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Effect of selected impurities on the high temperature mechanical properties of hot-pressed silicon nitride

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The effect of impurities on the high temperature mechanical properties of hot-pressed silicon nitride has been determined. Selected impurity additions were made to both relatively pure α-phase and β-phase silicon nitride starting powders. These powders were hot-pressed to full density using 5 wt % MgO as the pressive additive. The silicon nitride hot-pressed from the α-phase powder exhibited higher strength at both 25 and 1400° C than that fabricated from the β-phase powder. The impurity additions had no effect on the room temperature mechanical properties. The CaO additions had the most significant effect on the high temperature mechanical properties. In both the material hot-pressed from the α-phase and β-phase powders, increasing CaO additions severely reduced the high temperature strength and increased the amount of non-elastic deformation observed prior to fracture. Although alkali additions (Na_2CO_3, Li_2CO_3, K_2CO_3) also tended to have the same effects as the CaO, the high volatility of these compounds resulted in a much reduced concentration in the hot-pressed material, thus minimizing somewhat their tendency to enhance the high temperature strength degradation. The Fe_2O_3 and Al_2O_3 had no apparent effect on the high temperature mechanical properties.

1. Introduction

Hot-pressed silicon nitride is a prime candidate for gas turbine and other high temperature structural applications. Although fabricated with a room temperature flexural strength exceeding 700 MN m^{-2} (> 100 000 psi) [1, 4], its strength rapidly decreases at elevated temperatures [2–4]. At these higher temperatures the load–deflection curves cease to be linear and a non-elastic permanent deformation occurs. Both the strength degradation and non-elastic deformation are more pronounced as the loading rate is decreased [3, 4]. Previous investigators have related the high temperature mechanical properties to the total impurity content [2] and/or calcium content [4] of commercial material, but no systematic study has been made to determine the effect of individual impurities.

Silicon nitride is currently fabricated using MgO (1 to 5 wt %) as a hot-pressing additive which is believed to react with the SiO_2 layer on each nitride particle to form a liquid magnesium silicate which results in full densification due to liquid phase sintering [5, 6]. On cooling, this liquid is believed to remain as a glassy grain-boundary phase. At high temperatures, fracture is preceeded by sub-critical crack growth due to grain-boundary sliding [4]. Any impurities that decrease the viscosity of the glassy grain-boundary phase would tend to accelerate this high strength degradation and increase the rate of non-elastic deformation prior to fracture.

Auger spectroscopy on freshly fractured Si_3N_4 surfaces has determined that Mg, O, Ca, Na and K are found predominantly in the grain boundaries while Al and Fe are evenly distributed throughout the material [7]. Those elements concentrated in the assumed glassy grain-boundary phase may, therefore, control the high temperature mechanical properties.

The purpose of this investigation was to determine systematically the effects of individual impurity additions on the high temperature mechanical properties of silicon nitride. A high purity β-phase silicon nitride powder was purchased commercially and the technique to produce a high-purity α-phase powder was developed. Selected cation impurities commonly observed in both Si and Si_3N_4 powders were incorporated into both the α- and β-phase silicon nitride starting poweders. After hot-pressing to full density with the aid of high purity MgO, flexural strength measurements were made at both 25 and 1400° C Flexural creep tests were also carried out on selected specimens.

2. Experimental

At present the highest strength silicon nitride is obtained when α-Si_3N_4 rather than β-Si_3N_4 is used as the starting powder [8, 9]. The reasons for this are not completely understood at present but the microstructure of silicon nitride hot-pressed from α-phase powder has many elongated grains and a high fracture toughness while starting with the β-Si_3N_4 results in an equi-axed grain morphology, a comparatively low fracture toughness, and a lower strength material [8]. A β-Si_3N_4 powder* containing only 180 ppm Ca and no detectable alkaline elements was obtained. A α-Si_3N_4 powder with only 160 ppm Ca and no detectable alkaline elements was produced at Westinghouse Laboratories. Powder composition is presented in Table I. The phase and cation impurity content of both powders were determined by X-ray diffraction and spectrographic analysis, respectively.

High purity MgO† (5 wt %) was used as the hot-pressing additive. Selected impurity additions in the form of oxides or carbonates were made prior to milling the blended powders in plastic bottles with *t*-butanol and tungsten carbide balls for 16 h. The powder was dried and mixed with a mortar and pestle to break up any large agglomerates. The powder was then hot-pressed for 2 h at 1750° C, 276.MN m^{-2} (4000 psi) in a nitrogen atmosphere to form an ~ 5 cm diameter, ~ 1 cm thick disc. In all cases, immersion densities > 98.5% of theoretical were obtained.

TABLE I Spectrochemical analyses of Si_3N_4 starting powders (wt % based on stoichiometric Si_3N_4)

	Westinghouse Si_3N_4 (> 90% α-phase)	Cerac Si_3N_4 (< 90% β-phase)
Al	0.08	0.10
Ag	< 0.001	< 0.001
B	0.001	0.0025
Ca	0.016	0.018
Cr	0.01	< 0.01
Fe	> 0.1	0.03
Mg	0.001	0.001
Mn	0.05	0.002
Mo	< 0.003	0.003
Ni	< 0.01	0.0015
Pb	< 0.01	< 0.003
Sb	< 0.01	< 0.01
Sn	< 0.01	< 0.01
Ti	0.01	< 0.003
V	0.0005	< 0.002
Zn	< 0.01	< 0.003

Six flexural strength specimens (~ 0.3 cm x 0.6 cm x 3.0 cm) were cut from each disc and ground with a 320 grit diamond wheel. Flexural strength measurements were performed in four-point loading as previously described [4]. Three specimens were fractured at room temperature and three at 1400° C in air. Owing to the small number of specimens, a single stressing rate (~ 1000 MN m^{-2} min^{-1}) was used at 1400° C.‡ Flexural creep tests in four-point loading were carried out on similar sized specimens. These were performed at 1400° C with an initial applied outer fibre stress of 103.4 MN m^{-2} (15 000 psi) as calculated from the elastic beam equation. The mid-span deflection of the bar specimen was measured optically through a view port in the furnace with a telescope-cathetometer arrangement. The outer fibre strain was calculated from the measured deflections. The total strain after the experiment was calculated by a direct measurement of the specimen's curvature. This value was ~ 10% less than the *in situ* optical measurement taken just prior to unloading.

3. Results and discussion

The results of the room temperature flexural tests on material hot-pressed from the high purity β-phase powder are shown in Fig. 1. The impurity additions are seen to have little or no effect on the room temperature strength. All the points fall within the scatter of 380 MN m^{-2} (55 000

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* Cerac, Inc.

† United Mineral & Chemical Corp, NY, (< 200 ppm total cation impurities).

‡ Owing to the slow growth of cracks at high temperature, the strength of Si_3N_4 is dependent on stressing rate [4].

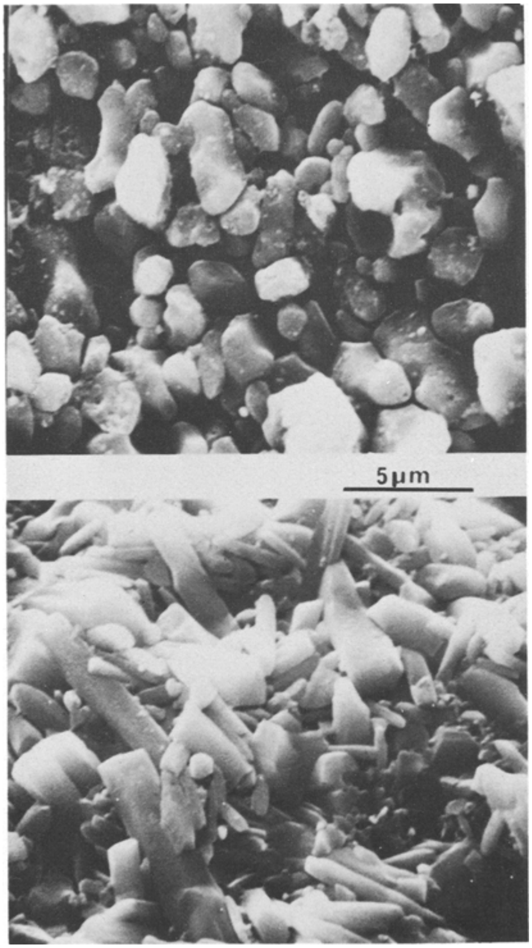

Figure 3 SEM micrographs of etched Si_3N_4 fracture surfaces for material hot-pressed with (upper) β-phase powder and (lower) α-phase powder.

The difference in the microstructures of material hot-pressed from the two starting powders is shown in Fig. 3. These fracture surfaces were etched in concentrated (48%) HF for 24 h to dissolve the silicate boundary phase and expose the Si_3N_4 grains. The β-phase powder produced a microstructure of equi-axed grains of 1 to 4 μm diameter. The α-phase powder, however, resulted in a hot-pressed material consisting of rod-shaped grains.

The results of flexural strength measurements of silicon nitride hot-pressed from the high purity α-phase powder are shown in Fig. 4. The impurity additions had no apparent effect on the room temperature strength. These data represent the average of three flexural tests and the vertical lines through individual points extend from the lowest to the highest values obtained. Somewhat more complex behaviour was obtained at 1400° C. The Al_2O_3 and Fe_2O_3 additions had no effect on the high temperature strength. The alkali additions (Li_2O, K_2O, Na_2O) seemed to reduce the high temperature strength but the effect may have been reduced substantially by losses due to the high volatility of these compounds. More specifically, although 0.113 wt% K was added to the powder (as K_2CO_3) no K was detected (< 0.01 wt%) by spectrochemical analysis. Thus, one cannot be certain of the effect of K_2O on the high temperature strength since it must have volatilized during hot-pressing. For the case of Li, 0.076 wt% was added but analysis revealed that 0.035 wt% Li remained in the hot-pressed disc. Nevertheless, the 1400° C flexural strength was reduced from about 481 MN m^{-2} (63 000 psi) to 350 MN m^{-2} (~ 50 000 psi). Similarly, while 0.217% Na was added only 0.025% wt% remained after hot-pressing. This quantity of Na, however, still produced a decrease in the 1400° C strength to 360 MN m^{-2} (~ 51 000 psi). It appears that while the alkali additions did tend to reduce the high temperature strength they also tend to volatilize during hot-pressing, thus minimizing the effect.

The CaO additions, however, remained totally in the hot-pressed product and had a very pronounced effect on the high temperature mechanical properties. As shown in Fig. 4, the strength was reduced continuously from 441 MN m^{-2} (~ 63 000 psi) to 210 MN m^{-2} (~ 30 000 psi) by additions of CaO up to 0.2 wt%. The effect of CaO on the high temperature creep behaviour is

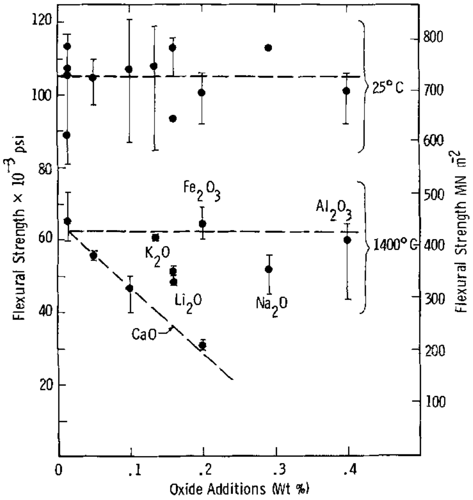

Figure 4 Effect of impurity additions on four-point flexural strength of Si_3N_4 hot-pressed from α-phase powder.

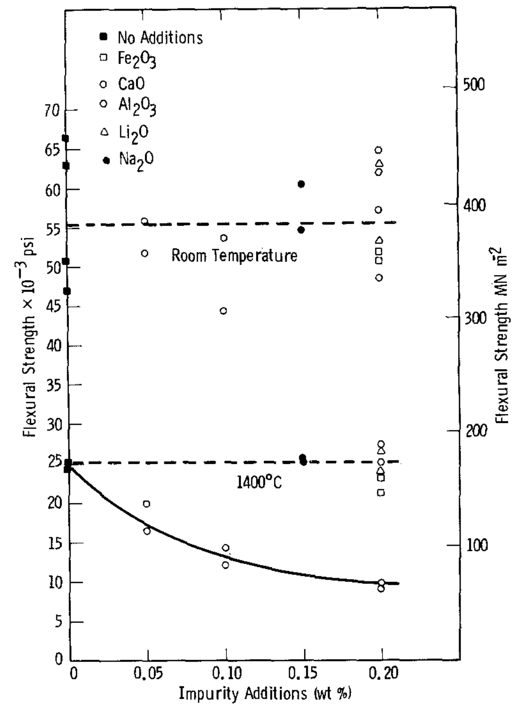

Figure 1 Effect of impurity additions on four-point flexural strength of Si_3N_4 hot-pressed from β-phase powder.

psi) ± 18%. Each point represents the average of three specimens from a single disc.

The most interesting results are those of the 1400° C flexural tests also shown in Fig. 1. Both Al_2O_3 and Fe_2O_3 had no significant effect on the high temperature strength. Surprisingly, the Na, which was shown by the Auger analysis [7] to be concentrated in the grain boundaries, and the Li, which similarly might be expected in the grain boundaries also had no apparent effect on the high temperature strength. However, spectrographic analysis of the hot-pressed material indicated a reduction in Li content to ~ 0.02% as compared to 0.093% added prior to hot-pressing; Na ($\ll 0.01\%$) was not detectable. The loss is attributed to the high volatility of the Li_2O and Na_2O under hot-press conditions.

CaO, however, does have a very significant effect on the high temperature strength of silicon nitride as shown in Fig. 1. With increasing additions of CaO, the strength decreases from a base line value of 172 MN m^{-2} (25 000 psi) to 62 MN m^{-2} (9000 psi) for an addition of 0.2 wt % CaO. The effect of CaO on the high temperature deformation is also quite apparent from the load–deflection curves as shown in Fig. 2. This figure presents the actual load–deflection curves from representative flexural specimens containing four different CaO contents. Since the samples vary slightly in size, the actual fracture stress is indicated adjacent to the appropriate curve. Note, that not only does the flexural strength decrease with increasing CaO content, but the non-elastic deformation appears to be much more pronounced This deformation behaviour is not only due to a change in the compliance of the specimen as slow crack growth occurs (by decreasing the load-bearing cross-section), but also it is a result of a homogeneous deformation within the specimen. On unloading a specimen just prior to fracture, one can easily observe both the permanent set due to homogeneous non-elastic deformation and the crack extending part way through the specimen. Thus, it appears that the CaO additions reduce the viscosity of the assumed glassy boundary phase which increases the materials's susceptibility to sub-critical crack growth to reduce its high temperature strength and increases the ease of homogeneous, non-elastic deformation by boundary separation and sliding.

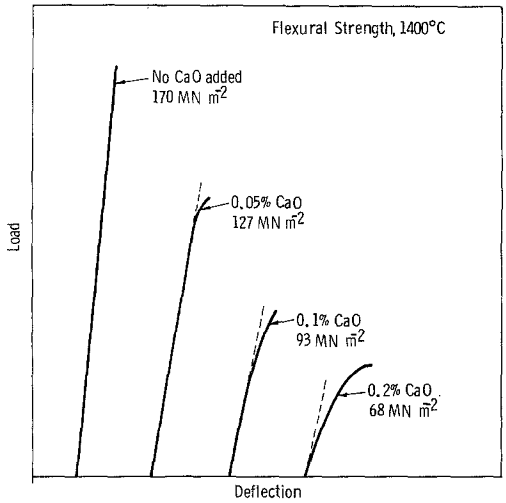

Figure 2 Load–deflection curves for Si_3N_4 with varying CaO additions prior to hot-pressing.

As mentioned previously, a higher strength silicon nitride is obtained when a α-Si_3N_4 rather than β-Si_3N_4 was used as the starting powder. The α-phase starting powder used here resulted in a hot-pressed material with a flexural strength of 735 MN m^{-2} (~ 105 000 psi) at room temperature and 421 MN m^{-2} (~ 63 000 psi) at 1400° C. As reported above, silicon nitride hot-pressed from the β-phase starting power exhibited much lower strengths at both temperatures.

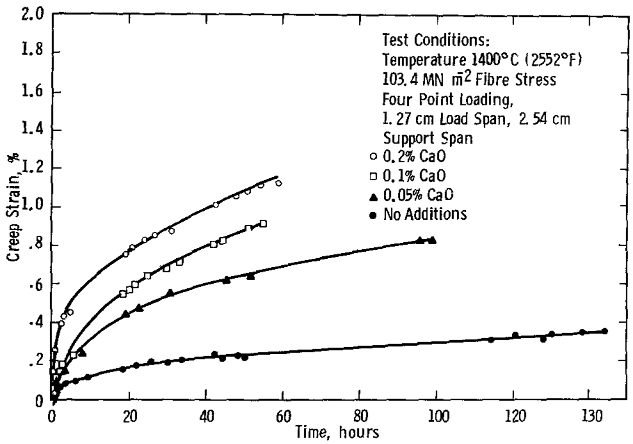

Figure 5 Flexural creep measurements at 1400° C as a function of CaO content.

shown in Fig. 5. These are the results of four-point flexural creep measurements made on four samples with varying Ca contents. Not surprisingly, the creep resistance decreased quite regularly as the CaO content increased. This is consistent with the observed decrease in the 1400° C strength and increase in the amount of non-elastic deformation that occurred prior to fracture as the calcium content was increased in both α and β powder. These results suggest that the CaO, Li_2O, Na_2O and K_2O decrease the viscosity of the glassy boundary phase at elevated temperatures thus increasing the amount of non-elastic deformation and reducing the high temperature strength.

4. Conclusions

(1) Silicon nitride hot-pressed from α-phase powder with 5% MgO additions results in a material with higher strengths at both room temperature and 1400° C than material fabricated similarly from a β-phase powder.

(2) Impurities such as Al_2O_3, Fe_2O_3, CaO, Li_2O, K_2O, Na_2O have no apparent effect on the room temperature mechanical properties of hot-pressed silicon nitride.

(3) CaO additions significantly increase the amount of non-elastic deformation occurring prior to fracture and decrease the flexural strength at elevated temperatures (1400° C). Additions of Li_2O, K_2O and Na_2O seem to have the same effects as the CaO but these compounds tend to volatilize significantly during hot-pressing thus reducing their effect.

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