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Received 9 December 1980
and accepted 5 February 1981

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The oxidation in air of sialon materials formed without densification aids

The importance of mobile cations at grain boundaries for the oxidation process in nitride ceramics has been convincingly demonstrated for the cases of hot-pressed silicon nitride containing magnesium oxide [1] and a commercial sintered sialon material [2]. In ceramics of these types there appears to be an ample reservoir of grain-boundary phase able to release cations such as Mg^{2+} and Y^{3+} to the surface oxide film to modify the properties of this film and to provide a basis for parabolic kinetics in the rate controlling diffusion of these ions from the grain boundaries.

Simple parabolic kinetics are, however, not always observed in the oxidation of sialon materials. In the course of recent studies on materials densified without the use of liquid-generating additives we have observed rather variable, but approximately linear, kinetics for a range of sialons with differing z values and O/N balances. While the data of Singhal and Lange [3], obtained with materials probably containing a much higher proportion of second phase than that present in our materials, do indicate parabolic kinetics, close examination of the published data of Arias [4] and of Hasegawa and co-workers [5] on the other hand shows that in these cases also, the parabolic rate law is not followed over the entire time range of the studies, particularly at longer times. Similar conclusions have been drawn by Brossard and co-workers [6, 7], from the examination of β'-sialon powders prepared with 60:40 and 70:30 balances of Si_3N_4:Al_2O_3, where it was observed that diffusion controlled oxidation kinetics were established only with difficulty at temperatures above 1300° C due in this case to crystallization of the protective amorphous oxide film.

Some of our own data obtained for oxidation of $z = 0.75$ sialons in laboratory air over the temperature range 1350 to 1550° C are presented in Fig. 1, and also, for convenience, in log–log form, in Fig. 2. The discontinuity in the curve at 1350° C is not an unusual, and so far not entirely explained, feature of the lower temperature oxidations. The mean value of the gradients of these plots is in the region of 0.81, and the apparent enthalpy of activation calculated at a constant extent of reaction has the very high value of 570 kJ mol^{-1}. Because the lines shown in Fig. 2 are approximately parallel, the enthalpy of activation is essentially independent of the extent of reaction up to times of the order of 16 h. These materials had been prepared by reaction hot-pressing at 1690° C mixtures of silicon nitride, aluminium oxide and aluminium nitride powders,

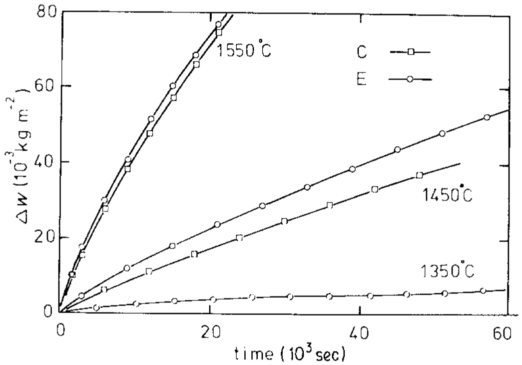

Figure 1 Weight gains (kg m^{-2}) plotted as a function of time (sec) for materials oxidized at 1350, 1450 and 1550° C.

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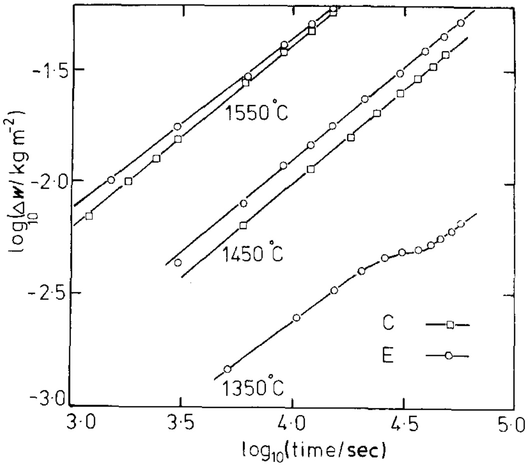

Figure 2 Data from Fig. 1 presented in the form $\log_{10}$ (weight gain) as a function of $\log_{10}$ (time).

of overall compositions corresponding to points slightly oxygen rich with respect to the β′-sialon phase line in order to achieve a reasonable degree of densification. Details of these starting compositions and products are provided in Table I. Analysis of the silicon nitride powder showed it to be contaminated to a small but significant extent by Fe (0.5 wt%), Ca (0.05 wt%) and Mg (0.04 wt%). Cubes of side 5 mm were cut from the hot-pressed discs and hand polished to < 1000 mesh silicon carbide and < 1 μm alumina before ultrasonic cleaning. Samples were usually suspended by a platinum wire basket and lowered rapidly to the pre-equilibrated hot zone of the furnace.

Subsequent X-ray and scanning electron microscope examination of the quenched oxide films showed them to be non-crystalline, and well-expanded by gas bubbles (Fig. 3a and b). There was a strong tendency at high temperatures for relatively isolated droplets of glass to be formed (Fig. 4). The porosity also seemed likely to be interconnected to a certain extent. The difficulties of estimating extents of reaction by measurements of film thickness are obvious. Energy dispersive X-ray analysis of selected outer surfaces of the glass layer indicated the presence (in addition to Al and Si) of trace amounts (at the limits of detection) of Ca and Fe.

It would therefore appear that in the absence of relatively large quantities of low valency grain-boundary cations the rate controlling process in these cases is in principle the diffusion of oxygen through an aluminosilicate glass film. The physical characteristics of this film, however, then have an over-riding influence on the oxidation kinetics observed. The film in fact appears to have a tendency to develop an effectively constant thickness (supported by Fig. 4). As far as the slow diffusion process is concerned, much of the materal forms either relatively isolated droplets, or contains channels through which rapid diffusion of gas can occur. Arguments concerning the nature of the rate determining step in the oxidation of silicon carbide have recently been revived [9], but in the present case the evidence is that the reaction takes place at the sialon–silicate interface, rather than the silicate–air interface, from the location of the source of the gas bubbles in the glass film. Relatively high values for the enthalpy of activation of oxygen diffusion through aluminosilicate glasses have previously been reported [10]. The enthalpy of activation values observed here are to be compared with those obtained (~ 130 kJ mol^{-1}) for the oxidation under similar conditions of reaction-bonded silicon nitride of a purity comparable with that used in the preparation of these sialons [11]. It is possible that the much higher values observed with the sialons are artificially inflated by changes in the physical nature of the aluminosilicate film with temperature, associated with changes in viscosity and surface tension.

It is of further interest that although the two compositions contained significantly different amounts (~ 7% and ~ 14%) of an oxide-rich second phase, they oxidized at closely similar

TABLE I

Material	Powder composition (wt %)			Equivalent % ratio of O/N	Estimated liquid phase content (%) [8]	Density (% theoretical)
	Si_3N_4	Al_2O_3	AlN			
C	87.4	9.0	3.6	0.98	7	86.7
E	84.6	14.0	1.4	1.14	14	95.5

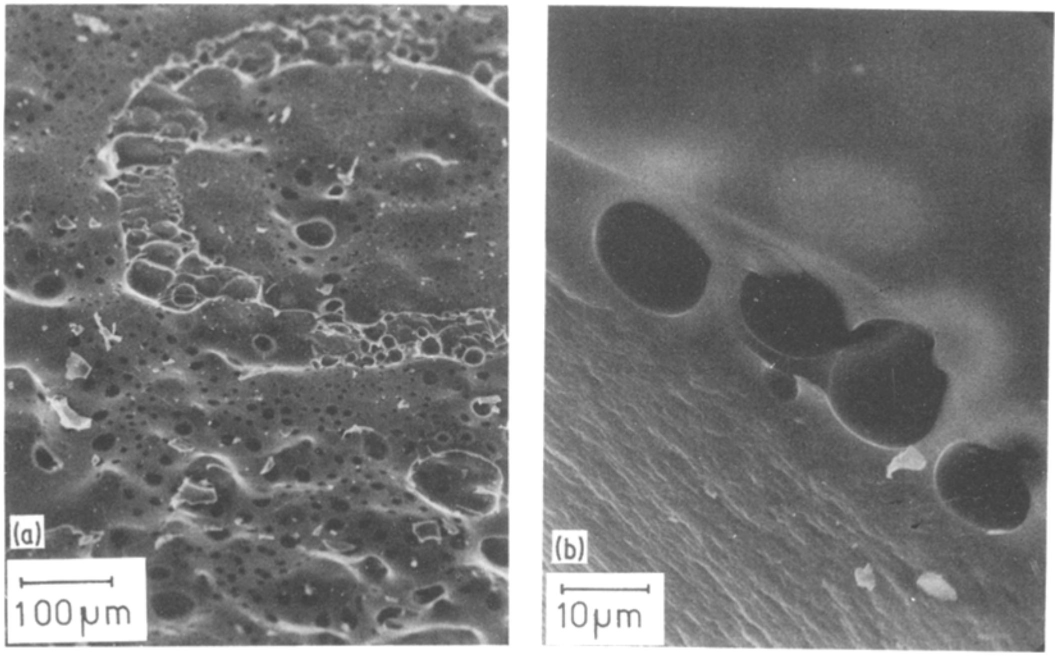

Figure 3 (a) Sample of surface oxidized for 15 h at 1350° C and (b) fracture surface of material shown in Fig. 3a.

rates over this range of temperatures. This would be in keeping with the view expressed above that the oxidation process is controlled in the present case more by the nature and composition of the surface oxide film (and therefore governed, primarily, by the z value of the sialon) than by the amount of composition of the grain boundary phase.

It seems clear therefore that the oxidation mechanisms and kinetics for sialon materials as a function of composition and purity level require further close scrutiny, and that it is unsafe to make the broad assumption that diffusion controlled, parabolic, kinetics are normal.

Acknowledgements

The partial support of this study by the DGRST is gratefully acknowledged. Assistance with

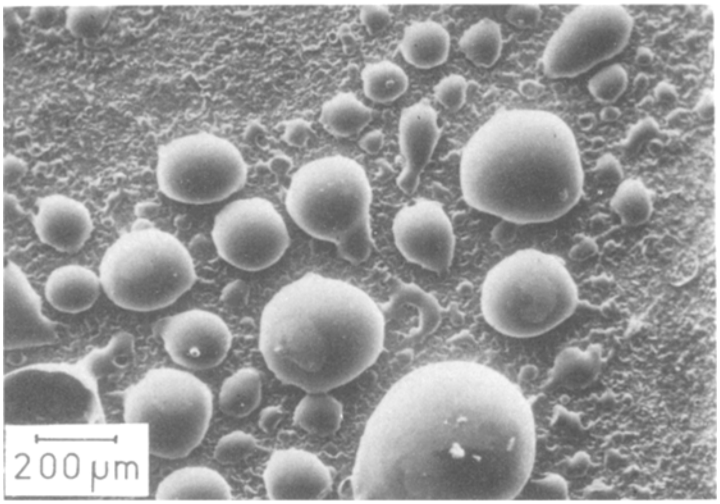

Figure 4 Surface of sample oxidized for 8 h at 1550° C.

scanning electron microscopy was provided by M. Lortholary. Analyses of the silicon nitride starting powder were carried out by F. Chukukere and hot-pressed sialon materials were prepared by M. N. A. Rahaman.

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Received 12 December 1980
and accepted 11 February 1981.

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ESR linewidths of some iron group ions in MgO

In a recent paper [1] the authors reported a study of intensity and linewidth measurements on the ESR spectrum of Fe^{3+} in MgO. It was shown that very little of the iron contributed to the Fe^{3+} cubic site spectrum, and that taking this into account and analysing the results by means of the Kittel and Abrahams' [2] dipolar theory the experimental linewidths were broadened, rather than narrowed as had been suggested previously [3]. Without more information regarding the bulk of the iron, which does not contribute to the cubic site spectra, it is difficult to say whether this line broadening is a result of interactions with the Fe^{2+} and the clusters, or whether there is some fault inherent in the model used.

In this context it is of interest to look at the linewidths of Co^{2+} in MgO, which were reported by Thorp *et al.* [4]. It would be a difficult proposition to count spins for Co^{2+}/MgO as this would require a dual low temperature cavity arrangement since the Co^{2+} signal only appears at temperatures less than 60 K. However, although Co^+ can be produced by X-irradiation [5] it is likely that under normal circumstances the cobalt will all be in the Co^{2+} state. We also expect that being divalent it will substitute directly for the Mg^{2+} ions, no vacancy compensation being required; furthermore, there is little likelihood of pairs forming or non-random clustering occurring, as may happen with Ti^{3+}, Cr^{3+} and Fe^{3+}. Consequently, it should be possible in the case of cobalt-doped magnesia to take the manufacturer's concentration, fit this directly into the appropriate calculation, and derive a reasonable comparison between theoretical and experimental linewidths.

Taking account of the Co^{2+} spin = 3/2 and the experimental value of $g = 4.2785$ [6] we obtain from the Kittel and Abrahams equations for second and fourth moments [2] the relationship between the peak-to-peak linewidths ΔH_{ms} and concentrations

$$\Delta H_{ms} = 0.6671 f \text{ (Tesla)} \qquad (1)$$

where f is the cation site fraction i.e. the fraction of magnesium sites occupied by Co^{2+} ions. Conver-

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