magnesium oxide single crystals, nor a concentration gradient of Mg ions in the reaction layer. This may mean that P and Mg ions do not form a solid solution with magnesium oxide and the reactant, respectively. Results of electron probe microanalysis of the specimens prepared with various ratios of magnesium oxide to P_2O_5, showed that the reactant had the approximate composition $3MgO{\cdot}P_2O_5$, and the composition was constant for heating times from 1 to 20h.

According to the phase diagram of the $MgO{\cdot}P_2O_5$ system [4], $3MgO{\cdot}P_2O_5$ is liquid at 1400° C. The wetting test of magnesium oxide single crystals by $3MgO{\cdot}P_2O_5$ at 1400° C showed spreading of the liquid on the magnesium oxide; $3MgO{\cdot}P_2O_5$ liquid completely wets the surface of magnesium oxide. The preferred interpretation of the welding is that $3Mg{\cdot}P_2O_5$ acts as a binder to connect the two single crystals of magnesium oxide.

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Effect of precursory solution anion on sintering of magensium aluminate

Highly homogeneous and reactive magnesium aluminate powder can be prepared by spray drying various precursor solutions followed by calcining [1]. A conventional ball-milling step was eliminated. The magnesium aluminate formed by using the precursor of $[MgSO_4 \cdot 7H_2O + Al_2(SO_4)_3 \cdot 18H_2O]$ can be sintered to a high density at a lower temperature than the temperature used to sinter conventional magnesium aluminate powder. The purpose of this note is to show the effect of sulfate precursor solution anion on the sintering property of magnesium aluminate.

Reagent grade $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $MgSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ were used to make the precursor solution. Precursor solutions (25 wt% of nitrate) of magnesium and aluminium nitrate $Mg^{2+}/Al^{3+} = 1:2$ were prepared by mixing 25 wt% $MgNO_3$ and $Al(NO_3)_3$ aqueous solutions which were obtained by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in de-ionized water. Other precursor solutions with 0.5:0.5 mole ratios of $[MgNO_3 \cdot 6H_2O + 2Al(NO_3)_3 \cdot 9H_2O]$ to $[MgSO_4 \cdot 7H_2O + Al_2(SO_4)_3 \cdot 18H_2O]$ and 1:1 of $MgSO_4 \cdot 7H_2O$ to $Al_2(SO_4)_3 \cdot 18H_2O$ were prepared in the same way as a mixed nitrate solution. The various precursor solutions were spray dried in a laboratory spray drier. The spray drier was held at 390° C. Spray-dried powders were calcined at 1150° C for 1h. A single phase of $MgAl_2O_4$ was obtained. Compacts formed by isostatic pressing the calcined powder to 20 000 p.s.i. were sintered at 1450° C for 20h. The specific area of the powders was determined by nitrogen adsorption using the B.E.T. technique. Sintered density was measured by mercury immersion. Spray-dried sulfate powder was further investigated by differential thermal and thermogravimetric analyses.

Fig. 1 shows the effect of precursor sulfate solution on the sintered density of $MgAl_2O_4$ and surface area of calcined spray-dried powder. Results indicate that the sintered density of $MgAl_2O_4$ and the surface area of the calcined powder were increased as the precursor sulfate solution anion was inceased. Bratton shows that sintering of high purity $MgAl_2O_4$ is governed by a volume diffusion equation [2]:

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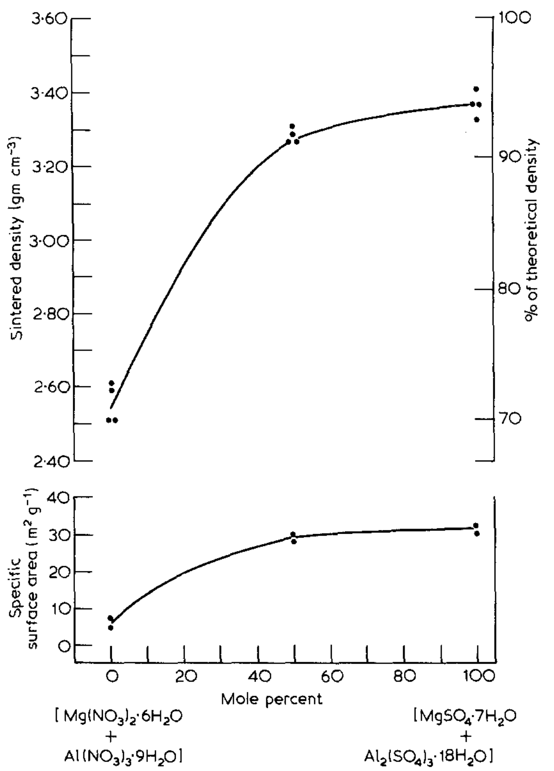

Figure 1 Effect of precursor sulfate solution on sintered density of $MgAl_2O_4$ and surface area of calcined spray drying powder.

$$\left(\frac{\Delta L}{L_0}\right)^2 = \frac{2\gamma a^3 D_v}{kTr^3}\,t$$

where $\Delta L/L_0$ = fractional shrinkage, t = time, r = sphere radius, T = absolute temperature, k = the Boltzmann constant, γ = surface energy, a^3 = vacancy volume and D_v = volume diffusion coefficient. At constant temperature and time, the equation can be rearranged as follows:

$$\left(\frac{\Delta L}{L_0}\right)^2 = \left(\frac{2a^3 D_v t}{kT}\right)\left(\frac{\gamma}{r^3}\right)$$

$$\therefore \quad \left(\frac{\Delta L}{L_0}\right)^2 = C\left(\frac{\gamma}{r^3}\right). \qquad (1)$$

Equation 1 indicates that sintering of $MgAl_2O_4$ at constant temperature and time is controlled by the surface energy and particle size of starting material. The surface energy can be represented by the following equation:

$$\gamma = \frac{\partial F}{\partial A_{T,P,n_1,n_2,\ldots}}$$

if γ is independent of surface area of A, upon integration

$$F = \gamma A. \qquad (2)$$

Thermal decomposition analysis is shown in Fig. 2. Results indicate that the temperature for formation of $MgAl_2O_4$ from $[MgSO_4 \cdot 7H_2O + Al_2(SO_4)_3 \cdot 18H_2O]$ is 1150° C. The forming temperature of $MgAl_2O_4$ from $[MgNO_3 \cdot 6H_2O + 2Al(NO_3) \cdot 9H_2O]$ found by Messier and Gazza was 400° C [3]. X-ray analysis of spray-dried material calcined at 1150° C shows that $MgAl_2O_4$ powder from the sulfate solution was poorly crystallized, while the $MgAl_2O_4$ from the nitrate solution is well-crystallized material. It appears that the surface area of $MgAl_2O_4$ formed by $[MgNO_3 \cdot 6H_2O + 2Al(NO_3)_3 \cdot 9H_2O]$ at 400° C was decreased by crystal growth as the material was calcined at 1150° C. Giauque has shown that very fine MgO has 800 cal mol^{-1} more free energy than well-crystallized MgO [4].

It is believed that finely-divided $MgAl_2O_4$ powder from the sulfate solution should have

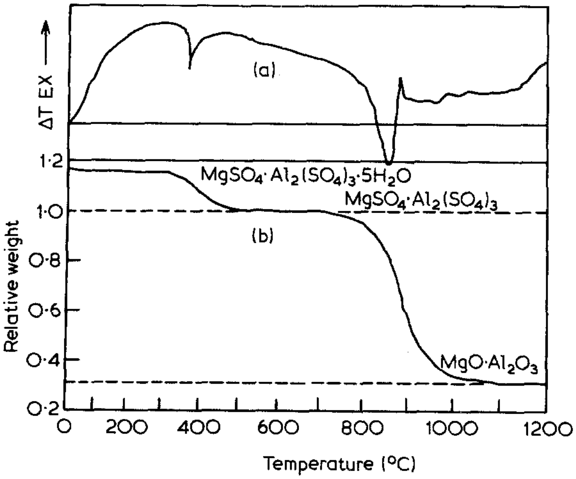

Figure 2 Thermal decomposition of spray-dried precursor solution of $[MgSO_4 \cdot 7H_2O + Al_2(SO_4)_3 \cdot 18H_2O]$. Curve (a). Differential thermal analysis. Curve (b). Thermogravimetric analysis.

higher free energy than $MgAl_2O_4$ from the nitrate solution. The higher free energy will have higher surface energy and surface area is shown in Equation 2. This note shows that the higher sinterability of $MgAl_2O_4$ powder from the sulfate solution as opposed to nitrate solution is attributed to the higher surface area (smaller particle size), which predominantly controls the sintering of $MgAl_2O_4$, as shown in Equation 1.

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The structure of the X phase in the Si–Al–O–N alloys

Recently, several works [1–3] have been published concerning the question of the X (or X1) phase, which appears in hot-pressed Si–Al–O–N compounds within a considerably large part of the high temperature (1760° C) isothermal section of the phase diagram. The pure X phase is hard to obtain. The exact composition of the X phase is controversial – the concentration values obtained by different authors (e.g. [2–4]) range between 12 to 20 wt% Si, 19 to 26 wt% Al, 44 to 52 wt% O and 6 to 16 wt% N. There are, however, reasons to assume that this is a definite stoichiometric compound. Several attempts have been made to determine its crystal structure. The following results were published:

(i) Triclinic [1] with $a = 9.9$ Å, $b = 9.7$ Å, $c = 9.5$ Å, $\alpha = 109°$, $\beta = 95°$, $\gamma = 95°$

(ii) Orthorhombic [2] with $a = 7.85$ Å, $b = 9.12$ Å, $c = 7.965$ Å

(iii) Monoclinic [3] with $a = 9.728$ Å, $b = 8.404$ Å, $c = 9.572$ Å, $\beta = 108.96°$, in addition to some earlier, less definite suggestions.

Suggestions (ii) and (iii) were worked out by X-ray diffraction, while (i) was deduced tentatively from TEM data. Most interestingly, the three suggested structures have many low-index reflections in common. Table I shows the lists of lattice spacings (*d*-spacings) calculated from the given parameters. If we compare only the few low-index lines that could be observed by X-rays, we may assume that all the results actually belong to the same structure, which was interpreted wrongly in several different ways because insufficient data were used. This is actually proved below.

We examined hot-pressed specimens which were prepared from Si_3N_4, SiO_2 and Al_2O_3 powders (about 18, 32 and 50 wt% respectively) by pressing at 30×10^6 N m^{-2} and 1780° C for 90 min. They lie close to the compositions suggested by Gauckler [4] and Naik *et al.* [5] and have a nearly pure X structure (Fig. 1). Specimens for transmission electron microscopy were prepared by the conventional methods for ceramics (e.g. [1]). After ion milling they were coated on one side by sputtering with a gold layer (6 nm thick), for the purpose of enhancing the electrical conductivity of the specimen and for camera-constant calibration. The specimens were examined in a JEM 200A electron microscope operated at 200 kV.

Sets of consecutive electron diffraction patterns from an individual X grain could never be indexed to fit any of the suggested structures. The triclinic structure [1] gave a close match for some diffractions but could not explain a complete set of results. We shall now examine the method of deducing the lattice constants from basic electron diffractions. Using the three basic patterns ([1 0 0], [0 1 0] and [0 0 1] zone axes) with their

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