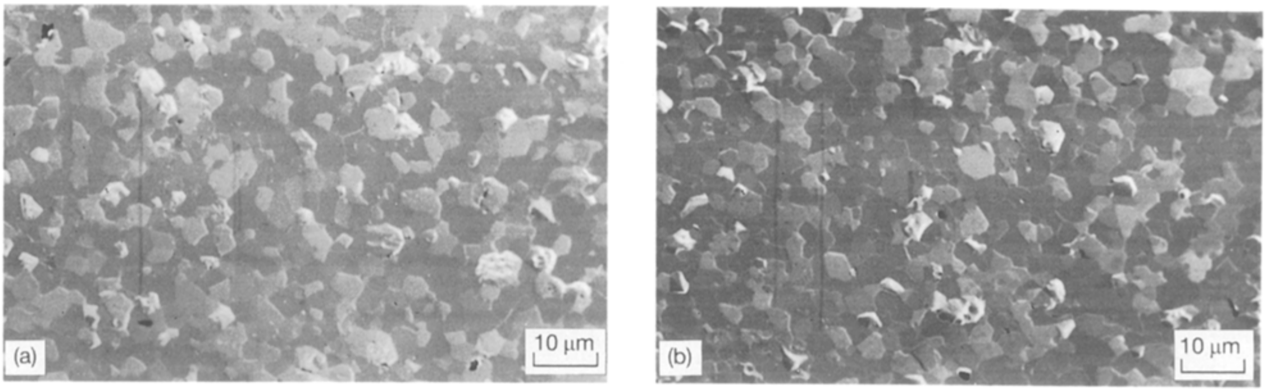

Figure 8 Surface morphologies of corroded AlN after immersion in CH_3COOH solution for (a) 12, and (b) 120 h.

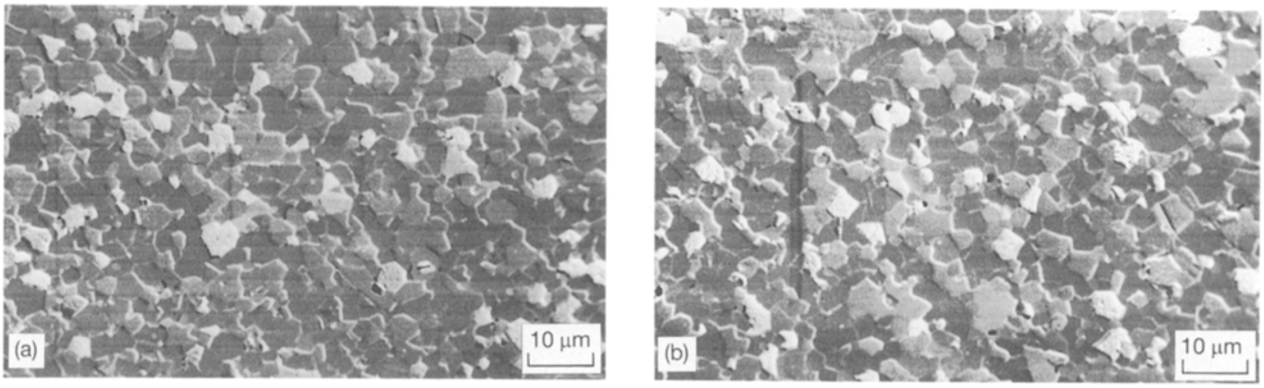

Figure 9 Surface morphologies of corroded AlN after immersion in HCOOH solution for (a) 12, and (b) 120 h.

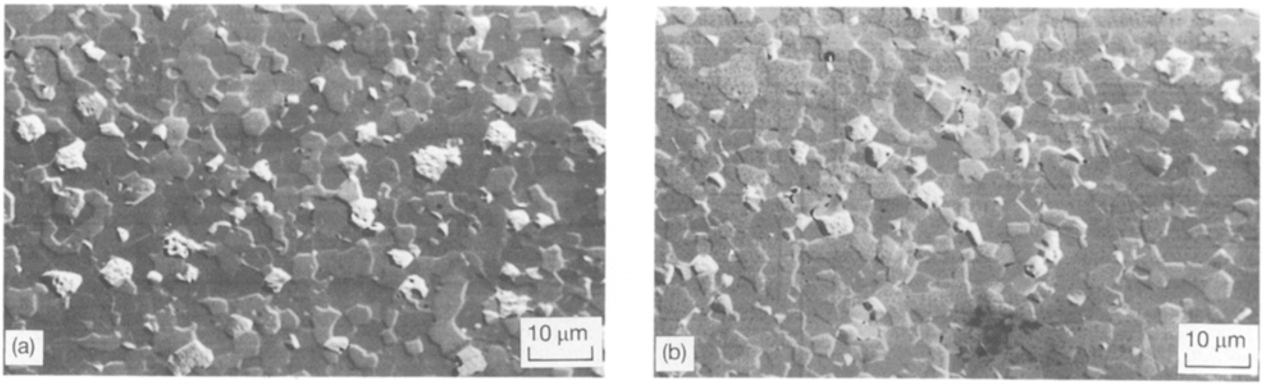

Figure 10 Surface morphologies of corroded AlN after immersion in HNO_3 solution for (a) 12, and (b) 120 h.

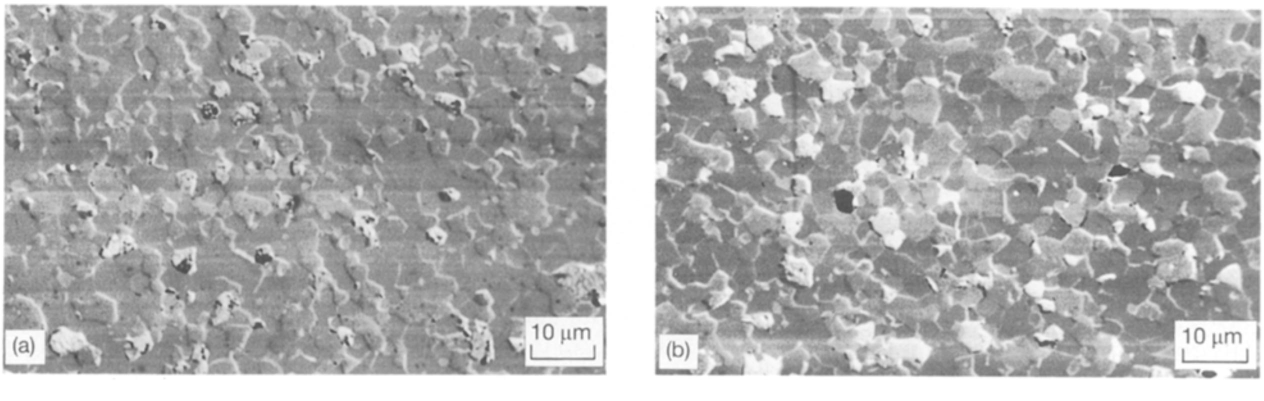

Figure 11 Surface morphologies of corroded AlN after immersion in HCl solution for (a) 12, and (b) 120 h.

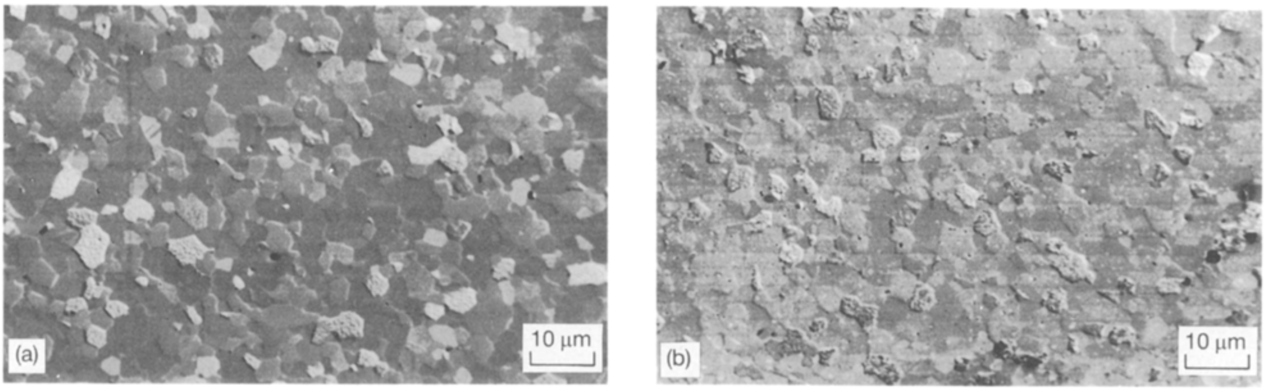

Figure 12 Surface morphologies of corroded AlN after immersion in H_2SO_4 solution for (a) 12, and (b) 120 h.

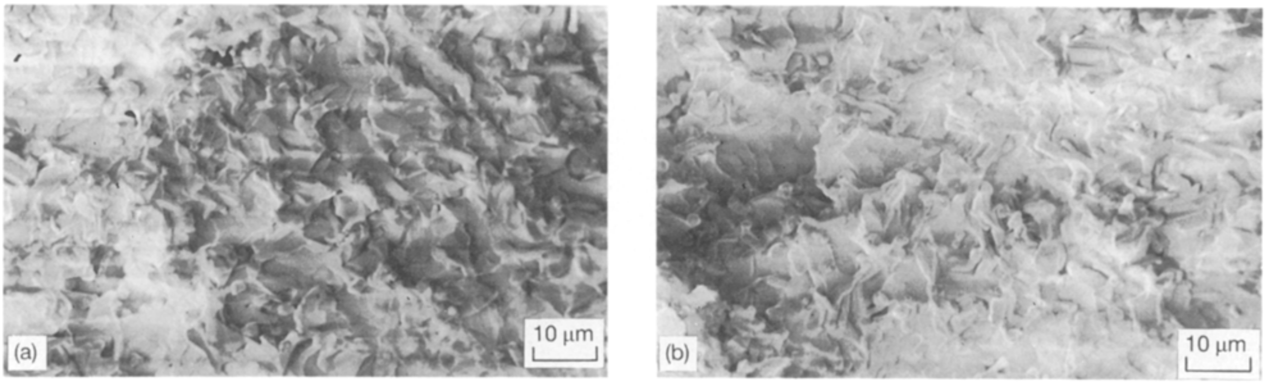

Figure 13 Surface morphologies of corroded AlN after immersion in NaOH solution for (a) 12, and (b) 120 h.

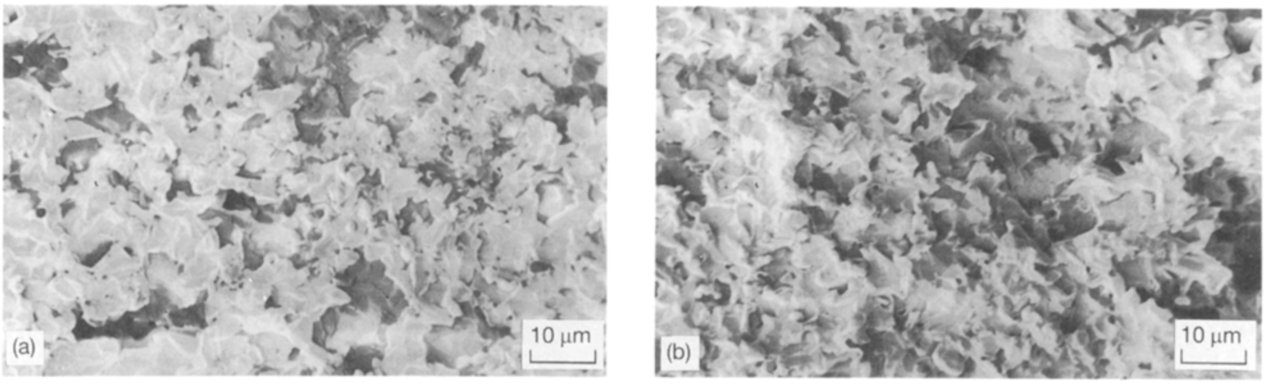

Figure 14 Surface morphologies of corroded AlN after immersion in KOH solution for (a) 12, and (b) 120 h.

Al–Y–O grains distributed on the surface form the tip of the AlN peninsula. Some Al–Y–O grains are situated away from the surface of the substrate due to the weak bonding strength of the connection between them and the porous etched AlN substrate. The porous structure inside the AlN substrate, as viewed from the middle of the cross-section of AlN, is shown in Fig. 17c and d, and is similar to the morphology of the etched surface indicated in Fig. 13. It is argued that after 5 days corrosion in NaOH solution, the whole AlN substrate is etched completely from the surface down to the inner part, to become a three-dimensional network. Chiou *et al.* [17] reported that surface roughness of AlN increased to 200 nm when it was etched by 4 wt% aqueous NaOH for 200 min, and even up to 800 nm for unpolished AlN after 80 min etching. The higher the concentration of the corrosive solution, the larger was the corrosion rate and the rougher was the etched surface. This implies that in a microelectronic package, a state of micro-etching can be retained by controlling the concentration of corrosion solutions and by the corrosion time, which are dilute and short, respectively. Because the immersion time exceeded 5 days, R_a values are not available; the probe of the α-step falls into a trap and is pinned by the very rough etched AlN surface.

No extra peaks exist other than AlN and Al–Y–O compounds in the XRD diagram of the AlN corroded in NaOH solution. To investigate further the mechanisms of the violent reaction between the NaOH solution and AlN, NaOH particles were placed on the AlN substrates to prepare the samples for analysis. Fig. 18 shows that the new compounds found after this corrosion reaction are Al_2O_3, Na_2O and $Na_2Al_2O_4 \cdot 6H_2O$. From thermodynamic considerations, the following reactions are proposed

$$2AlN + 2NaOH + 2H_2O \rightarrow Al_2O_3 + Na_2O + 2NH_3 \qquad \Delta G = -178\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

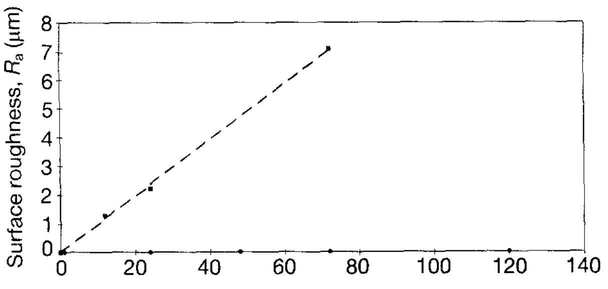

Figure 15 Effects of corrosion time on the surface roughness, R_a, of AlN immersed in (—■—) KOH and (—●—) HNO_3 solutions.

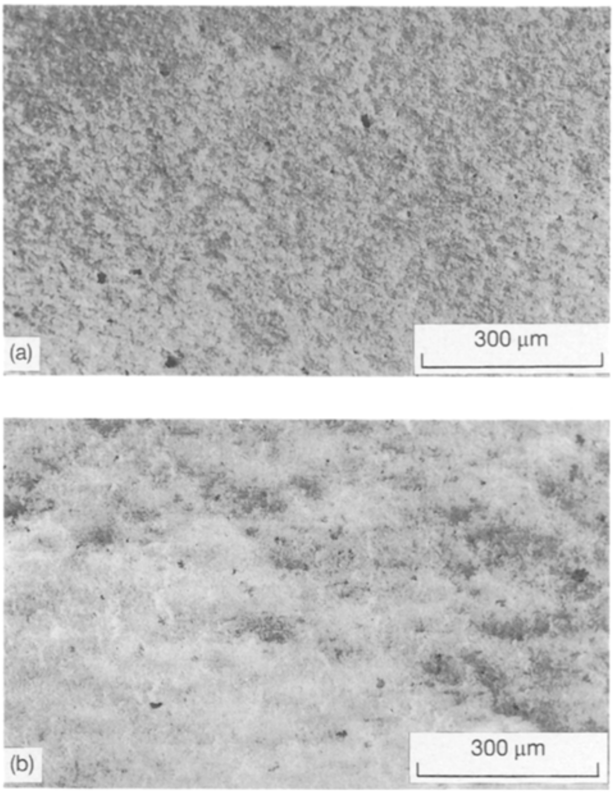

Figure 16 Macroscopic surface morphologies of AlN substrates after immersion in NaOH solutions for (a) 12 and (b) 72 h.

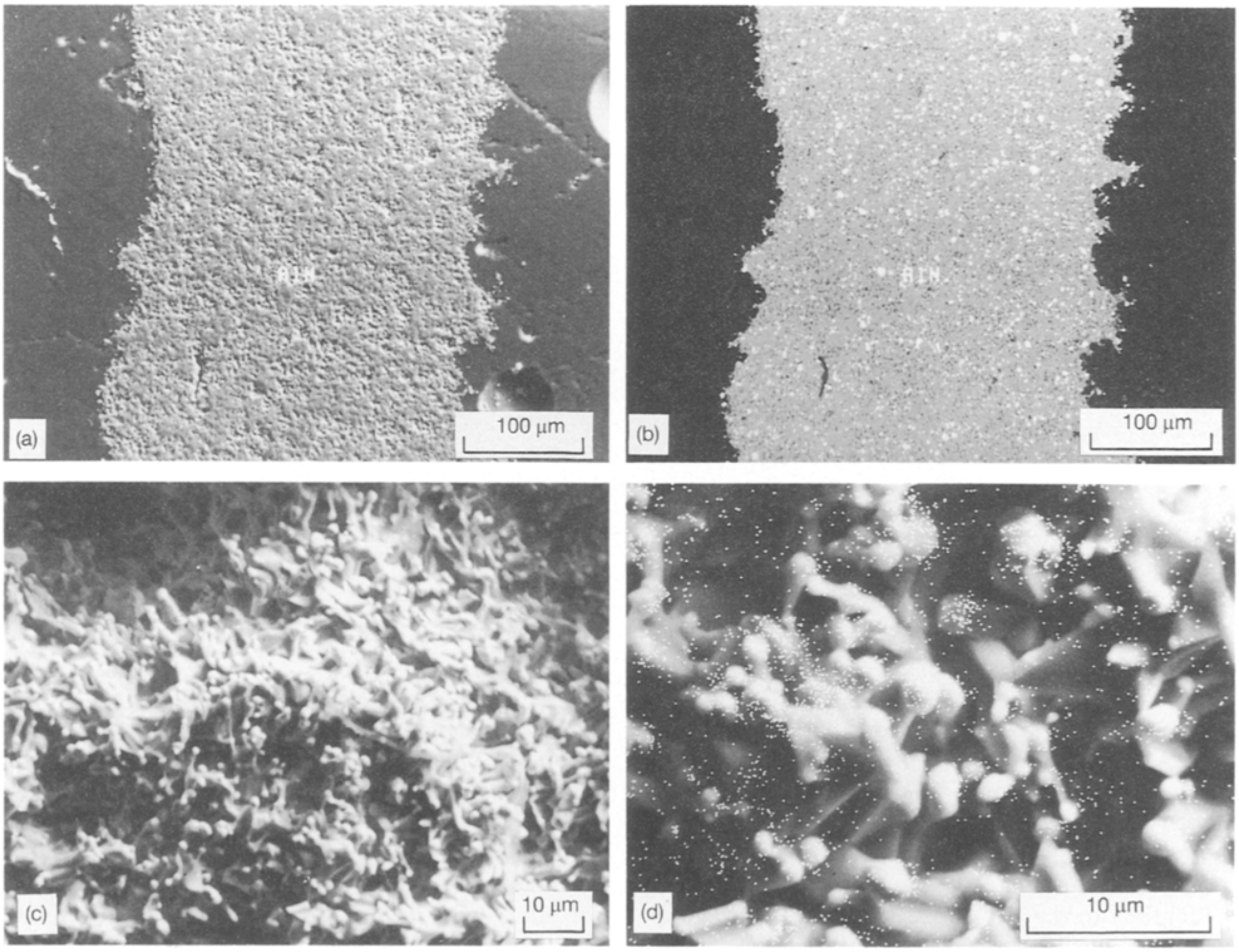

Figure 17 Cross-sectional view of AlN substrate after immersion in NaOH solution for 120 h. (a) Secondary electron image (SEI), (b) backscattering electron image (BEI), (c) magnification of (a), and (d) overlap of magnification of (c) and X-ray mapping of elemental yttrium.

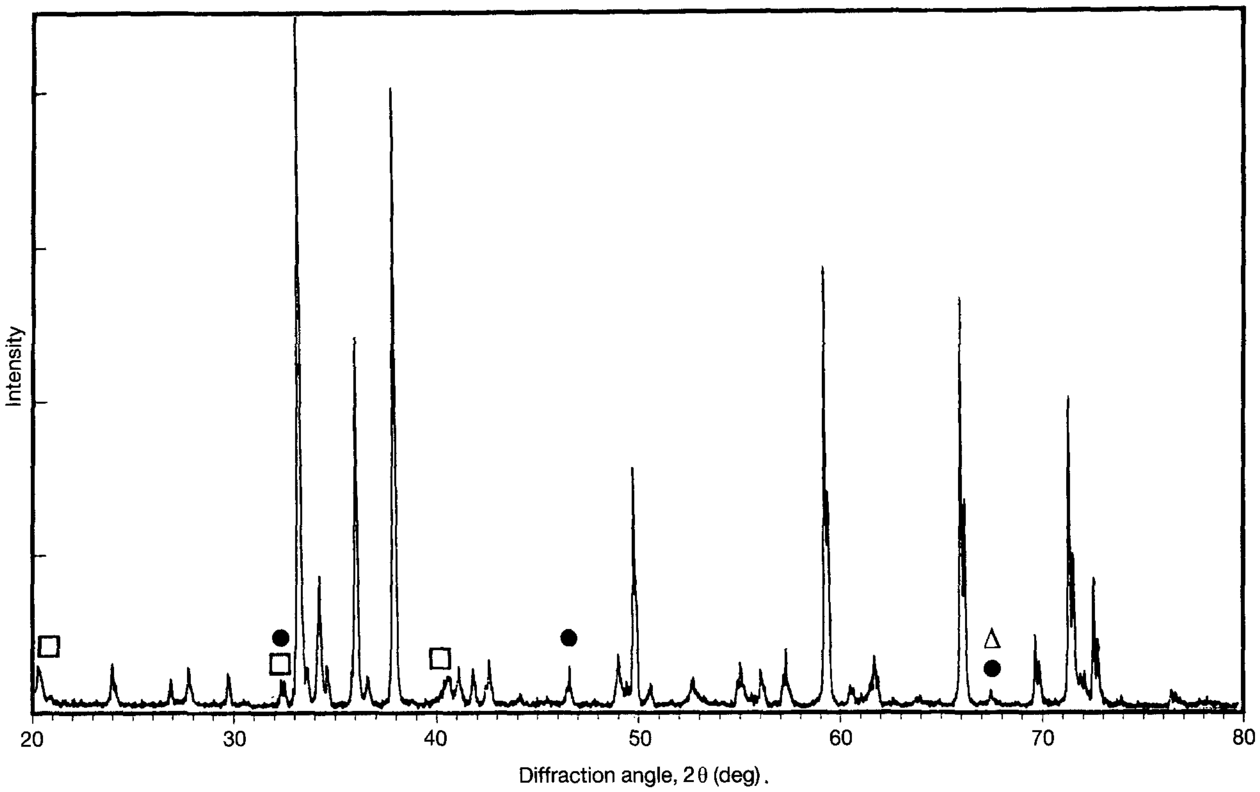

Figure 18 X-ray diffraction pattern of corroded AlN substrate after immersion in NaOH solution for 5 days. (●) Na_2O, (□) $Na_2Al_2O_4 \cdot 6H_2O$, (Δ) Al_2O_3.

Because Na_2O is unstable, a further reaction may take place

$$2AlN + 2NaOH + 8H_2O \rightarrow Na_2Al_2O_4 \cdot 6H_2O + 2NH_3 \qquad (2)$$

Osaka *et al.* [1] reported that $NaAl(OH)_4$ is the product of a reaction between AlN, NaOH and H_2O. Thus, the reaction

$$Na_2Al_2O_4 \cdot 6H_2O \rightarrow 2NaOH + 2Al(OH)_3 + H_2O \qquad (3)$$

will occur when AlN is immersed in NaOH solution. On combining Reactions 1–3, the overall reaction is

$$AlN + 4H_2O \xrightarrow{NaOH} Al(OH)_3 + NH_4OH$$
$$\Delta G = -\ 156.695\ \mathrm{kJ\,mol^{-1}} \qquad (4)$$

It is believed that NaOH plays an important role as catalytic agent to accelerate the reaction between AlN and H_2O. Na_2O, or $Na_2Al_2O_4 \cdot 6H_2O$, is the intermediate of the reaction. It is interesting to point out that H_2O is involved in the reactions. Without H_2O, the reaction may not occur because, the Gibb's free energy for the reaction below is positive

$$2AlN + 6NaOH \rightarrow 3Na_2O + Al_2O_3 + 2NH_3$$
$$\Delta G = +\ 108.481\ \mathrm{kJ\,mol^{-1}} \qquad (5)$$

In contrast to the acid cases, a violent chemical reaction (Equation 4) occurs in the base solutions, which results in an increased weight loss, and a rough and irregular surface morphology.

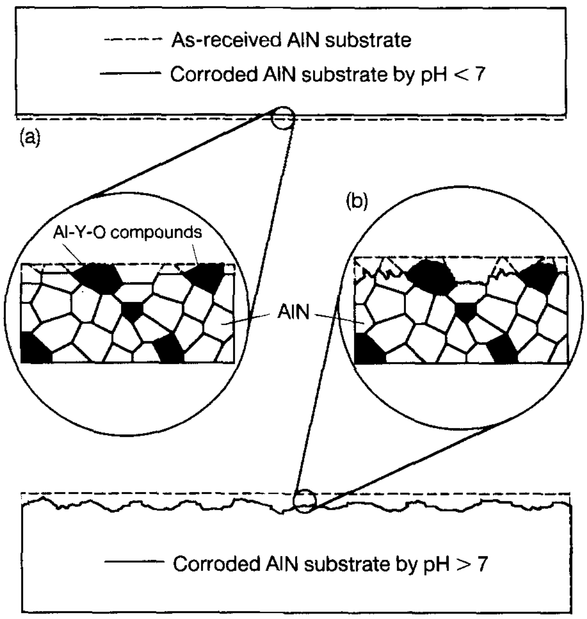

Figure 19 The sketch of a cross-section of the corroded Y_2O_3-doped AlN substrates at (a) pH $\leqslant$ 7 and (b) pH > 7.

On the basis of the above discussion, sketches of the cross-sectional views of the corroded AlN substrates after etching in the solutions with pH values $\leqslant$ 7 and > 7 are represeted in Fig. 19. In the case of pH $\leqslant$ 7 (Fig. 19a), each AlN grain is etched homogeneously and the etching rate depends on the crystal orientation of the grain. The more protrusive grains above the etched free surface of sintered AlN substrate, with dense and small pits on their surfaces, are the Al–Y–O compounds. A step feature appears perpendicular to the etching direction in microscopic view. However, for pH > 7 (Fig. 19b), AlN grains are attacked by the basic solutions randomly and rapidly, due to the violent chemical reaction (Reactions 1 and 2). No preference in the grain orientation is ever observed. The etched surface is hill-like in macroscopic view and a coral-like surface with random sharp edges shows up in the microscopic morphology.

4. Conclusions

1. The Y_2O_3-sintered-enhanced AlN substrate is corroded more quickly in basic solutions. The weight loss of AlN is around 70% after corrosion for 5 days and the surface roughness of AlN increase from 10 nm to 7 μm after 3 days immersion in alkaline aqueous solutions. The microscopic morphology appears coral-like with randomly distributed sharp edges.

2. In the corrosion conditions with pH $\leqslant 7$, the etching rates of AlN grains are different with respect to different crystal orientations. The mirror-like flat surface of polished AlN is etched away by only several atomic layers. The clear shapes and various height levels of AlN grains above the etched surface of the substrate result in a jigsaw puzzle morphology. After 5 days etching, the weight loss is negligible, yet the surface roughness increases from 11 nm to 14 nm.

3. An intensive chemical reaction occurs between the AlN, H_2O and alkali, which causes a violent corrosion of AlN in alkaline aqueous solutions. NaOH plays a role of catalytic agent, accelerating the reaction between AlN and H_2O. Na_2O, or $Na_2Al_2O_4 \cdot 6H_2O$, is the intermediate and $Al(OH)_3$ and NH_4OH are the resultant products in this reaction. A series of chemical equations is proposed to elucidate the reactions from the thermodynamic viewpoint.

References

1. T. OSAKA, N. HAGATA, E. NAKAJIMA, I. KOIWA and K. UTSUMI, *J. Electrochem. Soc.* **133** (1986) 2345.
2. K. K. SRIVASTAVA, M. ZULFEQUAR and A. KUMAR, *J. Mater. Sci.* **25** (1990) 2861.
3. K. K. SRIVASTAVA and A. KUMAR, *Mater. Sci. Technol.* **6** (1990) 137.
4. R. B. HESLOP and K. JONES, "Inorganic Chemistry" (Elsevier, Amsterdam, 1976) p. 341.
5. Y. KURIHARA, T. ENDOH and K. YAMADA, *IEEE Trans. Compos. Hybrids Manuf. Technol.* **12** (1989) 330.
6. R. CHANCHANI, *ibid.* **11** (1988) 427.
7. A. ABID, R. BENSALEM and B. J. SEALY, *J. Mater. Sci.* **21** (1986) 1301.
8. Y. PAULEAU, A. BOUTEVILLE, J. J. HANTZPERGUE, J. C. REMY and A. CACHARD, *J. Elect. Chem. Soc. Solid State Sci. Technol.* **129** (1982) 1045.
9. K. M. TAYLOR and E. LENIE, *J. Electrochem. Soc.* **107** (1960) 308.
10. G. LONG and L. M. FOSTER, *J. Am. Ceram. Soc.* **42** (1959) 53.
11. T. OSAKA, T. ASADA, E. NAKAJIMA and I. KOIWA, *J. Electrochem. Soc.* **135** (1988) 2578.
12. L. M. SHEPPARD, *Ceram. Bull.* **69** (1990) 1801.
13. G. A. SLACK and T. F. McNELLY, *J. Crystal Growth* **34** (1976) 263.
14. M. TRONTELJ and D. KOLAR, *J. Mater. Sci.* **8** (1973) 136.
15. N. KURAMOTO and [illegible]. TANIGUCHI, *J. Mater. Sci. Lett.* **3** (1984) 471.
16. B. S. CHIOU and C. D. YOUNG, in "42nd Electronic Components and Technology Conference", San Diego, CA, Electronic Industry Association; Components, Hybrides & Manufacturing Technology Society (IEEE, New York, 1992) p. 692.
17. B. S. CHIOU, J. H. CHANG and J. G. DUH, *Plat. Surf. Fin.* **1** (1993) 65.

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