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Corrosion of silicon nitride ceramics in aqueous HF solutions

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The leaching behaviours of hot-pressed Si_3N_4 ceramics containing Y_2O_3, Al_2O_3 and AlN as additives and hot isostatically pressed Si_3N_4 without additives were studied in 0.1 to 10 M HF aqueous solutions at 50 to 80° C. Silicon and aluminium ions were dissolved into the HF solutions, but yttrium ion did not dissolve at all and formed insoluble YF_3. The dissolution of silicon and aluminium ions was controlled by the surface chemical reaction and the apparent activation energies were 70.5 to 87.6 kJ mol^{-1}, respectively. The corrosion rate increased with increasing degree of crystallization of the grain boundary phases. The corrosion resulted in roughness of the surface and degradation of the fracture strength. Si_3N_4 ceramics containing an amorphous phase at the grain boundaries showed the most excellent resistance to corrosion with HF solution, and kept a fracture strength of above 400 MPa even after leaching 40% of the silicon ions.

1. Introduction

Since the non-oxide ceramics Si_3N_4 and SiC show superior mechanical properties such as fracture strength, fracture toughness, thermal shock resistance and chemical stability, they have received special attention for structural applications not only at high temperature but also at moderate temperature. As for the chemical properties of Si_3N_4 at high temperature, the corrosion of Si_3N_4 by high-temperature oxygen/air, coal slags, alkaline molten salts, etc, has been studied in detail [1], but few preliminary studies have been performed for the corrosion behaviour of Si_3N_4 ceramics at low temperature [1–4]. It was reported that Si_3N_4 ceramics were attacked by HF solution, but were stable in other acidic solutions [1]. Since Si_3N_4 ceramics were fabricated by using additives such as MgO, Y_2O_3, Al_2O_3 and AlN as sintering aids, these additives formed grain boundary phases in Si_3N_4. The physical and chemical properties of Si_3N_4 ceramics depended significantly on the amounts of the grain boundary phases and also their degree of crystallization. For example, it was reported that the fracture strength of Si_3N_4 ceramics with added Y_2O_3 and Al_2O_3 was improved by crystallizing the grain boundary phase [5]. It is considered that the chemical stability would be strongly affected by the grain boundary phase, but no systematic study of the effect of additives on the corrosion behaviour in Si_3N_4 ceramics has been reported. The aims of the present study are to report the effect of additives on the corrosion rate and the strength degradation of Si_3N_4 ceramics in HF aqueous solutions.

2. Experimental procedures

Hot isostatically pressed Si_3N_4 without additives and pressureless-sintered and hot-pressed Si_3N_4 with the addition of about 3.5 wt % Y^{3+} and 3 wt % Al^{3+} as Y_2O_3, Al_2O_3 and AlN were used as corrosion samples. The degree of crystallization of the grain boundary phase was adjusted to 100, 50 and 0% [5]. These samples were denoted SN-0, SN-1, SN-2 and SN-3, respectively, and the characteristics of the samples are summarized in Table I.

All samples were cut into rectangular coupons

TABLE I Characteristics of the samples

Sample	Additive (wt %)		Crystallization of the grain boundary phase (%)	Density (g cm^{-3})	σ_{3b} (MPa)	K_{IC} (MPa m$^{1/2}$)	H_v (GPa)	E (GPa)	Size (mm^3)
	Y	Al							
SN-0	0	0	–	2.67	240	4.0	6.7	129	2 × 5 × 20
SN-1	3.5	3.4	100	3.22	670	6.0	16.0	237	2 × 5 × 13
SN-2	3.6	2.7	50	3.23	605	6.6	15.7	232	2 × 5 × 11
SN-3	3.6	2.4	0	3.22	530	5.7	14.9	209	2 × 5 × 12

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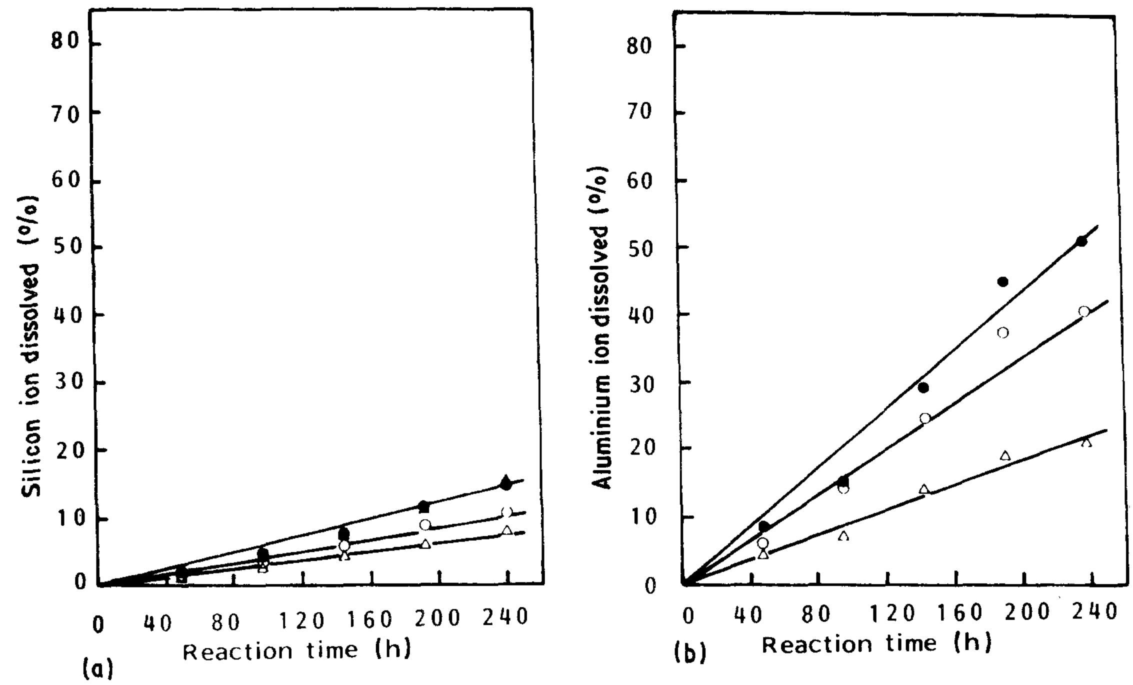

Figure 1 Time dependence of the degree of dissolution of (a) silicon and (b) aluminium ions from various Si_3N_4 ceramics in 1 M HF solutions at 70° C: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

2 mm × 5 mm × 12 mm ~ 20 mm and were polished to a mirror-like surface. In each corrosion test, a specimen and 20 ml of HF solution were put into a sealed polyethylene tube of 10 mm diameter and 150 mm long, then placed in a water bath regulated at the desired temperature. After maintaining the desired temperature and time, the tube was removed from the bath and the sample was quickly taken out and washed in hot water, and then dried. The amounts of silicon, aluminium and yttrium ions leached into the solution were determined by atomic absorption spectrometry. The microstructures of the samples were observed by scanning electron microscopy. The bending strengths of the samples were determined by three-point bending test with a span length of 10 mm and a crosshead speed of 0.5 mm min^{-1}.

3. Results and discussion

The four kinds of Si_3N_4 ceramic were dipped into 1M HF solution for 50 to 240 h at 70° C, and their

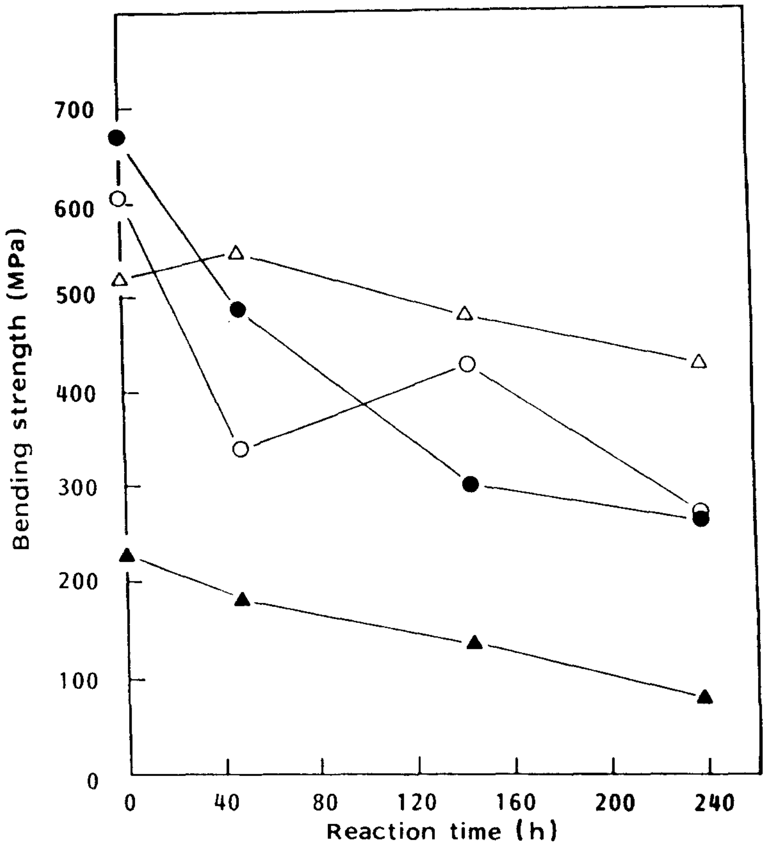

Figure 2 Time dependence of the fracture strength of various Si_3N_4 ceramics in 1 M HF solutions at 70° C: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

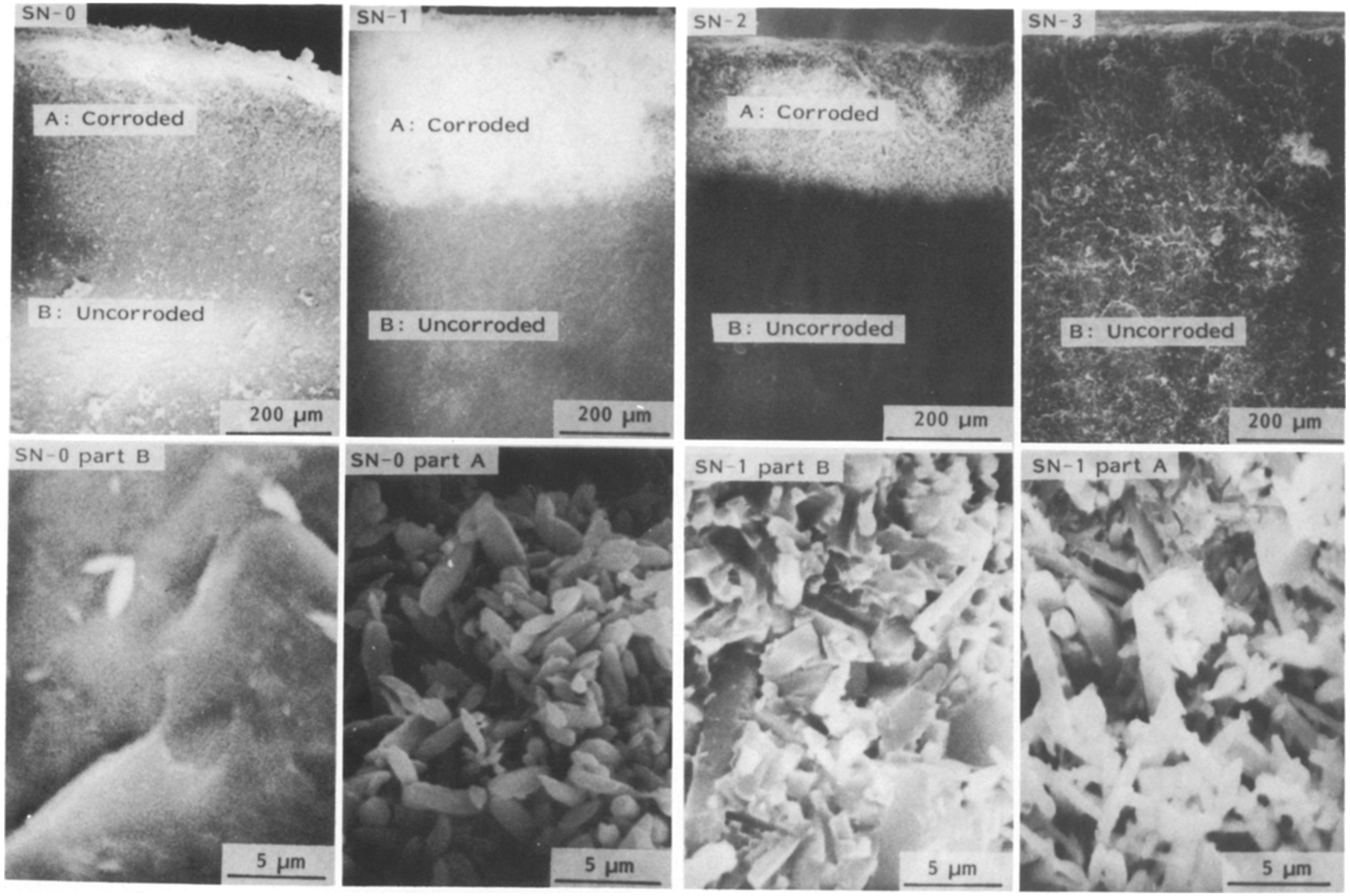

Figure 3 Scanning electron micrographs of cross-sections of Si_3N_4 ceramics corroded in 1 M HF solutions at 70° C for 240 h.

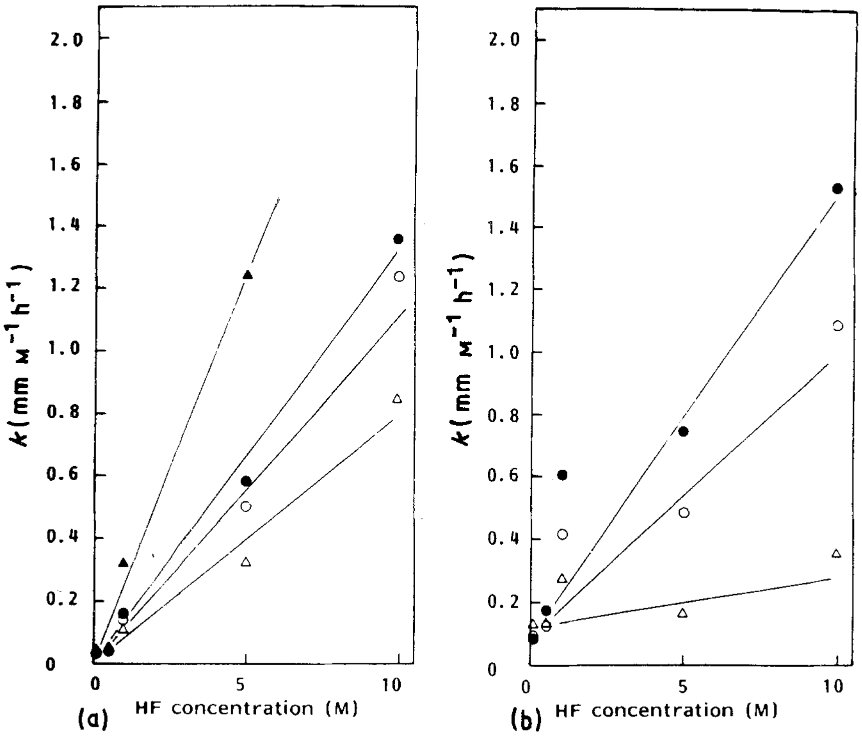

Figure 4 Relationship between the dissolution rate of (a) silicon and (b) aluminium ions and the concentration of HF at 80° C: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

corrosion behaviours were studied. Significant amounts of silicon and aluminium ions were leached into the HF solutions, but no dissolution of yttrium ion was observed. This might be due to the formation of insoluble YF_3. These reactions might be expressed as follows:

$$Si_3N_4 + 18HF = 3SiF_6^{2-} + 4NH_4^+ + 2H^+ \quad (1)$$

$$Al_2O_3 + 6HF = 2Al^{3+} + 6F^- + 3H_2O \quad (2)$$

$$Y_2O_3 + 6HF = 2YF_3 + 3H_2O \quad (3)$$

The time dependences of both the degree of dissolution of silicon and aluminium ions and the fracture strength are shown in Figs 1 and 2. Since the degree of dissolution of each ion was linear with reaction time, the flat-plate model expressed by Equations 4 and 4′ below could be adequately applied to the present dissolution reaction of both silicon and aluminium ions by assuming that the corrosion at the edge was negligible:

$$\frac{-dW}{dt} = k'SC \quad (4)$$

$$x = \frac{W_0 - W}{W_0} = \frac{kCt}{d_0} \quad (4')$$

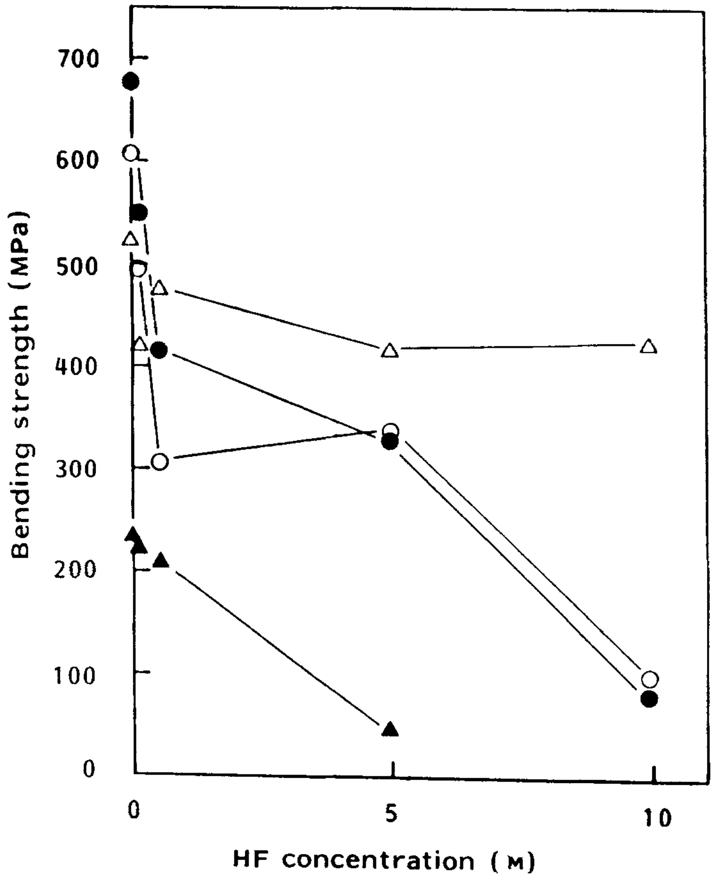

Figure 5 Bending strengths of Si_3N_4 ceramics corroded in various concentration of HF at 80° C for 120 h: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

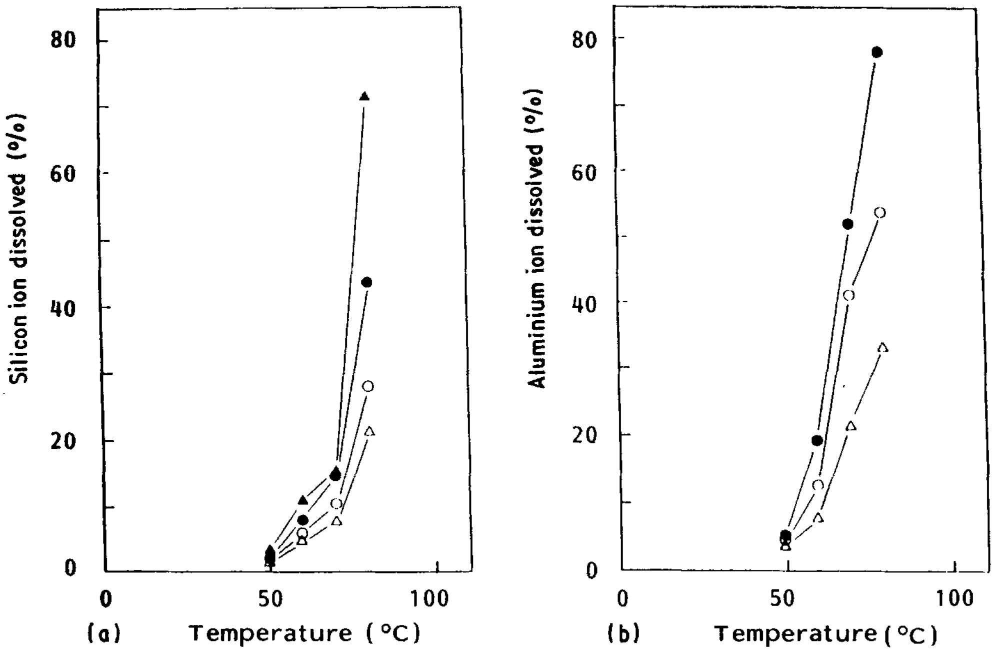

Figure 6 Degree of dissolution of (a) silicon and (b) aluminium ions from various Si_3N_4 ceramics corroded in 1 M HF solution at 50 to 80° C for 240 h: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

where k is the rate constant, W is the weight of the solid at time t, x is the fraction of ions dissolved, S is the surface area of the plate, C is the HF concentration and d_0 is the initial thickness of the sample. As seen in Fig. 1, since the degree of dissolution of aluminium ions was greater than that of silicon ions, aluminium ions at the grain boundaries seemed to dissolve more rapidly than silicon ions in the matrix. The dissolution rates of both ions decreased with decreasing degree of crystallization of the grain boundary phases, and was in the order of SN-0 > SN-1 > SN-2 > SN-3. The fracture strength of each sample was greatly degraded by the corrosion. The fracture strengths of SN-0, SN-1 and SN-2 corroded for 240 h were about 50% of the original values, while the fracture strength of SN-3 corroded for 240 h was 85% of the original value. Since the degradation behaviour of the fracture strength of SN-0 without additives was similar to those of SN-1, SN-2 and SN-3, it was expected that the degradation of the fracture strength was due to the formation of cracks accompanied by the dissolution of silicon ions in the matrix. It was also considered that the amorphous compound at the grain boundary inhibited the dissolution of silicon and

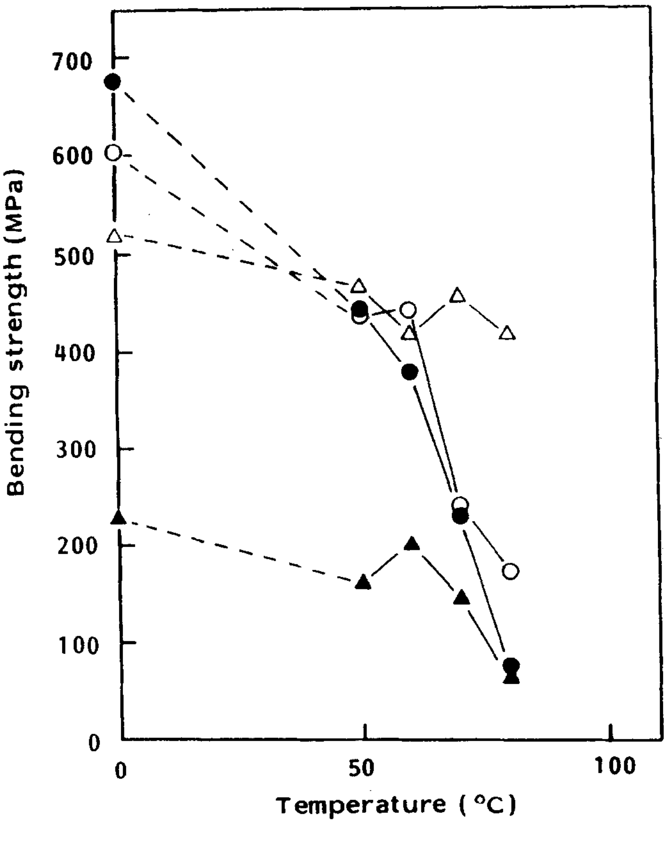

Figure 7 Bending strengths of Si_3N_4 ceramics corroded in 1 M HF solution at 50 to 80° C for 240 h: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

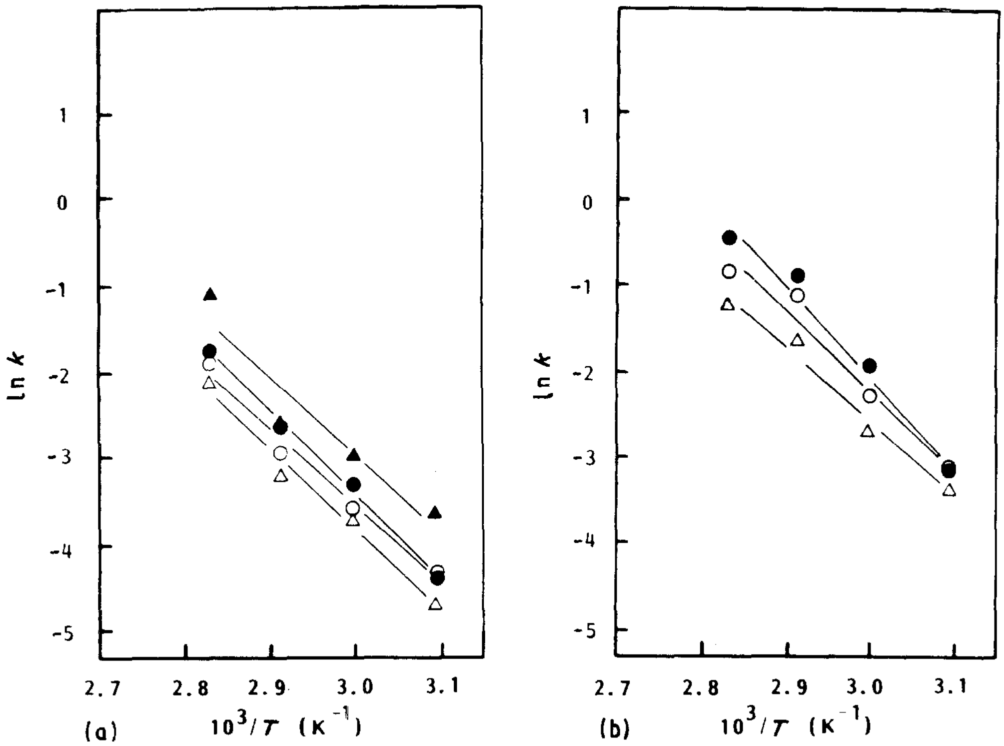

Figure 8 Arrhenius plots of the rate constant of the dissolution of (a) silicon and (b) aluminium ions in 1 M HF solutions: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

aluminium ions and the formation of large pits by corrosion reaction.

Scanning electron micrographs of a cross-section of each sample corroded in 1 M HF solution at 70° C for 240 h are shown in Fig. 3. Extensive roughening of the surface by the formation of large pits was observed. It was found that the corrosion layer thickness of SN-3 was smaller than those of other specimens.

The relationship between the HF concentration and the dissolution rates of silicon and aluminium ions at 80° C is shown in Fig. 4. As expected from Equation 1, the dissolution rate of both ions was first-order with respect to the HF concentration. The bending strengths of samples corroded in various concentrations of HF solutions at 80° C for 120 h are shown in Fig. 5. The bending strength of SN-0, SN-1 and SN-2 decreased with increasing HF concentration, and the bending strength was less than 100 MPa for the samples corroded in 10 M HF solution. On the other hand, the bending strength of SN-3 corroded by 0.1 to 10 M HF was almost constant at 400 to 500 MPa.

The corrosion behaviours of Si_3N_4 ceramics in 1 M HF solutions at 50 to 80° C are summarized in Figs 6 and 7. The dissolution of silicon and aluminium ions and the degradation of the fracture strength were greatly enhanced with increasing temperature. Arrhenius plots of the rate constants for the dissolution of the ions into 1 M HF solution are shown in Fig. 8. All data were well fitted to the straight lines expected from the Arrhenius equation, $k = A\exp(-\Delta E/RT)$. The apparent activation energies, ΔE, and the frequency factors, A, are summarized in Table II. Since the activation energies for the dissolution of silicon and aluminium ions were about 75.4 to 87.6 kJ mol^{-1},

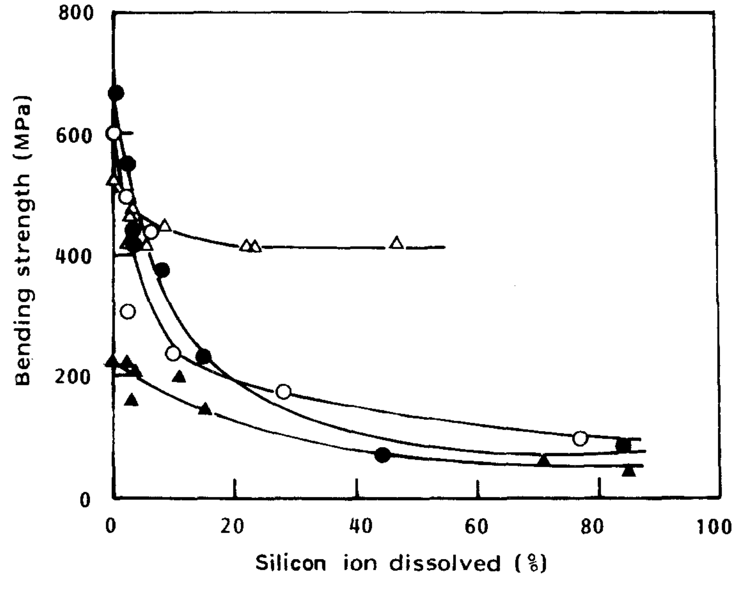

Figure 9 Relationship between the bending strengths of Si_3N_4 ceramics in HF solutions and the degree of dissolution of silicon ions: (▲) SN-0, (●) SN-1, (○) SN-2, (△) SN-3.

TABLE II Apparent activation energies and frequency factors for the dissolution of ions in HF solutions

Sample	Dissolution of silicon ions		Dissolution of aluminium ions	
	ΔE (kJ mol^{-1})	$10^3 A$ (mm M^{-1} h^{-1})	ΔE (kJ mol^{-1})	$10^3 A$ (mm M^{-1} h^{-1})
SN-0	77.4	49.8	–	–
SN-1	75.0	36.5	87.6	42.6
SN-2	74.1	13.6	77.7	42.5
SN-3	77.7	9.20	70.5	34.0

the corrosion reactions seemed to be controlled by the surface chemical reaction between Si_3N_4 ceramics and HF.

The relationship between the degree of dissolution of silicon ions and the fracture strength is shown in Fig. 9. The fracture strength of SN-0, SN-1 and SN-2 degraded to less than 200 MPa until the dissolution of 20% of the silicon ions. On the other hand, SN-3 maintained a fracture strength of more than 400 MPa, even after dissolving 50% of the silicon ions. It is considered that the corrosion reaction proceeded at structural discontinuities of the high-energy sites at first, and resulted in the formation of large pits [6]. Therefore, the excellent resistance of SN-3 to corrosive attack by HF might be attributed to many fewer structural inhomogeneities in the amorphous compound located at the grain boundaries.

4. Conclusions

From the results of corrosion tests of Si_3N_4 ceramics with added Y_2O_3, Al_2O_3 and AlN, the following conclusions may be drawn. Si_3N_4 ceramics suffered serious corrosive attack by HF solution. Silicon ions in the matrix and aluminium ions at the grain boundaries dissolved linearly with reaction time, but yttrium ions did not dissolve at all. The corrosion rate was first-order with respect to the HF concentration and increased with increasing degree of crystallization of the grain boundary phases. Si_3N_4 ceramics with amorphous phases at the grain boundaries showed excellent resistance to corrosive attack by HF solutions.

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