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# Wetting of silicon nitride by alkaline-doped $MgSiO_3$

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The wetting behaviour of $Si_3N_4$ by alkaline-doped $MgSiO_3$ was investigated by the sessile drop method. It is shown that the alkaline oxide additions improve the wetting of $MgSiO_3$ on $Si_3N_4$. The hot-pressing of $Si_3N_4$ is controlled by a liquid phase sintering process where the dissolution of $Si_3N_4$ in silicate glass promotes good wetting and a well bonded interface by lowering the liquid-solid interfacial energy. Controlling total alkaline impurity level between 50 and 100 ppm is suggested for an optimal strength performance.

## 1. Introduction

High strength, high density $Si_3N_4$ is produced by hot-pressing a blend of $Si_3N_4$ powder with 1 to 5 wt % MgO. It has been recognized [1-3] that the densification of $Si_3N_4$ is controlled by a liquid phase sintering process. Wild *et al.* [1] suggested that the liquid phase is $MgSiO_3$ (enstatite) which forms as a result of reactions between the added MgO and $SiO_2$ present in $Si_3N_4$. The presence of a grain-boundary glass phase in hot-pressed $Si_3N_4$ was confirmed [2, 4]. However, it was also pointed out [2] that the glass phase could not be the pure form of $MgSiO_3$ since the grain boundaries in hot-pressed $Si_3N_4$ contain from 10 to 20 mol % alkaline oxides, i.e. CaO, $Na_2O$ and $K_2O$. The bulk content of alkaline impurities in $Si_3N_4$ varies between 300 and 800 ppm.

It has been generally agreed that there are three distinguishable stages in a liquid-phase sintering process. These are rearrangement, solution-reprecipitation and coalescence. Rearrangement during hot-pressing of $Si_3N_4$ has been inferred from the experiments of Lange and Terwilliger [3], who found evidence for solution-reprecipitation as well. Microscopy evidence for partial grain dissolution was also observed [2]. The coalescence stage after the final few per cent of densification are complete is the last where microstructural modification occurs.

Whalen and Humenik [5] pointed out that a *good wetting* of the solid phase by the liquid phase during sintering *must* occur in order to sinter successfully with a liquid phase. It is well known [6] that alkaline impurities reduce the softening point of silicate glasses, lower the melting point of $MgSiO_3$ [7] and decrease sharply the viscosity of silicates. These effects must, in turn, influence the wetting characteristics of the liquid glass. On the other hand, it has been observed recently [2, 9-12] that significant improvements in the high temperature strength of hot-pressed $Si_3N_4$ can be achieved by a reduction in the total content of alkaline impurities. However, a recent experiment conducted in our laboratory showed that $Si_3N_4$ hot-pressed from very high purity powder* had, at room temperature, only a fraction of the strength normally obtained from a material hot-pressed from less pure powders containing 300 to 500 ppm alkaline impurities.

It thus became apparent that the role of the impurities is complex and should be analysed. Furthermore, the wetting characteristics of enstatite and alkaline-doped $MgSiO_3$ on $Si_3N_4$ need to be established. The purpose of this paper is to report on experiments that were aimed at establishing the wetting behaviour of $MgSiO_3$ on $Si_3N_4$ and the nature of the glass-solid interfaces. Some remarks concerning the hot-pressing process are also included.

## 2. Experimental

### 2.1. Compounds

Fourteen glass compositions (Table I) were prepared from high purity powders of $SiO_2$ and

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*Powder received from the Plessey Company, containing less than 10 ppm alkaline impurities.

TABLE I Composition and constitution of MgO . $SiO_2$ + alkaline compounds

| Compound no. | Composition of mixture (wt %) | | | Composition after melt (wt %) | | | Phases present | |
|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | MgO | Alkaline | $SiO_2$ | MgO | Alkaline* | Major | Minors |
| 1 | 60 | 40 | 0 | 60 | 39.8 | 0 | E | none |
| | | | *CaO* | | | *CaO* | | |
| 2 | 59.0 | 39.0 | 2.5 | 59.3 | 39.2 | 2.3 | E | D, F |
| 3 | 57.0 | 38.0 | 5.0 | 58.3 | 37.3 | 4.6 | F | D, E |
| 4 | 56.0 | 36.5 | 7.5 | 58.0 | 35.4 | 7.0 | F | D, E |
| 5 | 55.0 | 35.0 | 10.0 | 56.2 | 33.4 | 9.9 | D | F, E |
| | | | $Li_2CO_3$ | | | $Li_2O$ | | |
| 6 | 59.0 | 39.0 | 2.5 | 60 | 37.7 | 0.8 | E | F |
| 7 | 57.0 | 38.5 | 5.0 | 61.0 | 37.5 | 1.7 | F | E |
| 8 | 56.0 | 36.5 | 7.5 | 58.4 | 36.4 | 3.5 | F | E |
| | | | $Na_2CO_3$ | | | $Na_2O$ | | |
| 9 | 59.0 | 38.5 | 2.5 | 61.2 | 36.9 | 1.4 | E | F |
| 10 | 56.0 | 36.5 | 7.5 | 59.2 | 36.5 | 4.1 | F | E (trace) |
| 11 | 55.0 | 35.0 | 10.0 | 58.0 | 36.4 | 5.5 | F | E (trace) |
| | | | $K_2CO_3$ | | | $K_2O$ | | |
| 12 | 59.0 | 37.5 | 2.5 | 61.5 | 35.8 | 1.5 | F | E |
| 13 | 57.0 | 38.5 | 5.0 | 60.1 | 36.1 | 3.0 | F | E |
| 14 | 56.0 | 36.5 | 7.5 | 57.3 | 36.8 | 4.7 | F | E |

*Assuming that during melting, the carbonates convert to oxide: $M_2CO_3 \rightarrow M_2O + CO_2$, where M is the alkaline metal.

E = enstatite, D = diopside, F = forsterite.

MgO.† CaO was added in the oxide form, the other three alkalines were added in the form of carbonates.‡ The powders were dry milled with high purity $Al_2O_3$ balls for 48 h, then pressed into 15 mm diameter buttons and melted in graphite crucibles in purified $N_2$ atmosphere at 1550°C. After melting, the buttons were kept at temperature for 2 h and furnace cooled. Each button was separated from the others and only one particular batch of $MgSiO_3$ + alkali was melted at a time to avoid cross contamination. After removal from the furnace, each button was shattered and a few pieces were selected randomly for analyses. Phases were determined by Debye-Scherer powder X-ray diffraction, while the exact composition was determined by a wet chemical analysis. From the low background on the X-ray films, we concluded that the melted buttons were mostly crystalline.

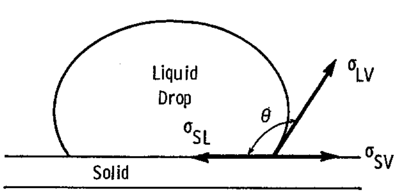

*Figure 1* Balance of forces, a liquid drop on a solid substrate.

### 2.2. Contact angle measurements

Wetting of a liquid upon a solid is defined by the contact angle, $\theta$, that a drop of the liquid forms at the point of contact with the solid (Fig. 1). A non-wetting configuration is one where the contact angle is equal to, or greater than 90 degrees. Full wetting is achieved when $\theta = 0$. The degree of wetting is determined by the surface forces acting on the system (Fig. 1) where

$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \tag{1}$$

where $\sigma_{SV}$, $\sigma_{SL}$ and $\sigma_{LV}$ are the surface energies, respectively, of the solid-vapour, solid-liquid and liquid-vapour interfaces. If $\sigma_{SL} > \sigma_{SV}$, the contact angle can never equal zero. However, when $\sigma_{SV} > \sigma_{SL}$, the degree of wetting is controlled by the $\sigma_{SL}$ term. The liquid-solid interfacial energy is thus of most interest in liquid phase sintering. Diffusion across the interface, mutual solubilities of the liquid and the

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†Fisher Scientific S-153 silica, M-51 magnesium oxide and C-117 calcium oxide.

‡CERAC P-1049 $K_2CO_3$; Johnson Mathey Chemicals, $Li_2CO_3$ Grade no. 1 and $Na_2CO_3$ grade no. 1.

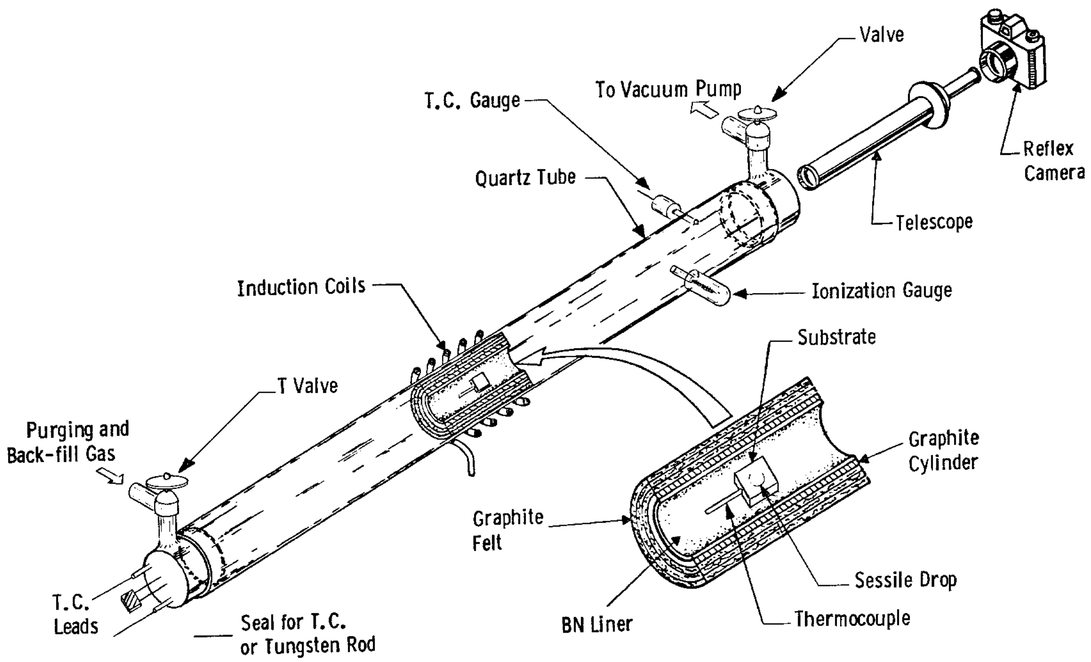

*Figure 2* Apparatus for measuring contact angle.

solid, and other chemical interactions across the liquid-solid interface affect the solid-liquid interfacial energy, and thus influence the degree of wetting.

The apparatus used to measure the contact angle is shown in Fig. 2. It consists of quartz tube 1.22 m long with provisions for evacuation, vacuum gauging and back-filling with a desired atmosphere. Heating is provided by an RF generator (450 kHz) connected to an induction coil. The substrate and liquid are heated by radiation from the boron nitride liner inside a graphite susceptor. Heating rate can be varied from an essentially equilibrium condition to a maximum rate of 400° C $min^{-1}$. The temperature is monitored by means of a thermocouple attached to the solid substrate near the liquid drop. The shape of the liquid drop is recorded on a photographic film. Contact angles are measured from the silhouettes of the drops magnified about 30 times.

Ideally, sessile drop experiments should be conducted on a single crystal of the solid substrate material. Since single crystals of $Si_3N_4$ are not available, we used the highest grade of hot-pressed $Si_3N_4$, i.e. Norton HS-130 grade $Si_3N_4$ containing 300 ppm of alkaline impurities, 0.5 wt % Fe, 0.8 wt % Al and 0.8 wt % Mg.

Small tiles, 12 × 12 × 2 mm, were machined from a block of $Si_3N_4$, then carefully polished and ultrasonically cleaned. The tile and a small piece of the desired glass were placed inside the susceptor. The telescope was first aligned against a sensitive water level, and then used to align the substrate in a horizontal position.

At the start of a test, the tube was evacuated and the assembly was degassed for 3 h at 150° C. The tube was then back-filled with purified $N_2$ gas and the temperature was raised to about 1300° C. Between 1300 and 1750° C the temperature was increased continuously at the rate of 10° C $min^{-1}$.

Ideally, the wetting angle should be determined in equilibrium, i.e. under isothermal conditions when $\theta$ is not changing with time. We chose, nevertheless, to examine $\theta$ during a continuous temperature increase for the following reasons: (1) $Si_3N_4$ is soluble in magnesium silicate; (2) surface reactions preclude the possibility of a true equilibrium; (3) preliminary tests showed that $\theta$ is not reversible, i.e. there is absolutely no retardation of the liquid glass drop upon cooling; (4) we wished to examine the behaviour of the glass-$Si_3N_4$ system under conditions similar to those encountered in the practice of hot-pressing where the temperature is

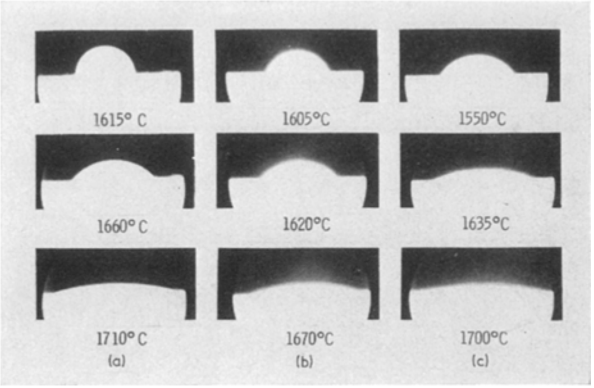

*Figure 3* Sessile drop shape as a function of temperature and composition, $Si_3N_4$ substrate, $N_2$ atmosphere, heating rate 10° C $min^{-1}$. (a) Pure $MgSiO_3$, (b) $MgSiO_3$ + 2.5% CaO, (c) $MgSiO_3$ + 7.5% CaO.

raised continuously at rates ranging from about 4 [13] to about 20° C $min^{-1}$ [14] or more.

## 3. Results

### 3.1. Compounds

Table I indicates very minute losses in the alkaline metal during preparation of the glasses. This allows us to assume that the gross chemical composition of the liquid glass drop remained unchanged during the duration of a test. The X-ray diffraction data are in a good agreement with published phase diagrams [7] and show that small additions of alkaline oxides to pure $MgSiO_3$ result in multiple phase mixtures where enstatite rapidly assumes the position of a minor phase.

### 3.2. Contact angle

Examples of the silhouettes of a few sessile drops are shown in Fig. 3. Note the increased spreading (lower contact angle) as the amount of CaO in $MgSiO_3$ is increased. The data for the contact angles versus temperature for all compounds are shown in Fig. 4. The data demonstrate the strong effect of alkaline impurity additions on the wetting of magnesium silicate on $Si_3N_4$.

Complete wetting, $\theta = 0$, is not achieved with $MgSiO_3$ (enstatite) even at the highest temperature. For a comparable addition of alkaline oxide, wetting improves moving from CaO to $Li_2O$, which parallels the effect of these additions on lowering the melting points and improving the viscosities of silicates [7, 8]. In the case of $Li_2O$

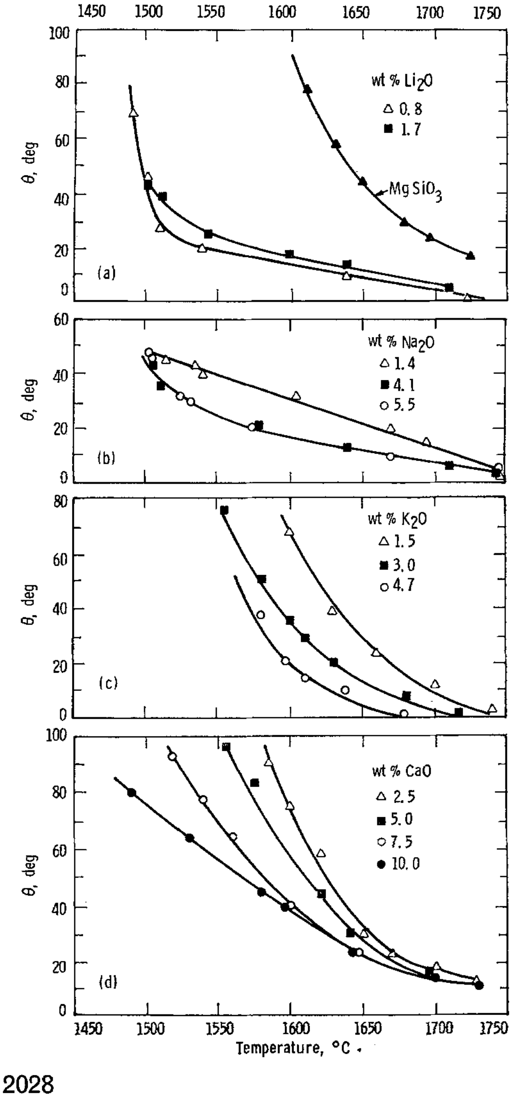

*Figure 4* Wetting of MgO · $SiO_2$ on $Si_3N_4$ as a function of temperature and additions of alkaline oxides. Nitrogen atmosphere, heating rate 10° C $min^{-1}$.

there seems to be a slight decrease in the degree of wetting with an increase in the amount of alkaline addition. This may be due to severe reactions at the liquid-solid interface.

After reaching the maximum temperature the furnace was turned down and the system allowed to cool at the rate of 75 degrees per min. In no case did we observe a change in the contact angle from the minimum attained at the maximum temperature.

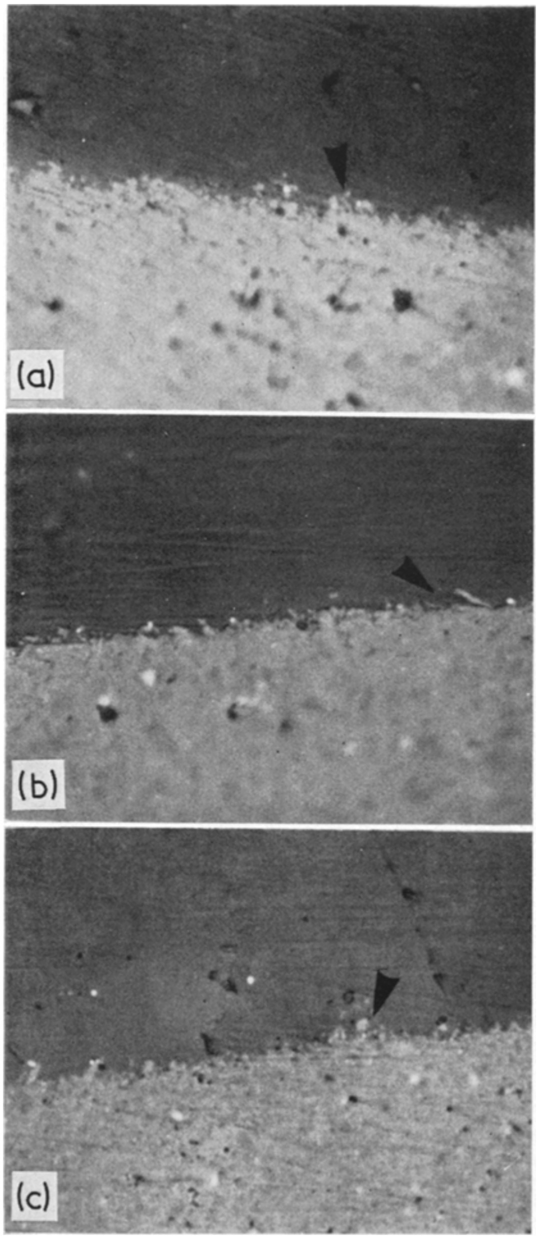

*Figure 5* Light micrographs of transverse sections through the glass-$Si_3N_4$ interface. Glass is at the top of each micrograph. (a) System 3, (b) system 10, (c) system 13 (Table I). (× 1000).

The liquid-solid interfaces were examined by light and scanning electron microscopy. The tiles were dissected in the middle, mounted in "Kold Mount" and mechanically polished with 1 μm alumina. Examples of the interfaces are shown in Fig. 5. In all three systems shown in Fig. 5 there is evidence of dissolution at the interface. The interface is rugged, and in many areas (arrows) particles of $Si_3N_4$ seem to be floating in the glass.

The nature of the interfaces are shown in more detail in the scanning electron micrographs of Fig. 6. A reaction zone of about 15 μm is seen in Fig. 6a. The original $Si_3N_4$ surface is marked by the large arrows in both micrographs. It is clear that well-bonded interfaces are formed between the silicate glass and the $Si_3N_4$ substrate.

The distribution of elements across the interface was examined by energy dispersive X-ray analysis. Readings were made at various points along the marked line in Fig. 6a. The results are summarized in Fig. 7. Diffusion of Mg, and to some extent of Ca, into the $Si_3N_4$ substrate has occurred. This phenomenon is demonstrated again in Table II which summarizes count readings at various marked points on Fig. 6b. These readings support the assignment of the original $Si_3N_4$ surface as marked and show that diffusion of Mg into the $Si_3N_4$ occurs, apparently, for all silicate systems. These findings support a previous observation [2] where diffusion of Mg into the grain during hot-pressing was indicated.

TABLE II Energy dispersive X-ray count ratios for Mg/Si and K/Si, system 13, Fig. 6b (corrected for background)

| Point no. | Mg/Si | K/Si |
|---|---|---|
| 1 | 0.61 | 0.008 |
| 2 | 0.55 | 0.007 |
| 3 | 0.62 | ND |
| 4 | 0.01 | ND |
| 5 | 0.61 | 0.009 |
| 6 | 0.03 | ND |
| 7 | 0.02 | ND |
| 8 | 0.01 | ND |
| 9 | 0.01 | ND |

ND = not detected

A few systems richer in $SiO_2$ were also examined. 80 $SiO_2$–20 MgO, 95 $SiO_2$–5 MgO and

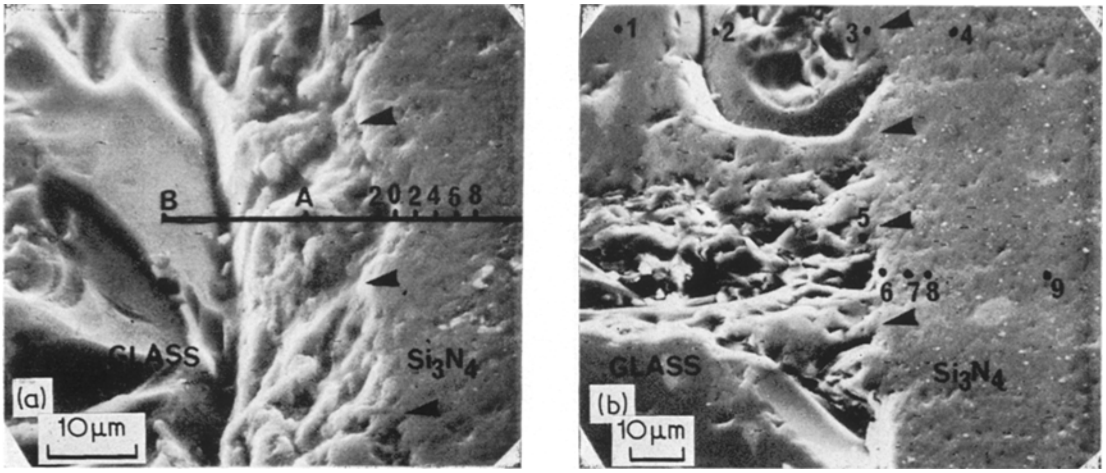

*Figure 6* Scanning electron micrographs showing the glass-$Si_3N_4$ interface. (a) System 5, (b) system 13 (Table I). Original $Si_3N_4$ surface is marked by arrows. Scale bars ≡ 10 µm.

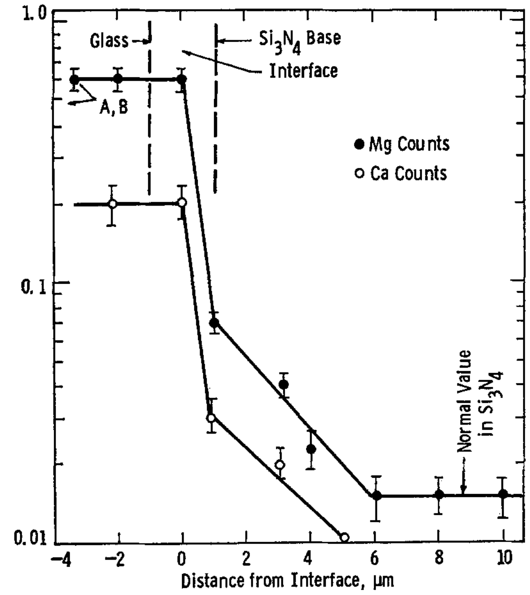

*Figure 7* Mg and Ca concentration, system 5 (Table I), along the trace marked in Fig. 6a.

95 $SiO_2$–5 CaO glass mixtures were tested following the same procedure as described above. Poor wetting was obtained with all three systems at temperatures up to 1800° C. However, the interfacial reactions observed with the $MgSiO_3$-base systems (Fig. 6) also must have occurred with the high $SiO_2$ systems. These are illustrated in the three SEM micrographs of Fig. 8. Well-bonded interfaces are seen in Fig. 8a and b, although the poor wetting is clearly visible at the left edge of Fig. 8b (high contact angle). The original $Si_3N_4$ surface, marked by the dotted lines, was determined by energy-dispersive X-ray analysis. Diffusion of Mg across the interface was observed in both Fig. 8a and b.

A somewhat rougher interface is seen in the $SiO_2$ + 5 CaO system (Fig. 8c). However, the general appearance is that of a well-bonded interface. It seems, therefore, that the glass-substrate interfacial reactions are mainly a result of dissolution of $Si_3N_4$ in $SiO_2$ base glasses.

## 4. Discussion

### 4.1. Wetting behaviour

The time element is significant in the development of the wetting angle, specifically where strong surface reactions are involved. It was essential, therefore, to determine the development of wetting as a function of time under isothermal conditions. Fig. 9 illustrates the results of measurements conducted on three systems. No detectable time effect is shown for the $MgSiO_3$–$Si_3N_4$ system at 1720° C, with $\theta$ reaching a constant value in less than 1 min at 1655° C. The $MgSiO_3$ + 4.7 wt % $K_2O$ system is another example of the change of $\theta$ with time where, as above, equilibrium seems to occur in less than 1 min. We can conclude, therefore, that the interfacial reactions are fast and do not affect the spreading of the glass beyond the first minute

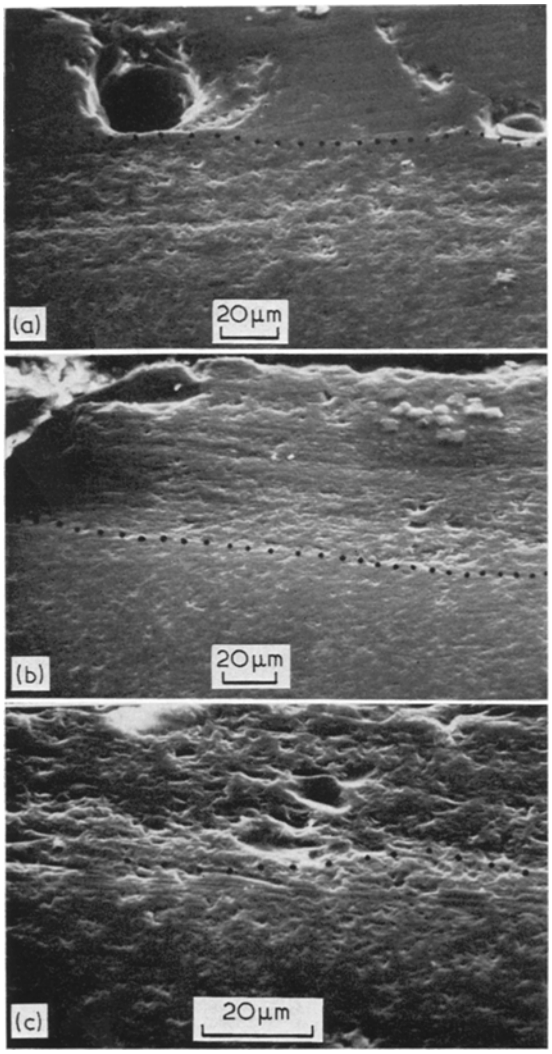

*Figure 8* SEM micrographs of transverse sections through the glass-$Si_3N_4$ interface. Glass is at the top of each micrograph. (a) 80 $SiO_2$ + 20 MgO, (b) 95 $SiO_2$ + 5 MgO, (c) 95 $SiO_2$ + 5 CaO. Dotted lines mark the original $Si_3N_4$ surface. Scale bars ≡ 20 µm.

or so. This observation lends credit to our measurements which were conducted during a continuous increase in temperature.

Few correlations, of general nature, have been reported between cos $\theta$ and the energy terms in Equation 1. Zisman [15] showed that cos $\theta$ increases linearly with decreasing surface energy of the liquid. This relation holds for a series of homologous liquids at a constant temperature. Rhee [16] found a linear relationship between cos $\theta$ and temperature and suggested that this

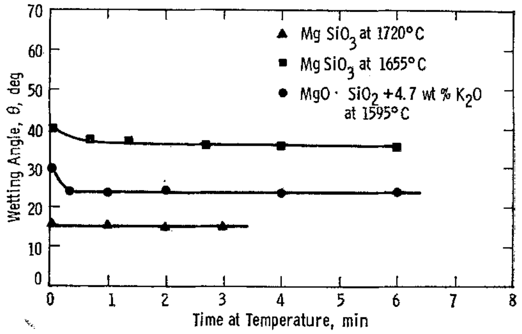

*Figure 9* Wetting angle as a function of time at a constant temperature.

rate is applicable to many liquid metal-ceramic systems.

Cos $\theta$ as a function of alkaline oxide additions is plotted in Fig. 10 where the data indicate a linear dependence of cos $\theta$ on alkaline additions. The four lines in Fig. 10 extrapolate to two common points which agree well with the value of cos $\theta$ for the pure $MgSiO_3$ system. These results add credibility to the data reported in Fig. 4. From the data in Fig. 10 we can write

$$\cos\theta = A + BX_a \qquad (2)$$

where $X_a$ is the fraction of alkaline addition, $A$ is the value of cos $\theta$ for pure $MgSiO_3$ and $B$ is the slope of the line. Both $A$ and $B$ are constants typical of the test temperature and the systems tested. Equation 1 indicates that cos $\theta$ depends on all three interfacial energies. However, the additions of alkaline oxide should not affect the

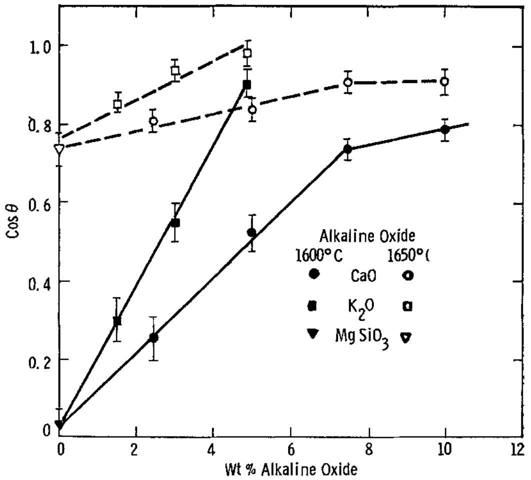

*Figure 10* Cos $\theta$ as a function of alkaline oxide content. Data cross plotted from Fig. 4.

solid-vapour energy at a constant temperature. Thus, we note, that for the series of tests represented in Fig. 10, $\sigma_{SV}$ = constant. Kingery [17] has shown that dilute mixtures of $SiO_2$ with alkaline oxides do not affect the surface energy of the liquid silica. We assume, therefore, that a similar behaviour will also hold for the $MgSiO_3$ system with small additions of alkaline oxides. Thus, we note that for the series of tests represented in Fig. 10, $\sigma_{LV} \approx$ constant. Equation 1 can be written as

$$\cos\theta = A' - B'\,\sigma_{SL}\,. \tag{3}$$

Combining Equations 2 and 3

$$\sigma_{SL} \approx \alpha - \beta\, X_a\,. \tag{4}$$

This is a significant result in that it indicates that the alkaline additions affect mainly the solid-liquid interfacial energy and that this energy term controls the wetting behaviour of the silicate glasses on $Si_3N_4$.

Similar reasoning can be applied to the work of adhesion, $W_A$, which defines the work necessary to separate the liquid from the solid and is, therefore, a measure of the strength of the liquid-solid interface. We note that [18]

$$W_A = \sigma_{SV} + \sigma_{LV} - \sigma_{SL}\,. \tag{5}$$

If $\sigma_{LV}$ and $\sigma_{SV}$ are about constant then, from Equations 4 and 5,

$$W_A \approx -\alpha + \beta X_a\,, \tag{6}$$

which indicates an increase in the strength of the liquid-solid interface due to additions of alkaline oxide to the magnesium silicate glass.

### 4.2. The hot-pressing process

The degree of dominance of the rearrangement stage during liquid phase sintering depends on the volume fraction of the liquid. When the volume fraction of the liquid is less than 5%, the amount of shrinkage due to rearrangement is negligible [5]. Since the volume fraction of the liquid glass in hot-pressed $Si_3N_4$ does not exceed 5%, we do not expect rearrangement to be a significant factor during densification of $Si_3N_4$. Indeed, analysis of densification data showed slopes of between $\frac{1}{2}$ and $\frac{1}{4}$ in plots of log density change versus log time [3]. These slopes are characteristic of a solution-reprecipitation process where the rate of densification is controlled by the solution rate of the solid at the liquid-solid interface [19]. Dissolution of the solid at the liquid-solid interface during hot-pressing of $Si_3N_4$ is inferred from transmission micrographs [2] and is clearly demonstrated by the micrographs in Figs. 5, 6 and 8.

Kingery [20] has emphasized the strong dependence of the solution and reprecipitation process on a low contact angle, $\theta$, and a low dihedral angle, $\phi$. The effect of alkaline oxides on lowering the contact angle has been demonstrated in the present experiments (Fig. 4). The dihedral angle, which is a measure of the degree of intergranular penetration by the liquid phase, is given by [5]

$$\cos\frac{\Phi}{2} = \frac{\sigma_{gb}}{2\sigma_{SL}}\,, \tag{7}$$

where $\sigma_{gb}$ is the grain-boundary energy. The very small grain size in hot-pressed $Si_3N_4$ [2] does not allow reliable measurements of $\Phi$. However, it is clear from Equation 7 that lowering the liquid-solid interfacial energy would have a significant effect on the results of the liquid sintering process. Equation 4 demonstrates how the alkaline oxide additions contribute to the lowering of $\sigma_{SL}$.

Lange and Terwilliger [3] recognized the significance of magnesium in promoting full densification of hot-pressed $Si_3N_4$, but could not discern its exact function. $Si_3N_4$ pressed with oxide mixtures other than MgO did not achieve full density. Our previous results [2] and the current experiments show that Mg diffuses from the liquid glass phase into the solid $Si_3N_4$. It is, therefore, quite probable that the final few per cent of densification are provided by a diffusional process whereby Mg ions are accommodated within the structure of $Si_3N_4$. From a crystallographic point of view, this is, indeed, feasible as Wild, *et al.* [1] show.

The detrimental effect of alkaline oxide impurities on the high temperature strength of hot-pressed $Si_3N_4$ are well documented [9-12]. On the other hand, the results of the present investigation suggest that a certain amount of alkaline addition is necessary to promote a fast and a full densification of $Si_3N_4$ coupled with a strong and cohesive structure. One possible solution is to control the alkaline impurities at an optimal level. Creep data [10, 11] suggest that lowering the total bulk alkaline level to below 100 ppm may result in a significant improvement in the stress-rupture strength of $Si_3N_4$ at 1300°C. It seems that the optimal level of the alkaline impurities may lie between 50 and 100 ppm.

Another possible solution is to add a compound to the $MgO-Si_3N_4$ blend which will increase the refractoriness of the grain-boundary glass phase. This was the route taken by Gazza [21], who reported improvements in the high temperature strength of $Si_3N_4$ hot-pressed with an addition of a few per cent of $Y_2O_3$. Auger analysis performed on this material showed [22] that Y is indeed present in the boundary glass phase.

## 5. Summary and conclusions

We have shown that hot-pressing of $Si_3N_4$, most probably, is controlled by a solution-reprecipitation stage during the liquid-phase sintering process. The liquid-solid interfacial energy is the dominant parameter that controls densification, probably as a result of strong reactions at the interface of solid $Si_3N_4$ and the liquid glass phase. More specifically, the results of this paper show that:

1. Alkaline oxide additions improve the wetting of magnesium silicates on $Si_3N_4$ significantly.
2. The alkaline impurities lower the liquid-solid interfacial energy and improve the work of adhesion.
3. Dissolution of $Si_3N_4$ in silicate glass promotes good wetting and a well bonded interface.
4. Full densification is apparently achieved due to the diffusion of Mg from the boundary glass phase into the $Si_3N_4$ grain.
5. Controlling the total alkaline impurities between 50 and 100 ppm is suggested for an optimal strength performance.

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