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EFFECT OF SELECTED IMPURITIES ON THE HIGH
TEMPERATURE MECHANICAL PROPERTIES OF HOT-PRESSED
SILICON NITRIDE

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Westinghouse Electric Corporation

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Technical Report #2, October 18, 1974

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EFFECT OF SELECTED IMPURITIES ON THE HIGH TEMPERATURE
MECHANICAL PROPERTIES OF HOT-PRESSED SILICON NITRIDE

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Pittsburgh, Pennsylvania 15235ABSTRACT

The strength of commercial hot-pressed silicon nitride has been shown to degrade severely at elevated temperatures. As the temperature is increased the amount of non-elastic deformation occurring prior to fracture has been found to increase significantly. This reduction in high temperature strength and creep resistance is believed to be associated with impurities. Selected impurities were therefore added as oxides or carbonates (Al_2O_3 , CaO , Fe_2O_3 , Li_2CO_3 and Na_2CO_3) to both a relatively pure α -phase silicon nitride powder and a relatively pure β -phase silicon nitride starting powder. These powders were then hot-pressed to full density using 5 wt % MgO as the pressing additive. The silicon nitride hot-pressed from the α -phase powder exhibits higher strength at both 25°C 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 that from the β -phase silicon nitride powders, increasing amounts of CaO severely reduced the high temperature strength and increased the amount of non-elastic deformation observed prior to fracture. Although additions of the alkali compounds (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 ($> 100,000 \text{ psi}$),⁽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 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 on the high temperature mechanical properties.

Silicon nitride is currently fabricated using MgO (1 to 5 wt %) as a hot-pressing additive that 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 preceded 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 temperature strength degradation and increase the amount 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 systematically determine the effects of individual impurity additions on the high temperature mechanical properties. A high purity silicon nitride starting powder was necessarily a pre-requisite for any such impurity study. A high purity β -phase powder was purchased commercially and then a technique was developed to produce a high purity α -phase powder since none was available commercially. Selected cation impurities commonly observed in both Si and Si_3N_4 powders were incorporated as either oxides or carbonates (viz., CaO , Al_2O_3 , Fe_2O_3 , K_2CO_3 , Li_2CO_3 and Na_2CO_3) to both the α and β -phase silicon nitride starting powders. 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 the β - Si_3N_4 results in an equiaxed grain morphology, a comparatively low fracture toughness, and a lower strength material.⁽⁸⁾ A relatively pure β - Si_3N_4 powder was obtained* containing only 180 ppm Ca and no detectable alkaline elements. A relatively pure α - Si_3N_4 powder was produced at Westinghouse Laboratories with only 160 ppm Ca and no detectable alkaline elements. The phase content, determined by X-ray analysis, and the cation impurity content, determined by spectrographic analysis, of both powders are presented in Table 1.

* Cerac, Inc.

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 composite powders in plastic bottles with t-butanol and tungsten carbide balls for 16 hours. The powder was dried and mixed with a mortar and pestle to break up any large agglomerates. A 5.08 cm (2 in.) diameter disc, approximately 0.954 cm (.375 in) thick was then hot-pressed for 2 hours at 1750°C, 27.6 MN/m² (4000 psi) in a nitrogen atmosphere. In all cases, immersion densities > 98.5% of theoretical were obtained.

Six flexural strength specimens (~ 0.3 x 0.6 x 3.0 cm) were cut from each disc and ground with a 320 grit diamond wheel. Flexural strength measurements were performed in 4-pt loading as previously described.⁽⁴⁾ Three specimens were fractured at room temperature and three at 1400°C in air. Due to the limited number of specimens, a single stressing rate (~ 1000 MN/m²/min) was used at 1400°C.** Flexural creep tests in 4-pt loading were carried out on similar sized specimens. These were performed at 1400°C with an initial applied stress of 15,000 psi fiber stress as calculated from the elastic beam equation. The mid-span deflection of the bar specimen was measured optically through a viewing port in the furnace with a telescope-cathotometer arrangement. The outer fiber 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

* United Mineral & Chemical Corp., NY, NY (< 20 ppm total cation impurities).

** Due to the slow growth of cracks at high temperature, the strength of Si₃N₄ is dependent on stressing rate.⁽⁴⁾

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 psi) $\pm 18\%$. 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 boundary and the Li which might be expected to do the same had no apparent effect on the high temperature strength. However, spectrographic analysis of the hot-pressed material indicated a Li content of ~ 0.02 compared with the 0.093% added prior to hot-pressing, and no detectable Na ($\ll 0.01\%$). This is most probably due to the high volatility of the Li_2O and Na_2O .

The CaO, however, does have a very significant effect on the high temperature strength 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 fracture stresses are indicated next to the appropriate curve. Note that not only does the flexural strength decrease with increasing CaO content but the non-elastic deformation also becomes much more pronounced. This deformation behavior 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 it is also a result of 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 partway through the specimen. Thus it appears that the CaO additions reduce the viscosity of the assumed glassy boundary phase which increases the

material'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.

As mentioned previously, a higher strength silicon nitride is obtained when 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 ($\sim 105,000 \text{ psi}$) at room temperature and 421 MN/m^2 ($\sim 63,000 \text{ psi}$) at 1400°C . As reported above, silicon nitride hot-pressed from the β -phase starting powder resulted in much lower strengths at both temperatures. The difference in the microstructures of material hot-pressed from the two starting powders is shown in Fig. 3. The fracture surfaces shown were etched in concentrated (48%) HF for 24 hours to dissolve the silicate boundary phase, thus exposing the Si_3N_4 grains. The β -phase powder produced a microstructure of equiaxed grains of 1-4 μ 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. Each data point represents the average of three flexural tests and the vertical lines through the data points extend from the lowest to the highest values obtained. Somewhat more complex behavior 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 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 ($< 0.01 \text{ wt } \%$) 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 only 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/m² (~ 50,000 psi). Similarly while 0.217% Na was added only 0.025% wt % remained after hot-pressing. This quantity of Na, however, still resulted in a decrease in the 1400°C strength to 360 MN/m² (~ 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 this 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/m² (~ 63,000 psi) to 210 MN/m² (~ 30,000 psi) by additions of up to 0.2 wt % CaO. The effect of CaO on the high temperature creep behavior is shown in Fig. 5. These are the results of 4 pt flexural creep measurements made on 4 samples with varying Ca contents. Not surprisingly the creep resistance decreased quite regularly as the CaO content increased. This is consistent with the previously 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. These results suggest that the CaO, Li₂O, Na₂O and K₂O 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 Al₂O₃, Fe₂O₃, CaO, Li₂O, K₂O, Na₂O 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 Li₂O, K₂O and Na₂O 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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TABLE I
Spectrochemical Analyses of Si₃N₄ Starting Powders

	<u>Westinghouse Si₃N₄</u> (> 90% α-Phase)	<u>Cerac Si₃N₄</u> (> 90% β-Phase)
Al	.08	.10
Ag	< .001	< .001
B	.001	.0025
Ca	.016	.018
Cr	.01	< .01
Fe	> .1	.03
Mg	.001	.001
Mn	.05	.002
Mo	< .003	< .003
Ni	< .01	.0015
Pb	< .01	.003
Sb	< .01	< .01
Sn	< .01	< .01
Ti	.01	< .003
V	.005	< .002
Zn	< .01	< .003

FIGURE CAPTIONS

- FIG. 1 -- Effect of impurity additions on 4-point flexural strength of Si_3N_4 hot-pressed from β -phase powder
- FIG. 2 -- Load-deflection curves for Si_3N_4 with varying CaO additions prior to hot-pressing
- FIG. 3 -- SEM micrographs of Si_3N_4 etched, fracture surfaces for material hot-pressed with (upper) β -phase powder and (lower) α -phase powder
- FIG. 4 -- Effect of impurity additions on 4-point flexural strength of Si_3N_4 hot-pressed from α -phase powder
- FIG. 5 -- Flexural creep measurements at 1400°C as a function of CaO content

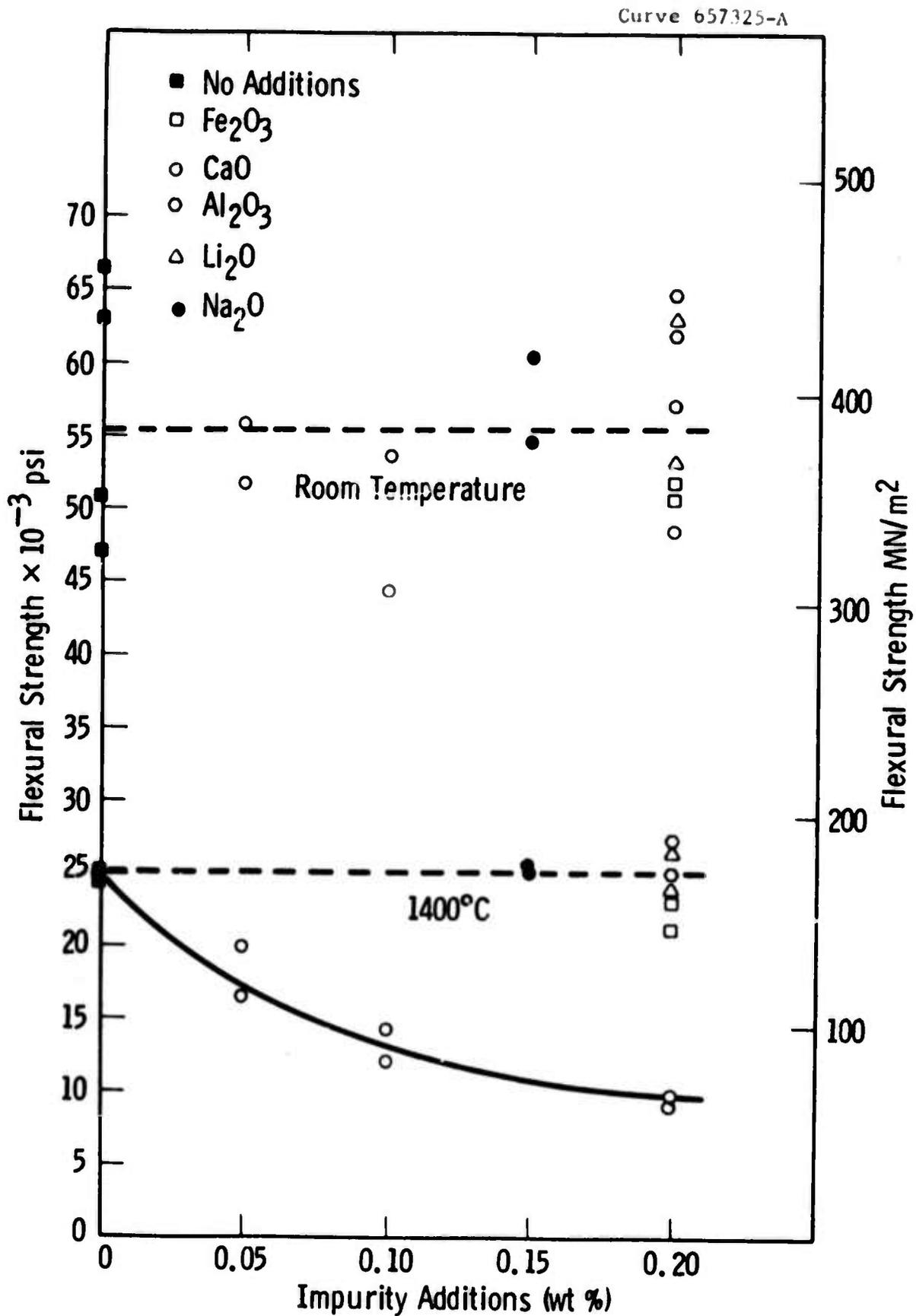


Fig. 1—Effect of impurity additions on 4 pt. flexural strength of Si_3N_4 hot-pressed from β -phase powder

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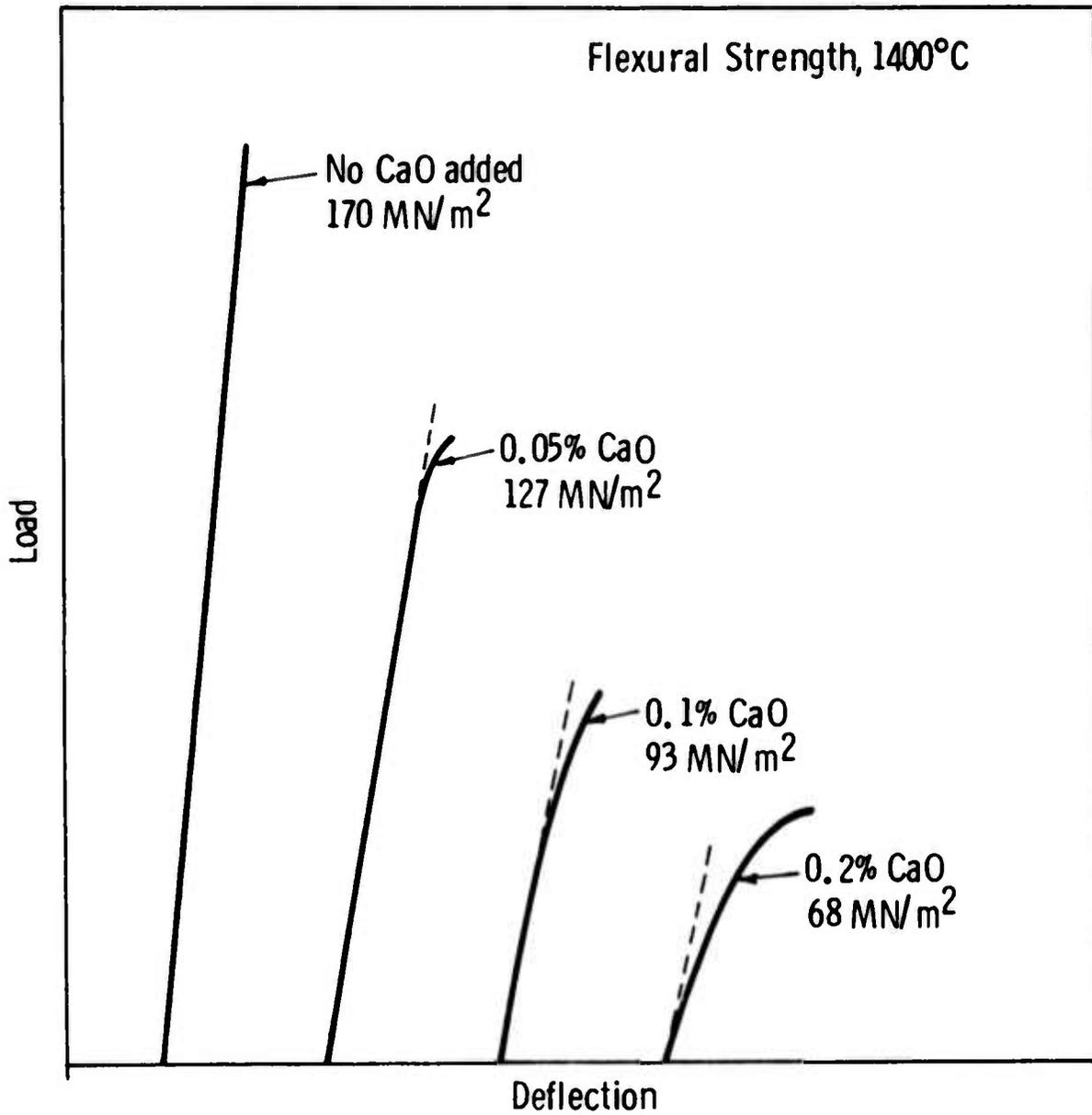
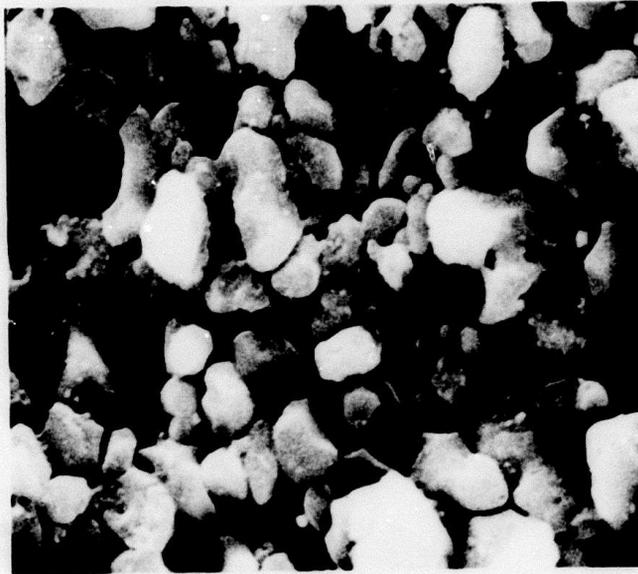


Fig. 2— Load-deflection curves for Si_3N_4 with varying CaO additions prior to hot-pressing



5 μ m



FIG. 3 -- SEM micrographs of Si₃N₄ etched, fracture surfaces for material hot-pressed with (upper) β -phase powder and (lower) α -phase powder

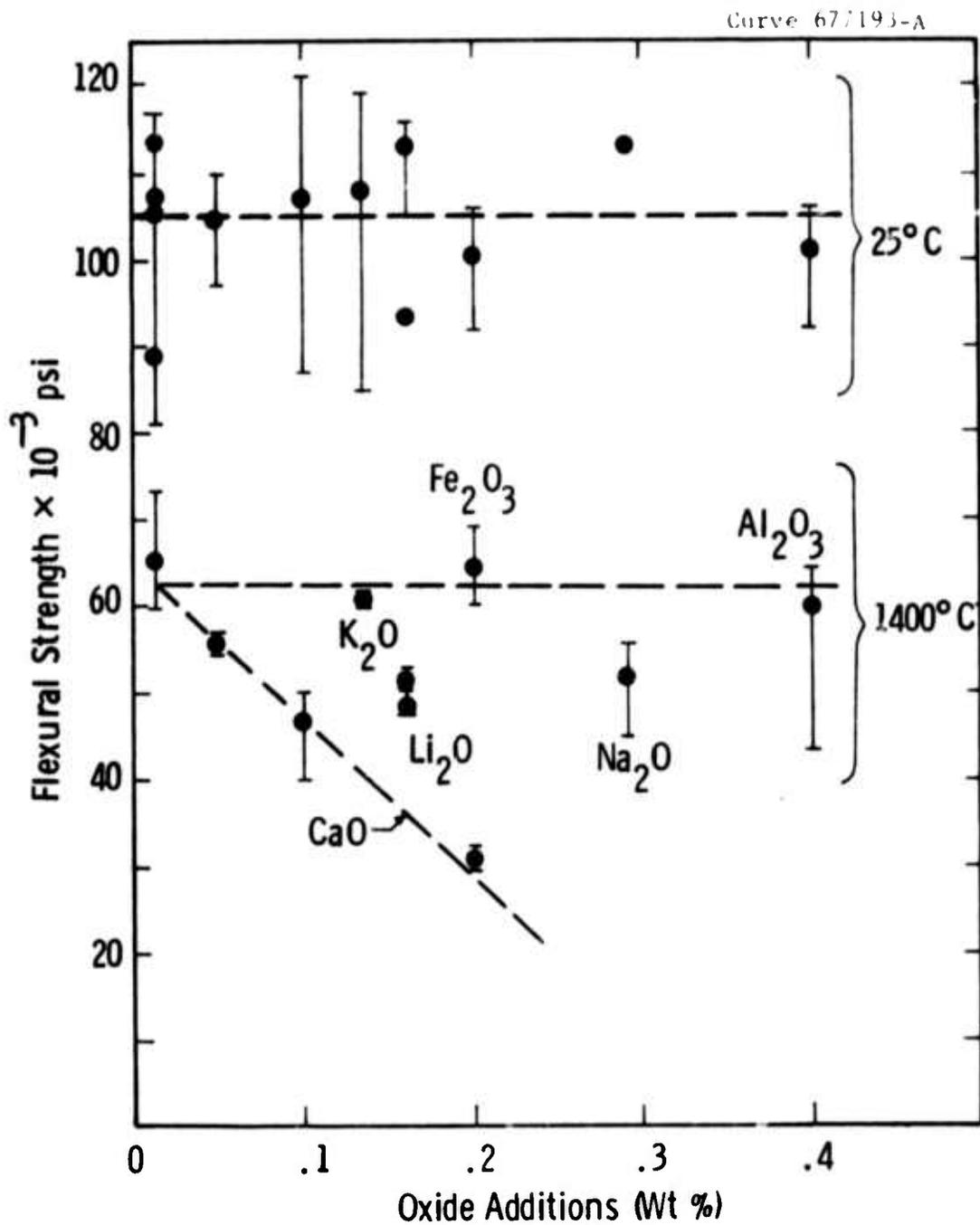


FIG. 4 -- Effect of impurity additions on 4-point flexural strength of Si_3N_4 hot-pressed from α -phase powder

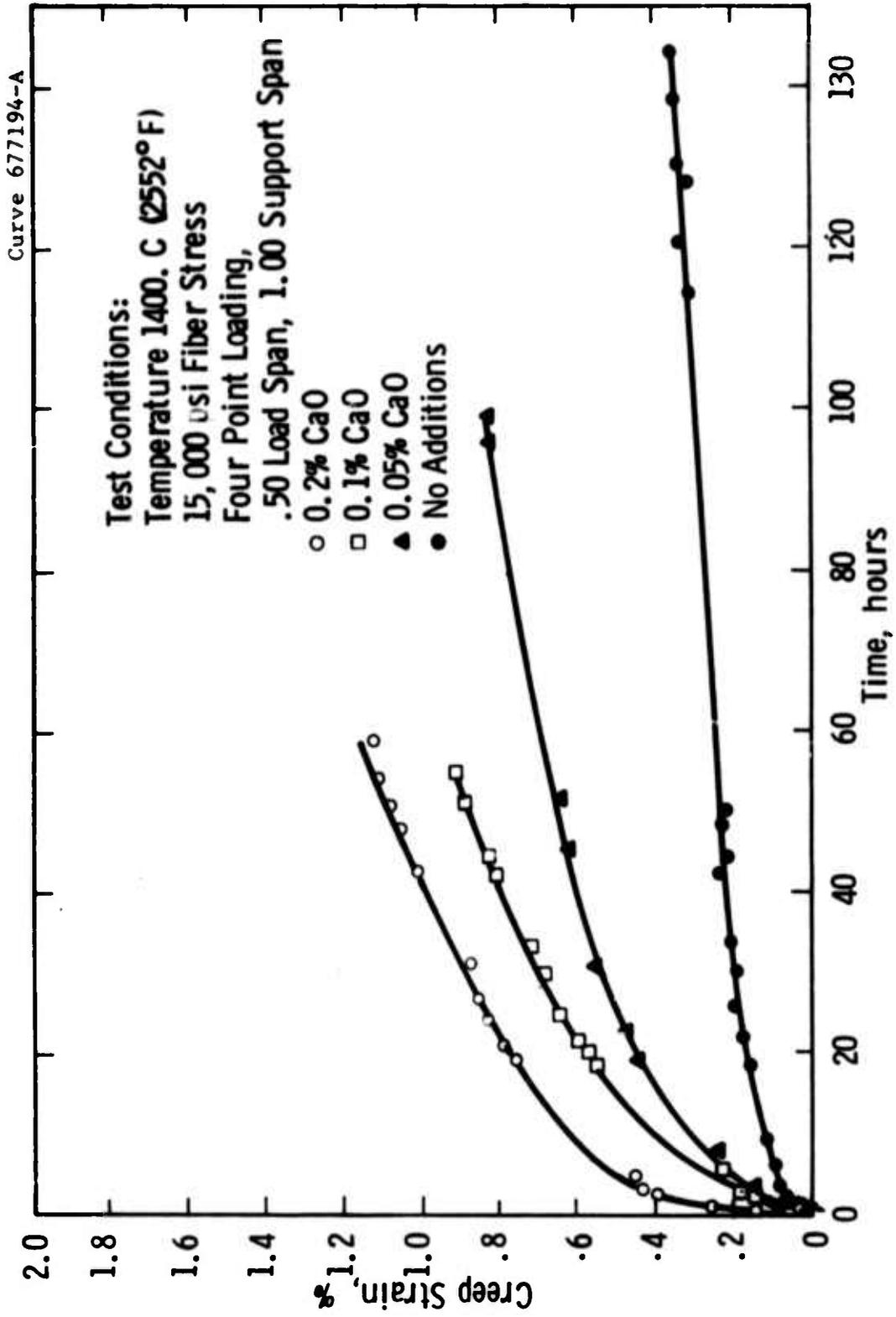


FIG. 5 -- Flexural creep measurements at 1400°C as a function of CaO content

14