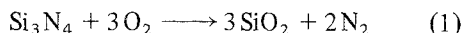


On the influence of a gaseous boundary layer on the oxidation of reaction-bonded silicon nitride at 1400° C

The oxidation of reaction-bonded silicon nitride (RBSN) in air in the temperature range 1000 to 1400° C has been the subject of several studies which all point out the formation of silica both within the pores (internal oxidation) and on the outer surface of the samples (external oxidation) [1, 2]. Internal oxidation seems to be favoured at low temperatures, but as yet this has not been clearly explained. Neither has the increasing weight gain of the oxidized samples as a function of surface roughness, other conditions remaining the same [3, 4].

It has been claimed [2] that the oxidation of this kind of material should be discussed in the same way as pure silicon oxidation [5], which has already been successfully done for silicon carbide [6]. Following this approach, the partial pressure of oxygen at the sample surface would be limited by its diffusion rate through a gaseous SiO boundary layer and in some cases so strongly reduced that the reaction:



might become thermodynamically impossible. The purpose of this paper is to give some experimental support to this assumption and to show that it may lead to a better understanding of RBSN oxidation.

The material used for this study was obtained from Si + 6 wt % Al compacts nitrided in flowing nitrogen (total pressure: 1.2 atm.; flow rate: renewals per hour) containing 450 to 1000 p.p.m. oxygen. The densities of the nitrided specimens varied between 2.4 and 2.7. The major phase was β -Si₃N₄ (in fact β' -sialon [7]). Free silicon (less

than 15 mol % irrespective of porosity) and traces of AlN could also be found. The specimens were machined into 25 mm × 5 mm × 1.5 mm test bars, the faces of which were systematically ground. These were divided into two groups; the first was oxidized in still air in alumina boats; the second was set in the hot zone of the furnace at the end of a vibrating alumina rod (Fig. 1), so that the test bars could not be protected by any gaseous layer which might form. Oxidation treatments were carried out at 1400 ± 5° C during 50 h in a horizontal furnace whose mullite core was open at both ends. It took two hours to introduce the samples into the pre-heated furnace and to draw them out at the end of the heat treatment.

X-ray diffraction analyses reveal that in both cases oxidation products are silica (detected as α -cristobalite) and a small amount of mullite, which is in agreement with previous observations relative to the oxidation of hot-pressed or sintered β' -sialon [8]. Samples from both groups exhibit decreasing final weight gains as density increases (Fig. 2). However the two plots are not exactly similar: weight gains and the amplitude of their variations are less important in the second case than in the first. Major differences between both groups are brought to light by microstructural observations on a plane normal to the surface. The oxidation of samples from the first group seems to be mainly internal: irregularly shaped oxidized zones seem to have grown at the expense of the initial material at some distance from the surface (Fig. 3a). On the contrary, samples from the second group possess a regular superficial oxidized layer (Fig. 3b).

The different behaviours of the two groups of samples with respect to superficial oxidation points out the formation of a gaseous boundary layer in still air which results in a strong decrease of the oxygen partial pressure $P_{\text{O}_2}^*$ at the surface

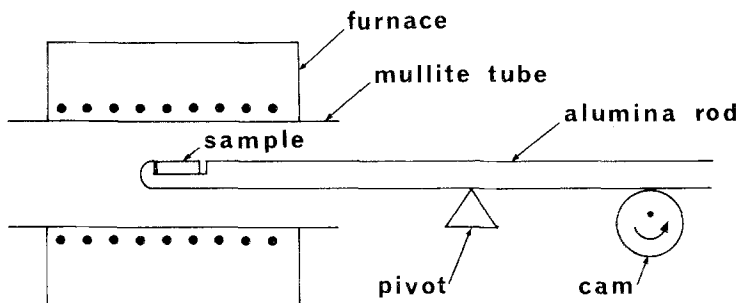


Figure 1 Vibrating device used during oxidation treatments.

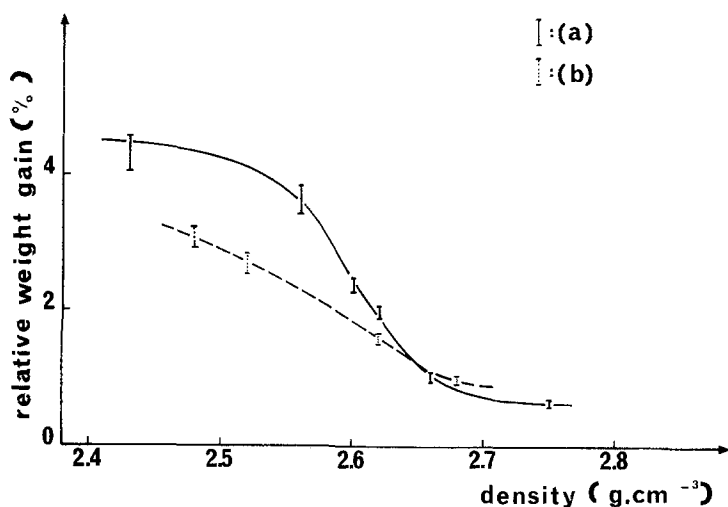
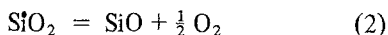


Figure 2 Final weight gains versus density plots (a) in still air; (b) using the vibrating device.

of the samples. Assuming that the gas flow is laminar within the boundary layer and the Gibbs enthalpy for the equilibrium



is given by: $\Delta G_2^0 = 192\,300 + 6.45T \log T - 82.9T$ [9], it is possible to calculate $P_{\text{O}_2}^*$ as a function of temperature [5]. The results are shown in Fig. 4 and can be compared with the minimum oxygen partial pressure $P_{\text{O}_2}^0$ allowing Reaction 1 to occur, knowing the corresponding Gibbs enthalpy: $\Delta G_1^0 = -469\,800 + 5.76T \log T + 28.2T$ [9], taking $P_{\text{N}_2} \approx 1$ atm. and substituting successively 1 and 10^{-3} for Si_3N_4 activity (the latter value, which is rather low in spite of the small amount of aluminium and oxygen in our β' solutions, has been suggested by a simplified thermochemical model for the Si-Al-O-N system [10]). It can thus be noted that $P_{\text{O}_2}^*$ is still smaller than $P_{\text{O}_2}^0$ at

1400°C, whatever the Si_3N_4 activity may be. External oxidation has however been observed at 1200°C on pure RBSN samples [1], as a result of thermogravimetric experiments in a vertical furnace where convection flows are important and probably reduce the protective role of the gaseous boundary layer.

It must then be considered that pores opening on the surface may induce local discontinuities in the boundary layer so that oxygen can have access to silicon nitride within the porous medium; this explains why the weight gains of samples from the first group are strongly dependent on density. This effect is less marked when external oxidation is favoured (second group of samples), presumably because the SiO_2 superficial layers partly fill the pores and reduce the gas penetration. Surface finish effects reported elsewhere [3,4] can be similarly explained: roughness may disturb the

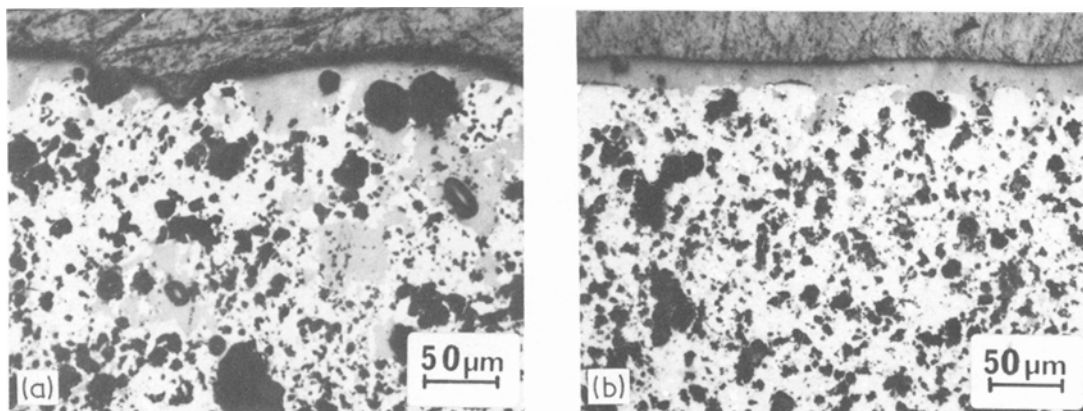


Figure 3 Microstructures of oxidized samples (density = 2.56) (a) in still air; (b) using the vibrating device.

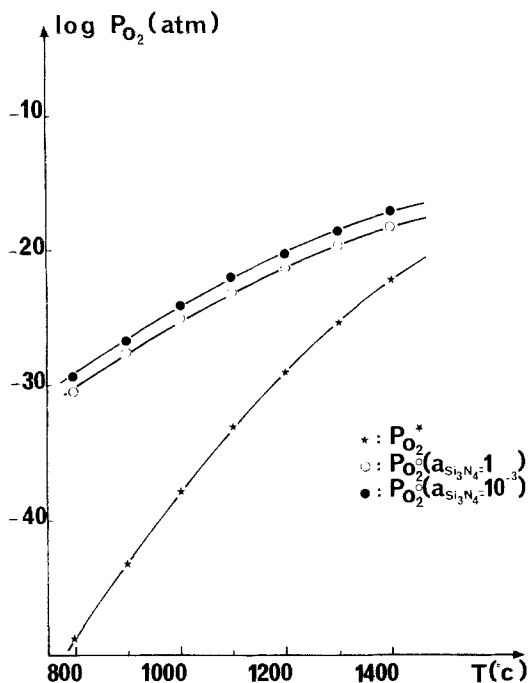


Figure 4 Oxygen partial pressures calculated from Wagner's model ($P_{O_2}^*$) [5] and from Gibbs enthalpy for Si_3N_4 oxidation ($P_{O_2}^0$) [9].

boundary layer and modify the rate of oxygen diffusion through it.

In summarizing the present work is believed to show that a gaseous boundary layer is formed during the oxidation of RBSN in still air. As a consequence, the observed behaviour is closely dependent on sample preparation (porosity, surface finish) and also on the type of furnace used, all factors which may influence the gas flow within the boundary layer and modify the oxygen

partial pressure at the gas–solid interface. Apparent kinetics may thus only be valid for given experimental conditions.

Acknowledgements

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Measurement of craze density by quantitative transmission electron microscopy

The density of crazed matter has generally been measured by Kambour's [1, 2] method of total internal reflection. This technique has the disadvantage that it averages over quite large craze volumes so is not suitable for measuring the variation of density along a craze or the density near the tip of a craze. These densities are of

interest because it is not clear how crazes grow in width. They are thought to grow by a combination of crazing new material and elongating the pre-existing craze. Beahan *et al.* [3] suggested from electron microscope observations on polystyrene that the majority of craze width growth is by crazing new material but they did observe a change in morphology as the craze neared its maximum width.

The purpose of this letter is to describe an electron microscope technique for measuring