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Vapour transport of magnesia into reaction-bonded silicon nitride

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Magnesia, as a sintering additive, can be introduced into reaction-bonded silicon nitride (RBSN) via vapour-phase transport. The principal process variables were studied; a controlling factor was found to be the amount of silica on the internal surfaces of the ceramic. Through a controlled oxidation of the RBSN, the amount of magnesia introduced to the compact was increased to ≈2 wt% allowing a post-sintered density of 93% theoretical to be achieved. Further increases in internal oxidation, and consequent magnesia uptake, were limited by the oxidation of Si_3N_4 whiskers on the surface of the RBSN and in its pore structure.

1. Introduction

Reaction-bonded silicon nitride (RBSN) is a ceramic made by a relatively low-temperature net-shape fabrication process involving the direct nitridation of silicon powder compacts. Owing to the dependence of this process on a continuous network of internal porosity to allow transport of the nitrogen throughout the compact, RBSN typically contains ≈ 20% porosity. This limits its strength and its oxidation/corrosion resistance. However, RBSN can be further densified by a subsequent heat-treatment process [1] yielding "post-sintered RBSN" (PSRBSN). In order to achieve this densification, sintering additives are required which react to form a liquid phase at high temperature. This liquid phase serves as a relatively fast diffusion path for mass transport during the solution–precipitation process responsible for densification.

The sintering additives can be introduced into the RBSN in one of three ways: firstly, by addition to the starting silicon powder, prior to reaction-bonding; secondly, by incorporation into the nitrided compact as soluble salts, and thirdly, by vapour diffusion from a powder bed. Although the first method is favoured by most workers [2], problems can arise due to additive agglomeration and inhomogeneous distribution and, in some cases, to incomplete conversion of silicon [3]. Solution impregnation is often not satisfactory because several impregnations are required and non-uniform additive distribution is a commonly encountered problem. In the present research, the third method, namely vapour-phase transport, was studied using magnesia, well documented for its role as a liquid-phase forming additive in the sintering of silicon nitride ceramics [4] and its high volatility [5], as a sintering aid. The work was part of a study to test the feasibility of an integrated high-temperature processing system taking a shaped, argon-sintered, silicon compact through to a full, dense ceramic, without cooling [6].

Although well known as a stable refractory oxide, magnesia becomes appreciably volatile above 1400 °C [7]. On consideration of the various vaporization mechanisms [8] and under the conditions of atmosphere, temperature and pressure set in the study, congruent vaporization (Equation 1) was considered most probable, i.e.

$$\mathrm{MgO_{(s)}} \rightarrow \mathrm{MgO_{(g)}} \qquad (1)$$

In a vacuum, the rate of vapour transport away from a surface is limited by the rate of evaporation–condensation, whereas in a gas at 1 atm pressure, as in the present case, it may be controlled by diffusion of the vapour away from the source through the gas. The interdiffusion coefficient, ($D_{\mathrm{MgO},\mathrm{N}_2}$), for MgO through nitrogen at 1 atm and at 1550 °C was estimated to be $1.5 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$. This value, compared with the evaporation kinetics, suggested diffusion was not limiting the transport process. The third stage of the vapour-impregnation process is the diffusion of "MgO" into the compact. The mean free paths of the various magnesia-bearing species were estimated to be in the range 0.5–1.7 μm. The average size of pores in the RBSN, as measured by mercury-intrusion porosimetry, was 0.1–0.2 μm. This gives a ratio of average channel radius to mean free path of 0.2–0.06 suggesting Kundsen flow rather than "viscous" flow through the pore structure. In Knudsen flow, gas diffusion is governed by collisions of molecules with the channel walls and is little affected by collisions between gas molecules.

The chance of chemical reaction of the magnesia vapour with the silica-coated walls of the compact at the experimental temperatures (∼ 1500 °C) is high and further complicates the process. It is this reaction

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that is believed to be the factor controlling the amount of magnesia introduced to the RBSN. The surface silica acts as a “sink” for magnesia vapour, the two reacting to form magnesium silicates, as shown in Equations 2 and 3. Therefore, the amount of magnesia retained in the compact would depend on the initial amount of silica in the RBSN.

$$2MgO + SiO_2 = Mg_2SiO_4 \text{ (forsterite)} \quad (2)$$

$$MgO + SiO_2 = MgSiO_3 \text{ (enstatite)} \quad (3)$$

2. Experimental procedure

2.1. Materials

Impregnation experiments were carried out on short pieces (~ 1 cm) of a typical commercial RBSN rod (“Nitrasil”, Tenmat Ltd, Manchester, UK) of diameter 8 ± 0.15 mm, which had an average pore size of 0.1–0.2 μm and a density of 2.35 $Mg\,m^{-3}$. The specific surface area of the internal porosity, as measured by the BET method, was $1.4\,m^2\,g^{-1}$. The total surface silica content of the as-received material, determined by measuring weight-loss during a deoxidation treatment in $N_2/5\%H_2$ at 1350 °C, was 1.2 wt %. From this, the thickness of the silica layer was estimated to be ~ 3.5 nm, in good agreement with the value, 3 nm, quoted in the literature [9].

2.2. Procedure

For the impregnation experiments, the specimens were embedded in a powder comprising 50 wt % Si_3N_4, 40 wt % BN and 10 wt % MgO contained in a boron nitride crucible, the purpose of the powder bed being to suppress decomposition of the RBSN and to provide the magnesia source; the role of the boron nitride powder was solely to prevent sintering of the bed. Heat treatment and post-sintering were carried out in an induction-heated controlled-atmosphere furnace, described in detail elsewhere [10]. The furnace was evacuated and back-filled with nitrogen twice before heating to the processing temperature at a rate of 50 °C min^{-1}.

After MgO impregnation, the specimens were transversely sectioned, mounted and polished using conventional ceramographic methods and, after coating with carbon, they were analysed using an electron microprobe analyser (Jeol JXA-50A). The probe covered an area of approximately 50 μm x 50 μm; this larger than typical area was chosen to average out variations arising from microstructural inhomogeneities.

What are considered to be meaningful magnesium profiles, were obtained by averaging data from four traverses along different diameters.

Deoxidation and oxidation treatments were carried out in a controlled atmosphere thermogravimetric balance [11].

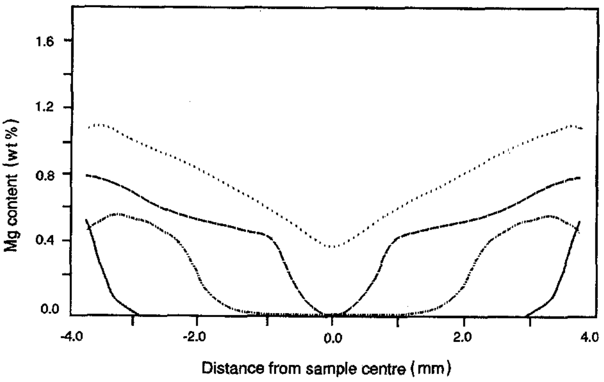

Figure 1 Magnesium concentration across samples annealed at 1450 °C, after (——) 3 h, (··——··) 5 h, (– – –) 10 h, (···) 15 h.

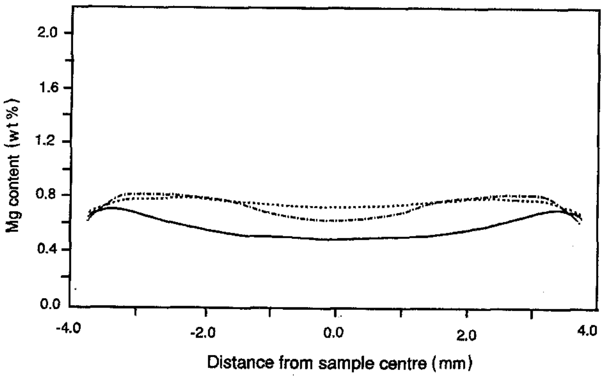

Figure 2 Magnesium concentration across samples annealed at 1500 °C after (——) 3 h, (·—·) 5 h, (···) 10 h.

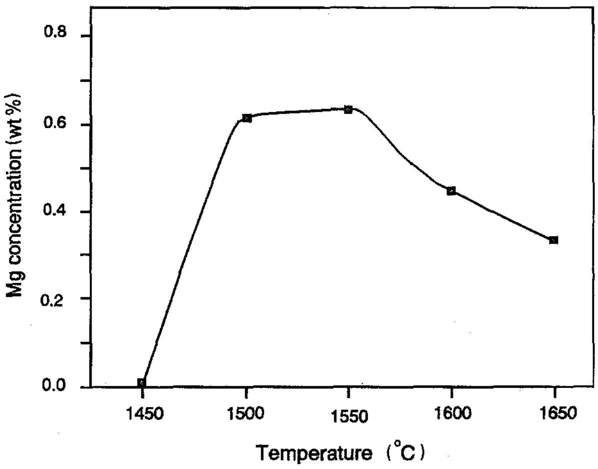

Figure 3 Magnesium concentration at sample centres after 5 h anneal.

3. Results and discussion

Initial experiments were carried out at 1450 °C for 3, 5, 10 and 15 h, and the magnesium concentration profiles obtained are shown in Fig. 1. The increase in magnesium content with annealing time is evident. Fig. 2 shows how the effects of time is markedly diminished at 1500 °C and that there is no significant difference in magnesium content following the 5 and 10 h anneals.

Fig. 3 shows that as the annealing temperature was increased from 1450 °C to 1550 °C, the magnesium concentration increased to ~ 0.65 wt % and was uniformly distributed (cf. Fig. 4). It is evident that impregnation falls off with increasing temperature above the optimum of 1500–1550 °C. One or both of two

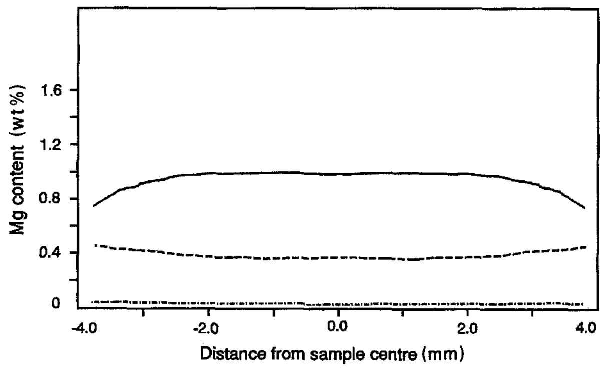

Figure 4 Magnesium concentration across samples annealed under various environments at 1550 °C for 5 h. (——) BN (N_2), (- - -) Al_2O_3 (N_2), (·—·) BN (N_2/H_2).

possible processes might account for this. If Knusden flow does occur then the inwards flux of MgO would decrease with increasing temperature. Also, the probability of reaction between the MgO and the surface silica would increase with increasing temperature, again diminishing the inward flux of MgO. Because the MgO–SiO_2 eutectic is at 1543 °C it seems more likely that it is the later process which is responsible for the observed decrease. It also has to be recognized that at the high temperatures involved, and especially if some free silicon is present, which is very likely, that the silica layers will be evaporating as SiO [12] removing the "sink" for MgO. In fact, annealing at 1650 °C resulted in an abundant growth of whiskers around the crucible lid, the coolest part of the immediate environment. Energy-dispersive X-ray analysis of these crystals identified them as magnesium silicates of varying composition indicating that volatilization of silicon oxide species as well as those of magnesium, was occurring.

Increasing the MgO content of the powder bed from 10 wt % to 25 wt % had no significant effect on the uptake of MgO after annealing at 1550 °C for 5 h, confirming that the rate-limiting step was diffusion into the compact.

The following experiments were carried out to confirm that the concentration of magnesia retained in the compact was dependent on the extent to which the RBSN was oxidized.

By heating the compact at 1350 °C in an N_2/5% H_2 mixture, the native silica was removed through the reaction

$$SiO_{2(s)} + H_{2(g)} \rightleftharpoons SiO_{(g)} + H_2O_{(g)} \qquad (4)$$

After the reduction process, which was followed directly on the thermal balance, and without giving the compact any opportunity to reoxidize, it was annealed in the MgO-containing powder bed. The resulting concentration profile in Fig. 4 shows that, as expected, the magnesium uptake was markedly reduced, from ~ 1 wt % to ~ 0.05 wt%. Also shown in Fig. 4 is the effect of different crucible materials on the amount of magnesium retained in the RBSN after impregnation. The magnesium content decreased by ≈ 50% when impregnation was carried out in an alumina crucible rather than the usual boron nitride crucible. Analysis confirmed that the alumina crucible was acting as a "sink" for the magnesia and silicon oxide vapours, thus resulting in a lower flux into the compact. This is not unexpected because eutectics in the MgO–SiO_2–Al_2O_3 ternary form at temperatures as low as 1355 °C [13].

The primary reason for impregnating the RBSN with magnesia is to promote the liquid-phase sintering of the silicon nitride in a subsequent heat treatment. The experiments indicated that the amount of magnesia normally introduced into the RBSN (≈ 1 wt %) was insufficient to achieve a high density during post-sintering. Because of the link between the amount of surface silica and the amount of MgO introduced to the compact, an effort was made to increase the MgO uptake by increasing the surface silica. This was achieved in a controlled way by progressively oxidizing RBSN compacts in the thermal balance at 950 °C in air [14].

Fig. 5 shows the magnesium profiles after annealing at 1550 °C for 5 h for RBSN materials with the following three silica levels: 1.2 wt % (as received), 3 and

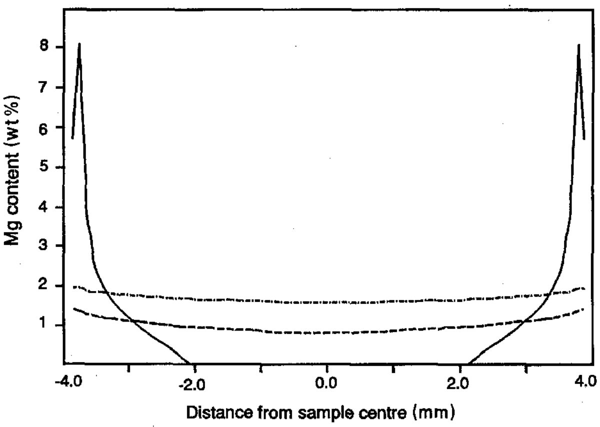

Figure 5 Magnesium concentration across samples after oxidation treatments. (——) 6 wt % silica, (·—·) 3 wt % silica, (- - -) unoxidized.

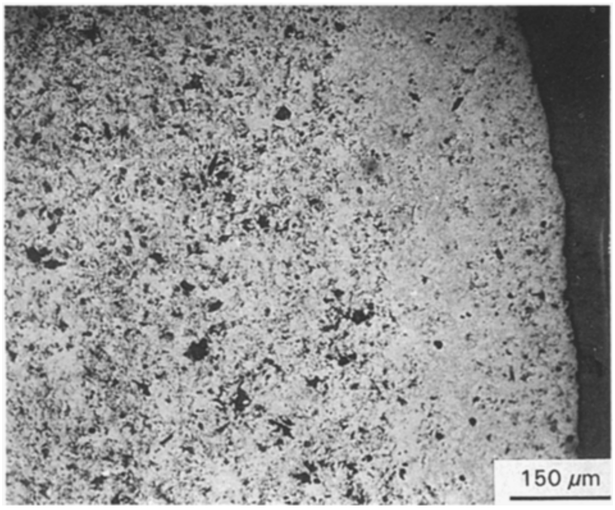

Figure 6 A section of an oxidized and magnesium-annealed sample showing density variations at sample edge (optical).

6 wt %. For the compacts with the least and intermediate silica contents, the magnesium uptakes are as expected; also the distributions of magnesium are uniform, indicating that the pore system had not been closed. The sample oxidized to 6 wt % silica gave a markedly different profile. The concentration of magnesium was high (7%–8%) near the surface, rapidly decreasing to zero within 2 mm from it. Microstructural examination (Fig. 6) showed the pore structure to be closed off during oxidation due to the volume expansion accompanying conversion of silicon nitride to silica. The following magnesium-impregnation process led to a magnesium-rich surface layer (~ 8 wt % Mg), as expected. The micrographs (Fig. 7) show that the blocking is caused by the oxidation of the sub-micrometre α-Si_3N_4 whiskers in the pore structure.

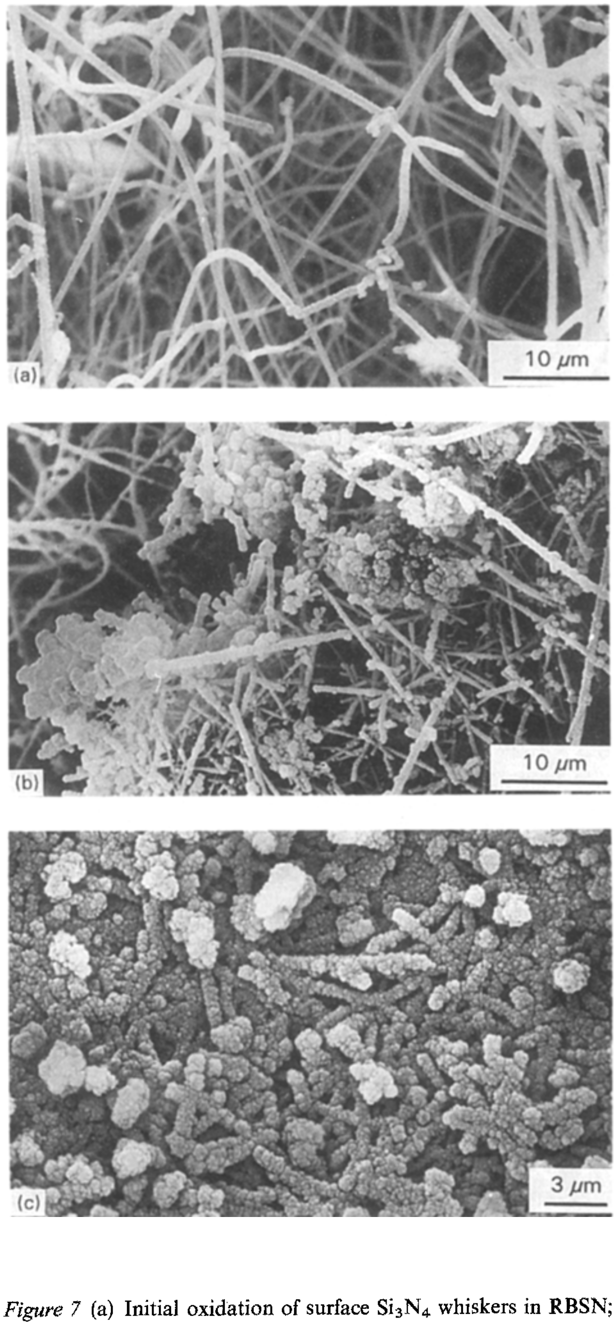

Figure 7 (a) Initial oxidation of surface Si_3N_4 whiskers in RBSN; (b, c) later stages of oxidation (scanning electron micrographs).

In the light of this experience, the magnesia uptake was limited to 2.5 wt % in the present experiment and specimens with this MgO content post-sintered at 1750 °C for 4 h in nitrogen attained densities of ≈ 93% theoretical. Values as high as 98% theoretical have been quoted in the literature for PSRBSN material [1] containing 5 wt % MgO.

4. Conclusion

The factors controlling the impregnation of reaction-bonded silicon nitride by magnesia vapour have been identified, the most important being the amount of silica on the internal surfaces of the RBSN pore structure. Magnesia vapour can be readily produced and can be transported into the compact, where it is localized by reaction with the surface silica. Limited success was achieved in increasing the silica content of the RBSN and thus the magnesia uptake by a prior oxidation treatment; the oxidation of fine Si_3N_4 whiskers present in the pores of the RBSN limited the achievement of a uniform internal oxidation of the RBSN and subsequent magnesia infiltration. If RBSN material can be produced free of these in-pore whiskers, possibly by changing processing conditions such as the nitrogen partial pressure during nitriding, then the above process of oxidation and infiltration of RBSN may prove to be a viable process for producing dense post-sintered RBSN. If the correct process conditions can be determined there appears to be no reason, in principle, why the envisaged multi-stage high-temperature treatment leading to a dense silicon nitride with minimum MgO content, could not be developed.

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