

Fig. 2. Calcium deposition vs weight of porous glass; glass was treated in 100 mL of NaOH solution with 0.001 mol  $\text{CaCl}_2$  addition at  $80^\circ\text{C}$  for 2 h.

Porous glass was crushed into small particles (20 to 35 mesh), etched with 5% HF for 2 min to remove surface contaminants, and dried in an oven at  $80^\circ\text{C}$ . Different weights of porous glass were immersed in 100 mL of NaOH solutions with various concentrations. Calcium chloride (0.001 mol) was added to each solution and the solution was oven-heated at  $80^\circ\text{C}$  for 2 h; a preliminary experiment showed that 2 h were sufficient to reach equilibrium.

The calcium concentration remaining in the solution after treatment was determined by atomic absorption analysis. The deposition, indicated by the ratio of calcium content remaining in a solution ( $C$ ) to the initial calcium content ( $C_0$ ), is shown in Fig. 2. Even without alkali solution, a small amount of calcium is deposited; this deposition probably comes from the nature of porous glass as a trace ion getter.<sup>6,7</sup> In alkaline solutions, the calcium deposition increases as the weight or surface area of porous glass increases. Also, the higher the alkalinity of a solution, the more calcium is deposited, suggesting that the reaction between calcium and silica is accelerated in more alkaline environments. When the higher calcium concentration or the larger amount of porous glass was used, a fleecy precipitate appeared in the solution. This precipitate was separated and dried in an oven. Measuring it by ir analysis showed silicate compound peaks and an X-ray diffraction pattern similar to that reported as C-S-H(I) ( $0.85\text{--}1.5\text{CaO}\cdot\text{SiO}_2\cdot 0.5\text{--}2.5\text{H}_2\text{O}$ ) by Taylor,<sup>8</sup> with other peaks identified as  $\text{CaCO}_3$  and other types of calcium silicate hydrates;  $\text{CaCO}_3$  may be a by-product in the drying process. The precipitate is probably a reaction product of calcium

and silica and entered the solution from the glass surface. The AES spectra also showed a calcium signal on the silica glass surface after the alkali solution treatment with  $\text{CaCl}_2$  (Fig. 3). In these spectra, signals assigned to Cl and C came from surface contaminants which are usually observed on a glass surface<sup>9</sup> and a signal of Cl was enhanced in spectrum (b) because of the addition of  $\text{CaCl}_2$ .

It was revealed that calcium in an alkaline environment reacts with glass surfaces to form insoluble calcium silicate compounds. This reaction can be intuitively speculated by checking glass surfaces after etching with and without calcium; the former was hazy, suggesting coverage with some film, whereas the latter was still clear. The amount of calcium deposited on the glass surface can be roughly estimated from the surface area of the porous glass as  $1.0\text{ Ca/nm}^2$  for 0.01N NaOH, 2.8 for 0.05N NaOH, and 3.6 for 0.1N NaOH.

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## The System $\text{Si}_3\text{N}_4\text{--SiO}_2\text{--ZrN--ZrO}_2$

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ZIRCONIUM DIOXIDE has been reported to be an effective additive for hot-pressing silicon nitride ceramics.<sup>1</sup> However, the reaction between these two compounds has not been studied. The present note reports the reactions between two pairs of compounds:  $\text{Si}_3\text{N}_4 + \text{ZrO}_2$  and  $\text{SiO}_2 + \text{ZrN}$ .

Appropriate amounts of chemicals were weighed and mixed for 1 h in a hard metal mill under acetone. After drying, the mixtures were pressed under a uniaxial pressure of 35 MPa. The pressed specimens were fired in BN-lined graphite crucibles in a graphite resistance-heated furnace. A mild flow of nitrogen was introduced during firing. Weight change after firing was recorded and the phases present were analyzed by X-ray diffraction (XRD). The relative amounts of different phases were compared with standard mixtures using XRD peak heights. A diffraction unit\* with monochromated (graphite)  $\text{CuK}\alpha$  radiation was used.

A mixture of 50 mol%  $\text{Si}_3\text{N}_4$  and 50 mol%  $\text{ZrO}_2$  was heat-treated at  $1400^\circ$ ,  $1600^\circ$ , and  $1700^\circ\text{C}$  for different lengths of time. No reaction was observed at  $1400^\circ\text{C}$ . The phases present after heat

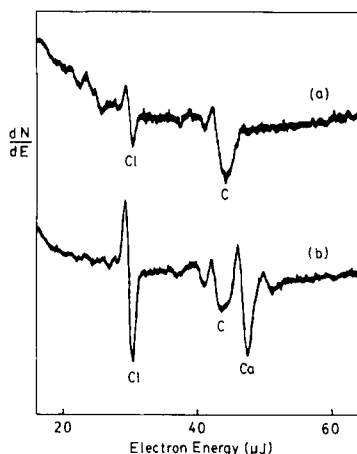


Fig. 3. AES spectra for silica slide glass etched in 100 mL 2.78N NaOH at  $80^\circ\text{C}$  for 12 h (a) without  $\text{CaCl}_2$  and (b) with 0.003 mol  $\text{CaCl}_2$  addition.

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treatment at 1600° and 1700°C are in Fig. 1. Weight loss was considered as the gas species in the figure. These results indicate that  $\text{Si}_3\text{N}_4$  and  $\text{ZrO}_2$  reacted, giving  $\text{ZrN}$  and gaseous species;  $\text{Si}_2\text{N}_2\text{O}$  was the intermediate phase.

Mixtures of 50 mol%  $\text{SiO}_2$  and 50 mol%  $\text{ZrN}$  were prepared in the same way and heat-treated at 1400°, 1600°, and 1700°C. No reaction was observed at 1400°C. The results for 1600° and 1700°C heat treatments are given in Fig. 2. The reaction at 1600°C was slow; it

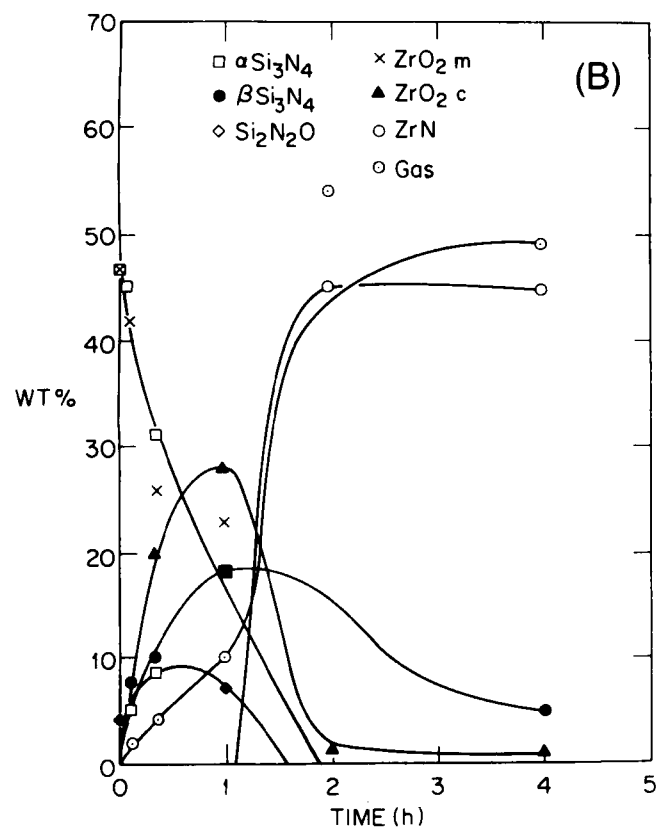
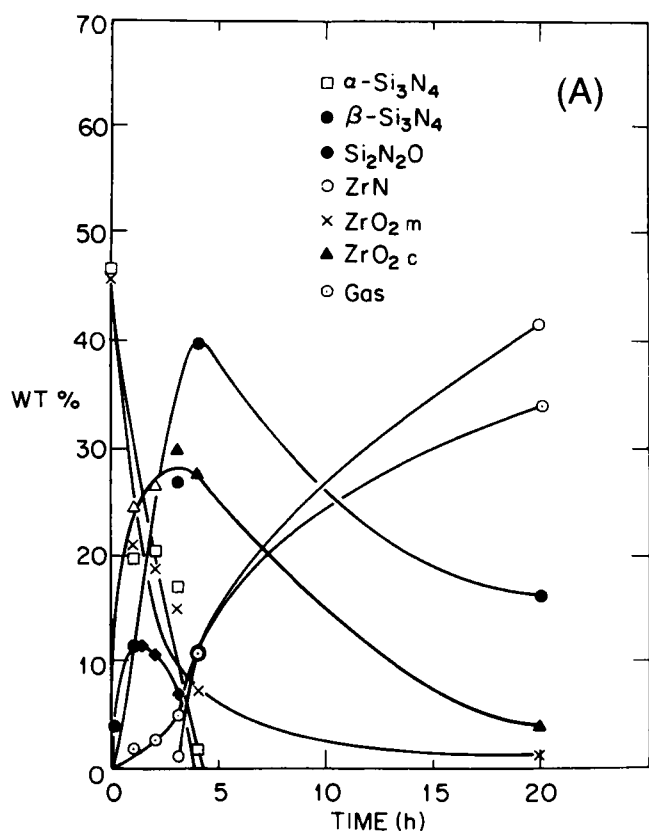


Fig. 1. Time dependence of phases present after sintering of  $\text{Si}_3\text{N}_4$ - $\text{ZrO}_2$  mixtures at (A) 1600° and (B) 1700°C.

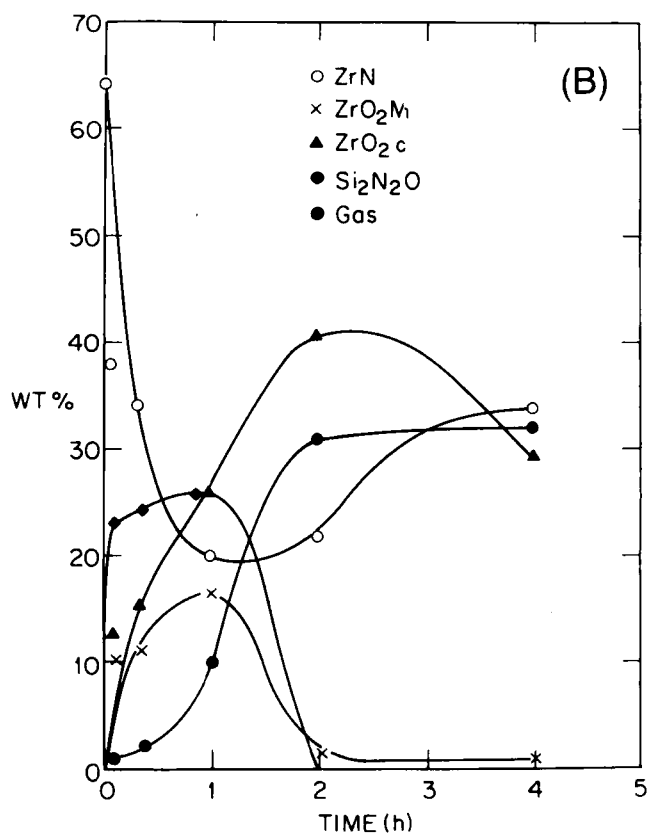
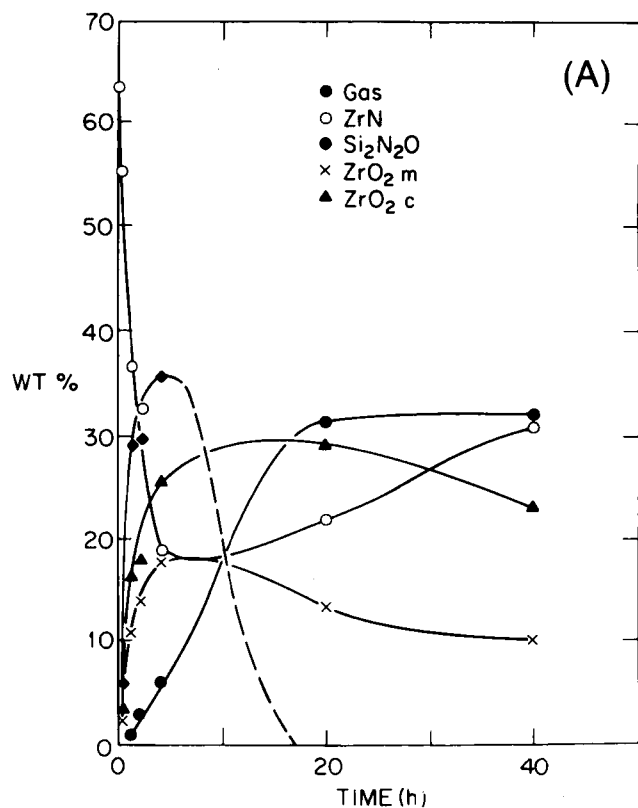
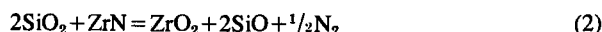


Fig. 2. Time dependence of phases present after sintering of  $\text{SiO}_2$ - $\text{ZrN}$  mixtures at (A) 1600° and (B) 1700°C.

was not completed after 40 h. However, from the trend it may be concluded that  $\text{ZrO}_2$  forms as an intermediate phase and  $\text{ZrN}$  will be the solid end product when fired in flowing nitrogen. These results suggest that the following reactions take place:



However, the actual reactions would be more complicated.

A computer program is being set up to calculate all gaseous species present in equilibrium with the condensed phase under a given condition in this system, using known free energy data.<sup>2</sup> The program used is the same as that suggested by Eriksson,<sup>3</sup> with modifications to suit local computers.

<sup>1</sup>Y. Inomata, Y. Hasegawa, and T. Matsuyama, "Role of  $\text{ZrO}_2$  as a Hot-Pressing Aid for  $\text{Si}_3\text{N}_4$ ," *Yogyo Kyokai Shi*, **84** [12] 600–604 (1976).

<sup>2</sup>(a) JANAF Thermochemical Tables, 2d ed. Edited by D. R. Stull and H. Prophet. No. NSRDS-NBS-37, U.S. Government Printing Office, Washington, D.C., 1971.

(b) A. Henry; pp. 183–85 in *Thermodynamics of Silicon Nitride and Oxynitride*. Edited by F. L. Riley. Noordhoff, Leyden, The Netherlands, 1977.

<sup>3</sup>G. Eriksson, "Thermodynamic Studies of High Temperature Equilibria," *Chemica Scripta*, **8**, 100–103 (1975).

## Effect of Carbon Impurity on the Thermal Degradation of an $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ Ceramic

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ALTHOUGH  $\text{Y}_2\text{O}_3$ -doped  $\text{Si}_3\text{N}_4$  exhibits improved high-temperature ( $>1300^\circ\text{C}$ ) properties, as compared with  $\text{MgO}$ -doped  $\text{Si}_3\text{N}_4$ , severe degradation of  $\text{Y}_2\text{O}_3$ -doped  $\text{Si}_3\text{N}_4$  occurs in an oxidizing environment at intermediate temperatures ( $\approx 1000^\circ\text{C}$ ). This effect has been shown<sup>1</sup> to be related to the existence of certain quaternary compounds in the material, e.g.  $\text{Si}_3\text{Y}_2\text{O}_3\text{N}_4$ ,  $\text{YSiO}_2\text{N}$ ,  $\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$ , and  $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$  (N-melilite, *K*, *H*, and *J* phase, respectively). To alleviate this problem for an  $\text{Si}_3\text{N}_4$  material containing 13 wt%  $\text{Y}_2\text{O}_3$ , Gazza *et al.*<sup>2</sup> reported a method involving post-heat treatment of specimens in a nitriding environment. Further studies with  $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$  compounds suggest that the instability of these compounds, principally  $\text{Si}_3\text{Y}_2\text{O}_3\text{N}_4$  in air at  $\approx 1000^\circ\text{C}$ , is greatly influenced by the presence of carbon in the material.

Two commercial  $\text{Si}_3\text{N}_4$  powders\* were used for producing the  $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$  compounds (Table I). Both powders were individually mixed with  $\text{Y}_2\text{O}_3$ <sup>†</sup> in a 1:1 molar ratio and ball-milled in ethanol for 20 h using polyethylene containers and WC balls. Chemical

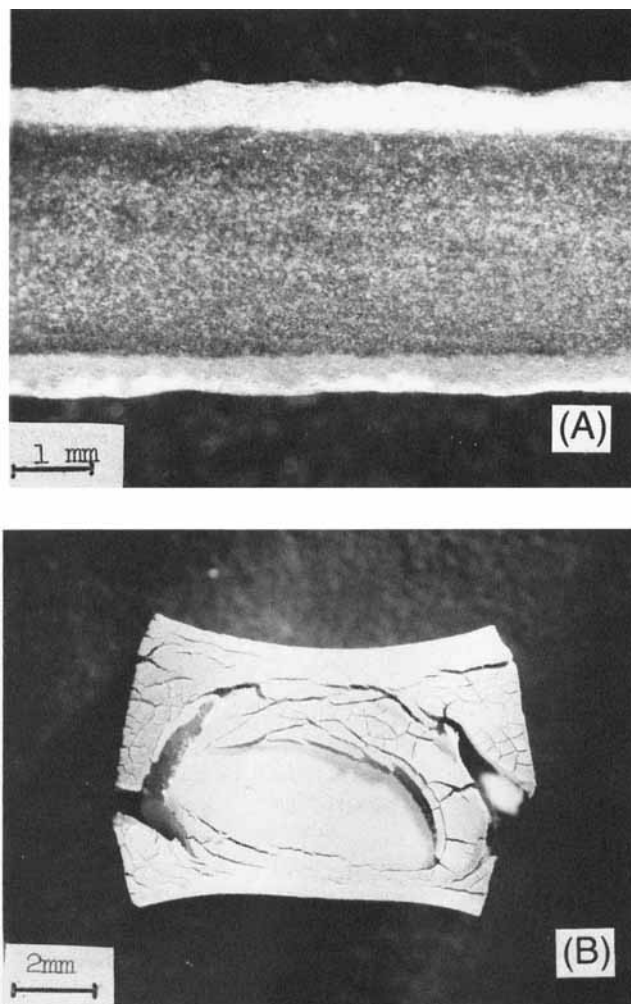


Fig. 1.  $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$  compounds (from powder B) after exposure at  $1000^\circ\text{C}$  in air. (A) B1 material, showing preferred oxidation (white layer) at as-hot-pressed surfaces after 117 h and (B) B3 material (2 wt% SiC) after 90 h.

analysis of the milled powder showed only 0.8 wt% tungsten in the samples. Therefore, the maximum amount of carbon introduced by milling is  $<0.06\%$ .

The milled and dried powders were hot-pressed in graphite dies for 90 min at  $1750^\circ\text{C}$  in  $\text{N}_2$  with an applied pressure of  $30 \text{ MN/m}^2$ . Some test bars for oxidation measurements were cut leaving as-pressed surfaces on opposite faces, whereas all faces were ground on the remaining specimens. The oxidation behavior was studied at  $700^\circ$  to  $1400^\circ\text{C}$  in air. During the oxidation treatment the samples rested on hot-pressed SiC pedestals with sharp edges.

X-ray analysis showed that all the hot-pressed materials studied were principally  $\text{Si}_3\text{Y}_2\text{O}_3\text{N}_4$  (N-melilite) with weak traces of  $\text{YSiO}_2\text{N}$  (*K* phase) present. The X-ray diffraction data obtained were in good agreement with those reported by Rae *et al.*<sup>3</sup> and Lange *et al.*<sup>4</sup> for N-melilite.

Initial oxidation experiments were conducted with specimens hot-pressed from powders A and B with  $\text{Y}_2\text{O}_3$  added (materials A and B1). Specimens tested had two as-cut and two as-pressed surfaces. Visually, the as-cut test specimens after oxidation at  $1000^\circ\text{C}$  in air appeared similar to that previously reported.<sup>1,5</sup> However, there was a peculiarity in the oxidation effect on the B1 material (Fig. 1(A)); only the surfaces which were in contact with the graphite die during hot-pressing showed signs of volume expansion and cracking. This result suggests that a reaction layer produced during hot-pressing strongly influences the oxidation behavior. The tests were repeated with A and B1 specimens in which the as-pressed surfaces were ground prior to testing. Specimens of material

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\*One (powder A) from H. C. Starck, Inc., Goslar, Federal Republic of Germany, and one (powder B) from GTE Sylvania, Inc., Towanda, Pa.

†Molycorp, White Plains, N.Y.

Table I. Impurity Concentrations of Starting  $\text{Si}_3\text{N}_4$  Powders

Impurities in unmilled powders	$\text{Si}_3\text{N}_4$ *A	$\text{Si}_3\text{N}_4$ <sup>†</sup> B
Al (ppm)	1800	$<30$
Fe (ppm)	700	$<10$
Ca (ppm)	1200	$<30$
Mg (ppm)	300	$<40$
Oxygen (%)	1.1	2.6
Carbon (%)	0.6	
Free Si (%)	$<2$	

\*H. C. Starck. †GTE Sylvania, Inc.