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Thermal decomposition of a Si_3N_4–22 wt% Al_2O_3 alloy

Materials near the Si_3N_4 corner of the Si_3N_4–AlN–Al_2O_3–SiO_2 quarternary, termed sialons, are candidate materials for high performance applications [1]. Hot pressed alloys in this system are useful because they possess high flexure strengths and good oxidation and creep resistance. However, since hot pressing reduces the ease with which these materials can be fabricated into complex shapes, procedures for sintering these materials to high density are required. A number of sintering studies performed on alloys within this system indicate that weight loss limits the density of the sintered product [2–4]. Thermal decomposition during sintering is undesirable because it competes against the densification process, enlarging pores that sintering tends to close. Nevertheless, despite the important effects it has on sintering Si_3N_4 based ceramics, the thermal decomposition reactions are not yet understood.

Mitomo and co-workers [3, 4], who examined the thermal decomposition of a β'-sialon, $Si_4Al_2O_2N_6$, noted that the dissociating species was SiO, and calculated the minimum SiO pressure required to inhibit weight loss. To maintain this pressure, they used a packing powder composed of Si_3N_4 and SiO_2. If this pressure was not maintained, the sample lost weight and its composition tended toward the AlN corner of the Si–Al–O–N system.

In this report, thermal decomposition studies of a Si_3N_4–22 wt% Al_2O_3 alloy are presented. When the SiO_2 in the Si_3N_4 powder is considered, the composition of this alloy falls within the β'–O′–X phase field in the phase diagram proposed by Jack [1].

The material was sintered under a variety of conditions designed to inhibit the weight loss. They are: (1) N_2 overpressure, (2) Reaction-bonded silicon nitride (RBSN) crucible liner, and (3) Buffered packing powder. The N_2 overpressure

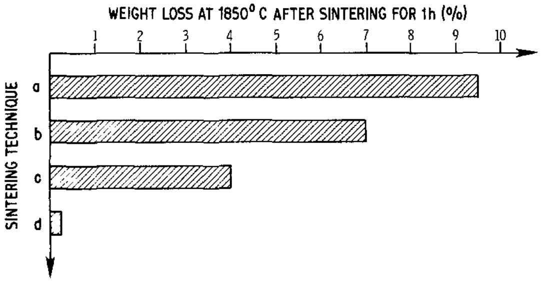

Figure 1 Comparison of the effectiveness of four different techniques used to inhibit the weight loss reactions. (a) Buffered powder, no crucible liner, $P_{N_2} = 2$ atm; (b) unbuffered poweder, no crucible liner, $P_{N_2} = 14$ atm; (c) unbuffered powder, RBSN liner, $P_{N_2} = 14$ atm; (d) buffered powder, no crucible liner, $P_{N_2} = 14$ atm.

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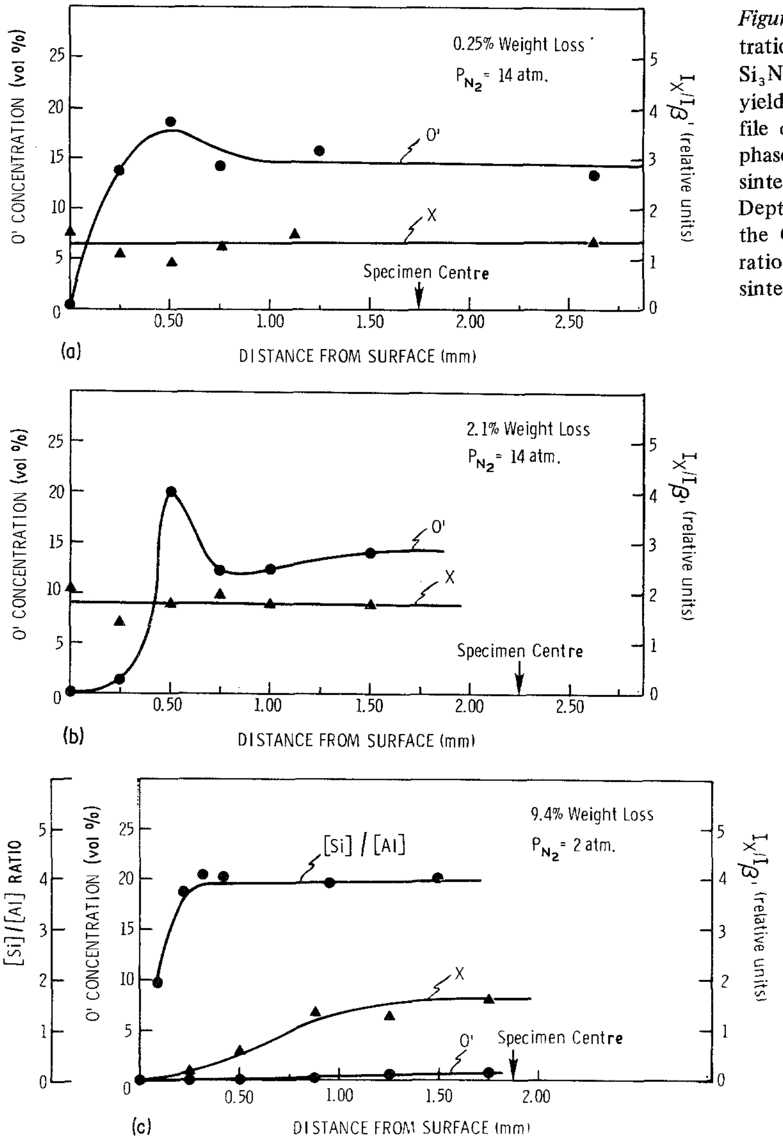

Figure 2 (a) Depth profile of the concentration of the O'- and X-phases in a Si_3N_4–22 wt% Al_2O_3 alloy sintered to yield 0.25% weight loss. (b) Depth profile of the concentration of O'- and X-phases in a Si_3N_4–22 wt% Al_2O_3 alloy sintered to yield 2.1% weight loss. (c) Depth profile of the concentration of the O'- and X-phases and the Si to Al ratio in a Si_3N_4–22 wt% Al_2O_3 alloy sintered to yield 9.4% weight loss.

reduces weight loss by inhibiting the generation of dissociated species. The RBSN crucible lines a graphite susceptor and acts as a barrier against reaction of the dissociated species and the carbon sink. The buffered packing powder, also composed of Si_3N_4–22 wt% Al_2O_3, generates the same dissociated species as the sample and therefore reduces the diffusion of the species away from the sample by reducing its concentration gradient in the vicinity of the specimen.

Fig. 1 shows the relative effectiveness, observed in this work, of four combinations of these techniques for reducing weight loss in this system. (In the figure the term "unbuffered packing powder" refers to pure Si_3N_4.) It is evident from a comparison of sintering techniques 1 and 4 that the N_2 overpressure is the most effective means of reducing weight loss. The buffered packing powder and a RBSN crucible liner also reduced weight loss, as suggested by a comparison of sintering techniques 2 and 4 and techniques 2 and 3, respectively.

Samples, sintered under a N_2 overpressure and packed in a buffered packing powder, were analysed for changes due to weight loss. Since initial work revealed phase inhomogeneities within specimens, depth profiles of the phase concentrations were performed. Structure factors were computed for the O- and β-phases from data in the literature

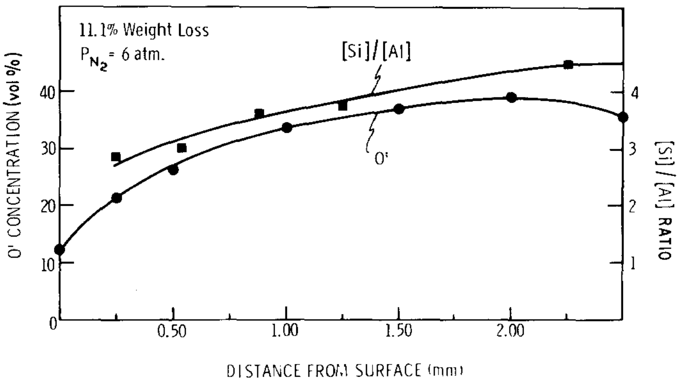

Figure 3 Depth profile showing correlation between the depletion of O′ and a decrease in the [Si]/[Al] ratio.

[5, 6] to determine the absolute magnitude of these phases in this material. For the analysis, the assumptions that the X-phase concentration is small (<10 wt%) and that the O- and β-phases yield similar integrated intensities to O′- and β′-phases were made. The relative amount of X-phase concentration, made by computing I_X^{102}/I_β^{210}, was also monitored. The depth profiles were performed by taking a diffraction pattern, grinding off 0.25 mm, and repeating until about half of the specimen was removed. The grinding was performed along the h direction in cylindrical specimens of volume $\pi r^2 h$.

The results for three specimens with weight losses ranging from 0.25% to 9.4% are shown in Figs 2a, b, and c. The results suggest that for samples exhibiting small weight losses, the surface becomes depleted of O′-phase but the X-phase distribution is not affected. For samples exhibiting about 9% weight loss, however, nearly complete depletion of the O′-phase occurs from the alloy, and partial depletion of X-phase concentrated near the surface is observed.

These results indicate that the concentration of the O′-phase in the surface material of the specimen is lower than in its interior. If this inhomogeneity is caused by the decomposition of surface O′ via the loss of SiO (and N_2), which Mitomo and co-workers [3, 4] and others [2] have suggested are the dissociating species, then the Si to Al ratio, [Si]/[Al], should be less at the surface than in the interior. To test this hypothesis, energy dispersive spectroscopy (EDS) measurements were made of the [Si]/[Al] ratio along the radial direction of the specimen. In specimens with a bulk O′ concentration of only 14 vol%, this effect was too small to be measured, but in a specimen with 40 vol% O′, a correlation was found between [Si]/[Al] ratio and the O′ concentration, as shown in Fig. 3. In addition, the specimen which lost 9.4% of its original weight on sintering was found to have a [Si]/[Al] ratio of only 2 near the surface, which is half of the bulk value. This suggests that significant dissociation of β′-phase occurred in this specimen because only dissociation of this major phase could account for such a large drop in [Si]/[Al] ratio.

The results indicate that dissociation and resulting weight loss lead to inhomogeneous specimens. Material loss comes primarily from near the surface (at least initially) thus causing differences between the composition of the surface material and the bulk. In these specimens, the O′-phase was found to be the least stable to dissociation and the β′-phase the most stable. This result is in accord with the conclusions of Mitomo *et al.* [4] that Si_2N_2O has a larger equilibrium SiO partial pressure than either the X-phase or the β′-phase. The inhibition of weight loss for these specimens can be accomplished effectively using a buffered packing powder and, more importantly, a N_2 pressure of about 14 atm. Lower N_2 overpressures used during sintering can result in a large weight losses, poor sintering rates, and undesirable composition inhomogeneities.

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Growth of Z centres in X-irradiated LiF:Mg

The enhancement of *F* centre formation by divalent impurities in alkali halides has been studied by several workers. Most of the data on this subject are confined to alkaline earth impurities such as Ca^{2+}, Ba^{2+} and Sr^{2+} in NaCl, KCl and KBr. There are comparatively few works on the effect of doping with Mg^{2+} in LiF in spite of the fact that this material is very important for thermoluminescent dosimetry. In this letter some interesting results on this subject are reported.

A sample obtained from a crystal doped with 0.2 wt% Mg in the melt and a size of 8 x 8 x 2 mm^3 was used for the study. The sample was first annealed for 1 h at 480° C, cooled to room temperature within 15 min and then thermally treated at 80° C for either 16 h (Procedure 1), 5 h (Procedure 2), or 2 h (Procedure 3). X-ray exposure after each thermal treatment was performed in steps between 0.026 and 0.52 $kC\,kg^{-1}$. After each irradiation the absorption spectrum was measured and resolved into a set of Gaussian shaped bands.

Figs 1a and b, show the influence of two different pre-irradiation annealing procedures on some selected radiation-induced optical absorption curves. As can be clearly seen, there is a strong dependence of the absorption regions on both sides of the *F* absorption band at 5 eV on the duration of the 80° C annealing. These regions are known to be connected to the different *Z* centre absorption bands, i.e. the 3.3 eV band, the Z_2 band at 4 eV and the Z_3 band at 5.5 eV [1]. According to Dryden *et al.* [2] it is considered that annealing Procedure 1 provides for a low concentration of dipoles (Fig. 1a), Procedure 2 for a medium concentration and Procedure 3 for a high concentration (Fig. 1b).

After computer analysis of all the absorption spectra, to determine the peak absorption coefficient for the different bands, the data were plotted as shown in Fig. 2. The abscissa dose *D*

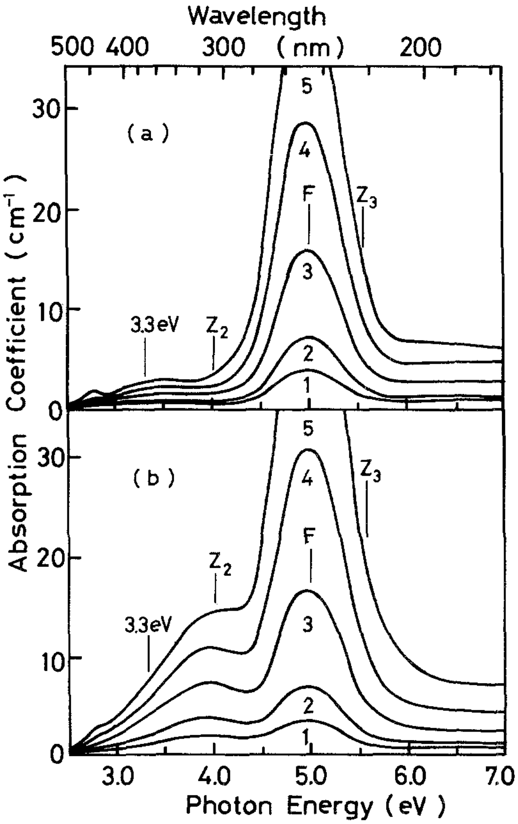

Figure 1 Absorption spectra of LiF : Mg after pre-irradiation annealing at 80° C for (a) 16 h and (b) 2 h and subsequent X-ray irradiation to different doses: (1) 0.026, (2) 0.052, (3) 0.13, (4) 0.26, (5) 0.52 $kCkg^{-1}$. The absorption spectra present prior to irradiation have been subtracted in all figures.

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