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# KINETICS OF THE THERMAL BEHAVIOUR OF HOT-PRESSED SILICON NITRIDE IN THE TEMPERATURE RANGE 1250 TO 1400°C

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## ABSTRACT

The isothermal oxidation behaviour of silicon nitride hot-pressed with magnesia (0.2–0.8 wt.%) was studied in air at 1250–1400°C. Reaction was followed by measuring the weight-changes of the specimens at intermittent periods of exposures. The surfaces of oxidized specimens were examined by X-ray diffraction analysis.

The oxidation rate follows the classical parabolic behaviour with an apparent activation energy of 98–235 kJ $mol^{-1}$ depending on the MgO content. The scales consist of a mixture of unoxidized silicon nitride, crystalline phases ($SiO_2$, Mg- and Mg–Ca-silicates) and a glass phase containing other elements. The data suggest that impurities greatly lower the oxidation resistance of $Si_3N_4$ in air. The oxidation results are discussed with regard to the chemical composition of the starting material.

## INTRODUCTION

Hot-pressed silicon nitride is of interest as a high temperature engineering material [1]. The most attractive properties include high-temperature strength, good oxidation resistance and good thermal-shock resistance [2,3].

Although many investigations were published on the oxidation resistance of hot-pressed silicon nitride containing MgO, the results are widely divergent as seen from Table 1. The present study was initiated to examine the reaction rates and oxidation mechanism over a wide range of temperature, time and composition to permit a more comprehensive evaluation of oxidation properties.

## EXPERIMENTAL

High purity silicon nitride with an $\alpha/B$ ratio of about 0.95 was mixed with MgO (0.2, 0.4, 0.6 and 0.8 wt.%) in a planetary ball mill for 30 h using

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TABLE 1

Results of previous studies on the oxidation resistance of hot-pressed silicon nitride containing MgO

| Author | Method [a] | Material | Atmosphere | Temp. (°C) | $\Delta G/A$ (mg cm$^{-2}$) | $K$ (mg$^2$cm$^{-4}$h$^{-1}$) | $R$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Wruss et al. (1975) [6] | TGA | $Si_3N_4$ + 5wt.% MgO | air, 40% moisture | 1060–1350 | 0.25–8 | $1.9\times10^{-10}$<br>$1.1\times10^{-6}$ | |
| Kiehle et al. (1975) [7] | XRD, SEM | HS 130 | air | 600–1450 | | | |
| Singhal (1976) [8] | TGA, XRD, SEM, EMP | HS 130 | 0.1 MPa dry $O_2$ | 1093–1370 | 0.03–0.5 | $1.6\times10^{-11}$<br>$4.6\times10^{-9}$ | 375 ± 25 |
| Singhal (1976) [9] | TGA | HS 130 | 0.1 MPa wet $O_2$ | 1200–1400 | | | 488 ± 30 |
| Tripp et al. (1976) [10] | TGA, XRD, SEM, EMP | HS 130 | 0.02 MPa dry $O_2$ | 1300–1500 | 0.42–1.2 | $2\times10^{-9}$<br>$1.3\times10^{-7}$ | 289 |
| Brennan (1977) [11] | TGA | NC 132 | air | 1350 | 0.935 | $4.0\times10^{-9}$ | |
| Schlichting and Gauckler (1977) [12] | TGA | $Si_3N_4$ + 5 wt.% MgO | static air | 1400 | 1.5 | $1.6\times10^{-7}$ | |
| Cubicciotti and Lau (1978) [13] | GCA, SEM, XRD, EMP | NC 132 | dry $O_2$ | 1248–1440 | | | 440 |
| Lange (1978) [14] | TGA | 0.755 mol fraction $Si_3N_4$ + varied MgO/SiO molar ratios | air | 1375 | 0.3–4.7 | | |
| Cramer (1980) [15] | TGA, XRD, SEM | $Si_3N_4$<br>$Si_3N_4$ + 0.25% MgO | air | 1200–1400 | 0.05–0.35<br>0.05–0.55 | $6.7–17\times10^{-11}$<br>$2.5–6.1\times10^{-10}$ | 87<br>182 |

[a] EMP = electron microprobe analysis; GCA = gas chromatographic analysis.

hexane as milling fluid. The dried pressed specimens were hot-pressed at 1850°C for 60 min with 80 MPa uniaxial pressure in BN coated graphite die. The method of preparation has been fully described previously [4,5].

The silicon nitride specimens in the form of rectangular bars were diamond sawed from the hot-pressed pellets. The specimens were polished with 600 grit SiC paper and ultrasonically cleaned in acetone and in alcohol. The stability of each hot-pressed composition in static air was investigated by placing the specimens (supported on knife-edged triangular prisms of RBSN) inside an electric resistance furnace. The specimens were heated at 1250, 1300, 1350 and 1400°C for $\simeq 100$ h. Mass-changes of the specimens were measured at intermittent periods of exposures. X-ray diffraction patterns of the surfaces were obtained with Cu $K_\alpha$ ratiation with Ni-filter.

## RESULTS AND DISCUSSION

### *Reaction kinetics*

The oxidation of silicon nitride to silicon dioxide can be simply expressed by

$$Si_3N_4 + 3\ O_2 \dashrightarrow 3\ SiO_2 + 2\ N_2$$

However, the oxidation of hot-pressed silicon nitride containing magnesia is much more complex because the reaction products include magnesium silicates as well as the above products. The weight-change measured in the reaction is a combination of gain from the oxygen reacted and weight-loss from the nitrogen evolved.

The weight-change data for HPSN-specimens oxidized at 1250–1400°C for $\simeq 100$ h in static air are summarized in Fig. 1. The results reveal the following deductions:

(1) an initial rapid increase in the weight of specimens was followed by a slower one. This is due to the formation of silica film in this passive oxidation which limits the rate of further oxidation;

(2) the increase in the MgO addition decreases the oxidation resistance of the specimens. The stronger effect of MgO is obtained as the oxidation temperature is increased.

The results are shown in Fig. 2 in a parabolic plot of the square of the weight-gain vs. time. The data were fitted to the parabolic equation

$$W^2 = Kt + C$$

where $W$ is the sample weight gain, $t$ the time of oxidation, $K$ the parabolic rate constant and $C$ a constant to account for the initial reaction. The value of $C$ equals zero because the specimens were inserted in the furnace at the desired temperature. However, the straight lines, which represent a region of

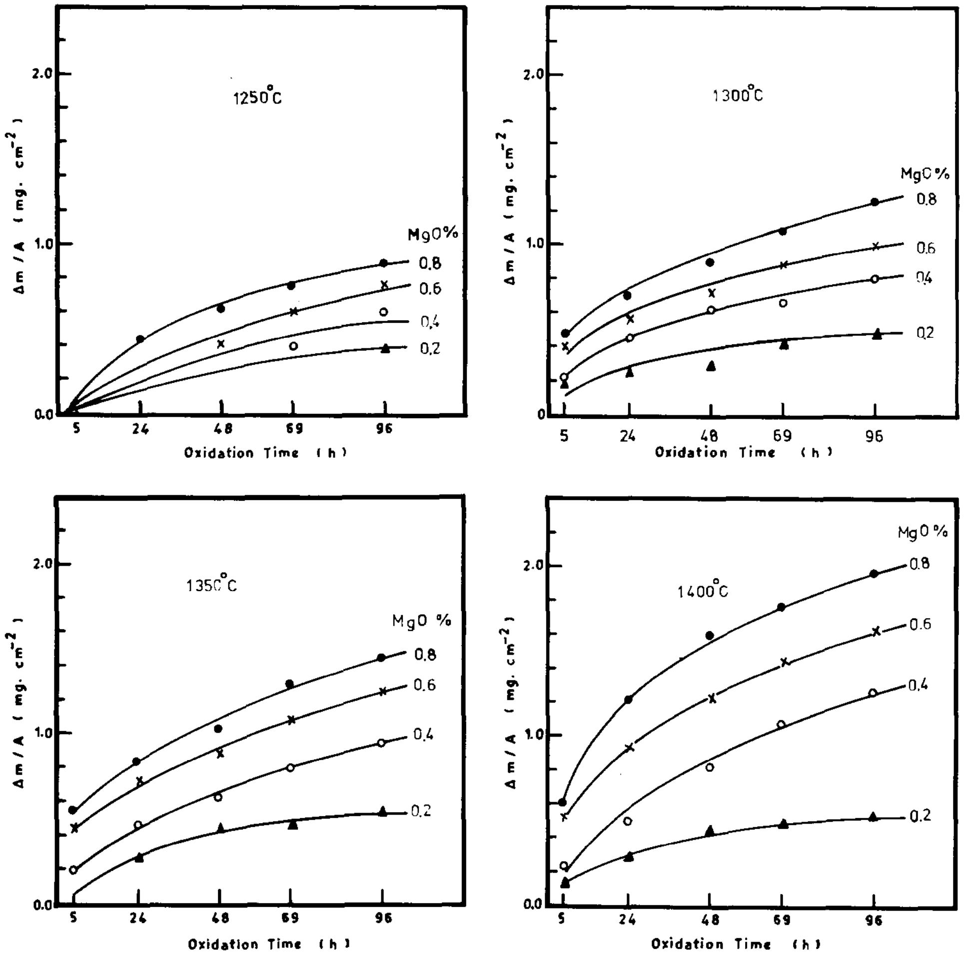

Fig. 1. Weight-change vs. time curves for HPSN specimens at temperatures indicated.

parabolic oxidation behaviour, intersect the ordinate at positive values. This indicates that the initial part of the curve was somewhat more rapid than parabolic. This appears clearly in the specimens containing higher amounts of MgO. The parabolic rate constant $K$ for the oxidation of HPSN specimens, obtained from the slopes of the straight lines in Fig. 2, is shown as a function of MgO in Fig. 3. The effect of MgO on increasing the oxidation rate is notable as the temperature of oxidation is raised.

The parabolic oxidation rate constants for the oxidation of the specimens are compared in the Arrhenius equation (Fig. 4)

$$K = A \exp(-E/RT)$$

where $E$ is the activation energy, $R$ is the gas constant and $T$ the absolute temperature. The present data approximate a straight line for each specimen

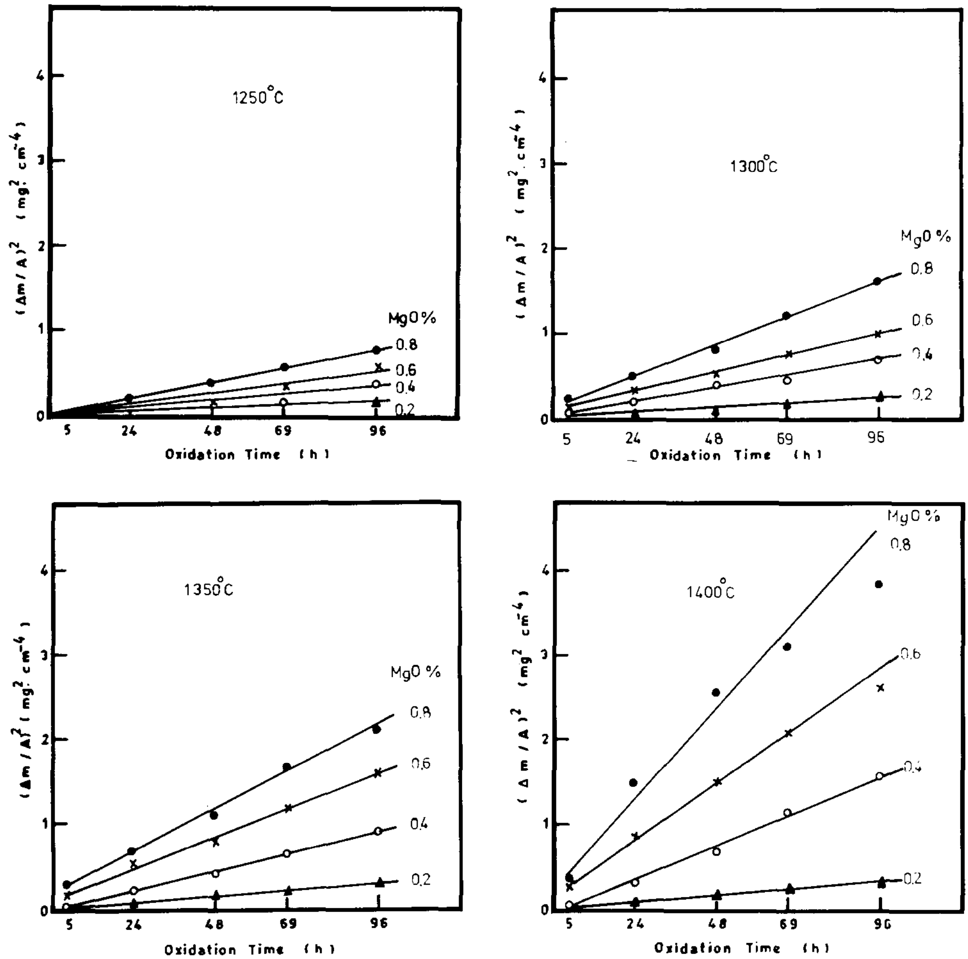

Fig. 2. Parabolic plots for the oxidation of HPSN specimens at temperatures indicated.

whose slope leads to the activation energy. The calculated activation energies are plotted as a function of the MgO% in Fig. 5. Results obtained by Singhal [8] and by Tripp and Graham [10] for HS 130, Cubicciotti and Lau [13] for NC 132 and Cramer [15] for especially prepared hot-pressed silicon nitride are also shown in Fig. 5. The activation energy increases with increasing MgO addition. Higher amounts than 0.4 wt.% MgO have little effect. While there is a conformity between the present results and those obtained by Cramer [15], the activation energies reported by other authors are higher, taking into consideration the amount of MgO used. This is discussed later.

### *Scale composition*

An X-ray diffraction examination was performed to determine the scale composition. The phase changes on the surface after oxidation at 1300 and

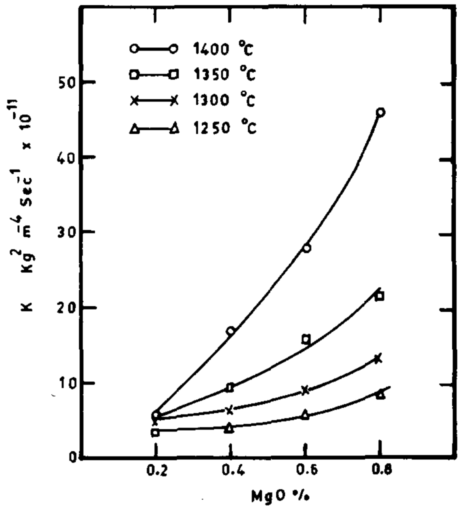

Fig. 3. Variation in the oxidation rate of HPSN specimens with MgO wt.%.

1400°C for 100 h are clearly shown in Figs. 6 and 7, respectively. Results reveal the following deductions: the amount of beta silicon nitride in the oxidation scale decreases with the increase of both MgO content and temperature of oxidation, $\alpha$-cristobalite was clearly identified as a main oxidation product; the magnesium silicate reaction products were identified as enstatite, $MgSiO_3$, and forsterite, $Mg_2SiO_4$, and the magnesium calcium silicates as akermanite, $Ca_2MgSi_2O_7$, and diopside, $CaMg(SiO_3)_2$; the sili-

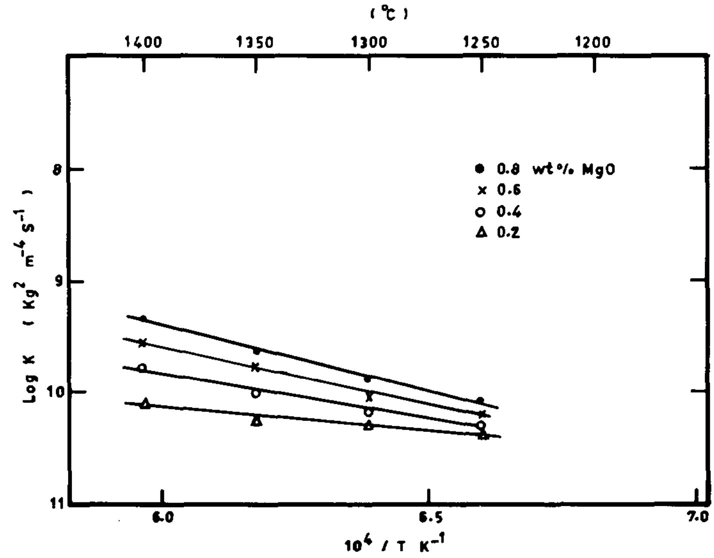

Fig. 4. Variation of rate constant with temperature.

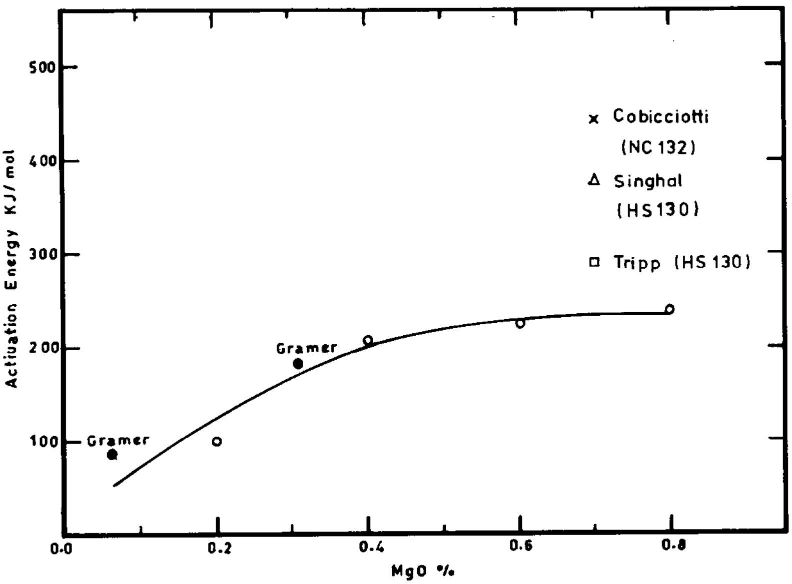

Fig. 5. Variation of activation energy with MgO wt.%.

cate crystals continue to grow as MgO and temperature were increased; the appearance of these phases represents a decrease in the amount of cristobalite, $SiO_2$, relative to CaO and MgO.

*Oxidation mechanism*

As above, the oxidation of hot-pressed silicon nitride obeys the parabolic rate law. This behaviour indicates that the rate of oxidation is diffusion-con-

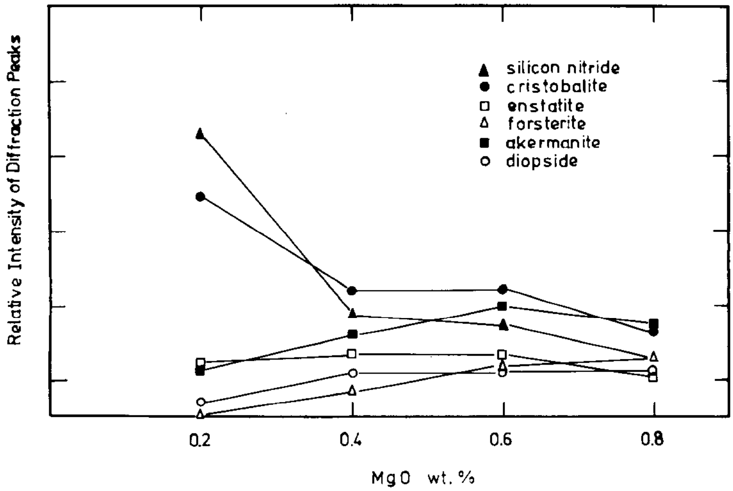

Fig. 6. Phase-changes on the surface of HPSN specimens oxidized at 1300°C.

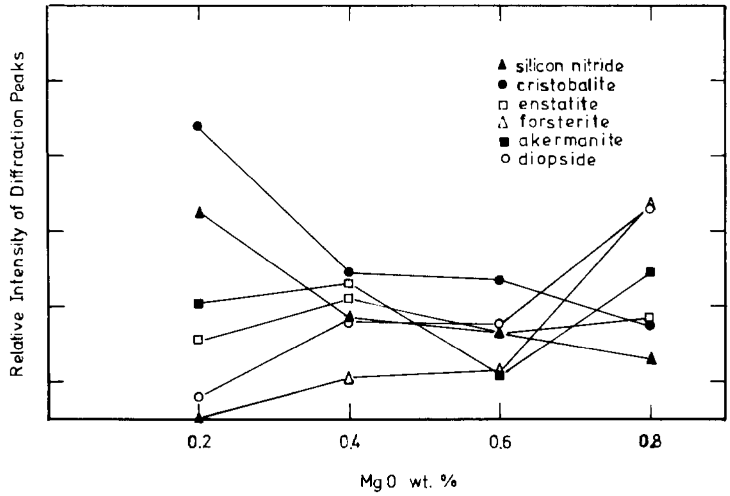

Fig. 7. Phase-changes on the surface of HPSN specimens oxidized at 1400°C.

trolled. There are some diffusional reactions which could occur during the oxidation of hot-pressed silicon nitride: (1) the inward diffusion of oxygen; (2) the outward diffusion of nitrogen; and (3) the outward diffusion of MgO and impurities from the grain boundary glass-phase into the oxidation scale.

Literature data are not available for $O_2$ diffusion in Mg or Ca–Mg silicates for comparison of the activation energies obtained. The fact [8], however, that the oxidation rate of HPSN is independent of oxygen flow rate in the range 1000 to 1400°C suggests that the diffusional mechanism other than inward oxygen diffusion is the rate-controlling mechanism. Furthermore, the reoxidation of HPSN material after removing the surface scale as described by Cubicciotti and Lau [13], showed that the oxidation proceeded along the same parabolic curve regardless of the thickness of the oxide scale. Therefore, the effect of $O_2$ or $N_2$ diffusion through the oxidation scale on the oxidation of HPSN may be limited.

The present results revealed that: (1) the oxidation rate of hot-pressed silicon nitride specimens increases as the MgO content is increased; (2) the oxidation scale was found to be enriched in Ca and Mg in the form of silicates; and (3) although any phase containing K, Al and Ti was not detected, these elements were difinitely present in the oxidation scale as indicated by energy dispersive X-ray analysis (Fig. 8). These elements may be reacted with silica and other elements to form an amorphous phase. These three facts from the present results prove that MgO and impurities diffuse from the grain boundary glassy-phase to the oxidation scale. A trial was performed to compare the present results for oxidation with those in the literature data based on the amounts of main impurities and composition of the liquid phase in HPSN materials. From Table 2 and Fig. 5, it is clear that the present silicon nitride contains the least impurities and, therefore, shows

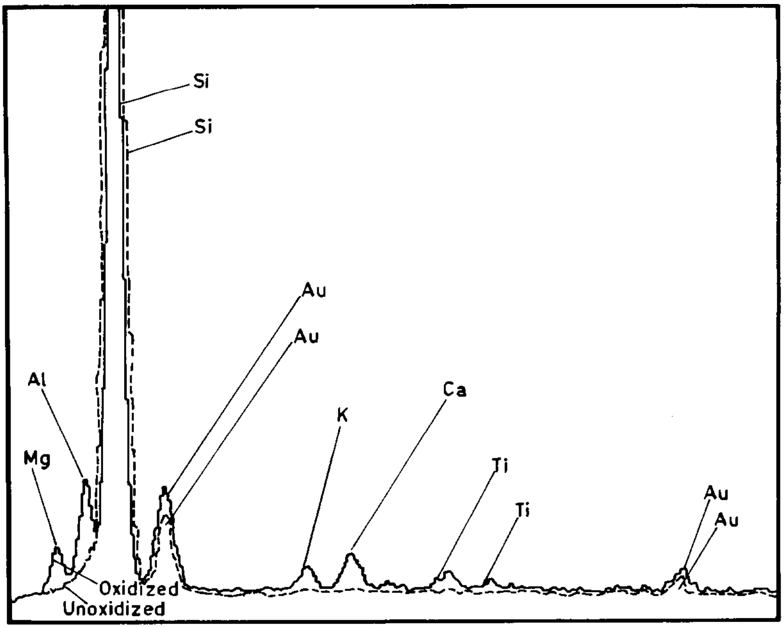

Fig. 8. Energy-dispersive X-ray analysis of HPSN specimen (0.8% MgO) oxidized at 1400°C.

the highest oxidation resistance. The NC-132 material, on the other hand, reveals the highest content of impurities and consequently the lowest oxidation resistance [13]. The difference between the activation energies obtained by Singhal [8] and Tripp and Graham [10] for the oxidation of HS 130 hot-pressed silicon nitride may be based upon a slight difference in the chemical composition of the material used in the two works (Table 2), as instead of definite chemical analysis data, a compositional range is given.

As mentioned above, MgO and impurities diffuse into the oxidation scale. They dissolve in the silicate glass formed in the oxidation scale and lower

TABLE 2

Main impurities and metal oxide concentrations in the glassy-phase in HPSN materials

| HPSN materials | Main impurities (%) | | | | | Metal oxides (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Ca | Fe | Mg | O | $Al_2O_3$ | CaO | FeO | MgO | $SiO_2$ |
| Present work [a] | < 0.05 | 0.01 | 0.05 | 0.7 [a] | 1.75 | 2.04 | 0.30 | 1.39 | 25.12 | 71.14 |
| NC 132 [13] | 0.14 | 0.01 | 0.22 | 0.70 | 1.2 | 6.65 | 0.34 | 7.11 | 29.19 | 56.68 |
| HS-130 [8,10] [b] | 0.07– | 0.02 | 0.1 | 0.70 | 2 | 2.54 | 0.53 | 2.47 | 22.29 | 72.15 |
| | 0.12 | 0.08 | 0.7 | | 5 | 1.92 | 0.94 | 7.63 | 9.84 | 79.64 |

[a] HPSN sample containing 0.7 wt.% MgO.

[b] Analytical values (wt.%) of HS-grades (Norton) [16].

their liquidus temperature, e.g., through the diffusion of calcium, the melting point as well as viscosity of the silicate melt are lowered. A recent study showed that the eutectic temperature in the $Si_3N_4$–$Si_2N_2O$–$Mg_2SiO_4$ compatibility triangle is 1515°C and that the addition of Ca impurity can reduce the temperature to as low as 1325°C [17]. Other impurities, e.g., Al, Fe and K have a similar effect on decreasing the liquidus temperatures and viscosity of the oxidation scale. These changes in the oxidation scale affect the dissolution of silicon nitride in the oxidation scale and its reaction with oxygen [13]. Thus, the different oxidation resistance behaviour of the two materials grades is based upon differences in the chemical composition.

## CONCLUSIONS

(1) The oxidation rate of silicon nitride hot-pressed with magnesia (0.2–0.8 wt.%) in air follows classical parabolic behaviour with an activation energy of 98–235 kJ $mol^{-1}$ in the temperature range 1250 to 1400°C.

(2) The oxidation rate is dependent on magnesia content. The impurities greatly lower the oxidation resistance of silicon nitride.

(3) The scales consist of a mixture of unoxidized silicon nitride, crystalline phases ($SiO_2$, Mg- and Mg–Ca-silicates and a glass-phase containing other elements.

(4) The chemical composition of starting material determines its oxidation resistance behaviour.

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