Fabrication of translucent magnesium aluminate spinel and its compatibility in sodium vapour

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The sintering behaviour of magnesium aluminate spinel on both sides of the stoichiometry has been investigated. It is found that the composition close to the stoichiometric composition, but slightly enriched in magnesia can be sintered to translucency in a free flowing hydrogen environment. The grain size decreases with magnesia content; the addition of yttria, however, results in a highly bimodal grain structure. Prolonged exposure of the spinel in a high temperature sodium vapour environment forms $Na_2O \cdot 5Al_2O_3$ and some traces of $Na_2O \cdot 11Al_2O_3$ predominately at the grain boundaries and near the surface of the specimen. Some possible sintering mechanism and factors affecting the in-line transmission are discussed.

1. Introduction

Since the introduction of translucent polycrystalline alumina (Lucalox) in 1959, research and development on high pressure sodium lamps has continued with almost unabated enthusiasm. The progress has been quite dramatic, resulting in the culmination of a family of light sources having a good colour rendition, luminous efficacy of the order of 120 lumens per watt and lamp life exceeding 6000 hours. The advent of transparent single crystal alumina tube (Corstar) has raised hopes of further improving the lamp efficacy. However, the high cost and the technical difficulties in making a reliable end seal present problems. Moreover, it is becoming increasingly apparent that the high temperature corrosion resistance of alumina in sodium vapour is reaching a threshold limit as the operating temperature of the arc tube exceeds 1200° C. In particular, the tendency of alumina to form β-alumina type compounds and the diffusion of sodium at high temperature impose certain limitations on the design configuration. This has consequently prompted further research for more refractory corrosion resistant and transparent ceramic oxides as envelope materials. Magnesium aluminate spinel is among one of the family of mixed oxides which appears to satisfy most of the

stringent environmental conditions operating within the arc tube. Besides its higher refractoriness and chemical inertness to alkalis, it has also a cubic structure with an isotropic expansion of the same order of magnitude as alumina. Being a face-centered cubic, pore-free single phase, polycrystalline spinel is expected to be as transparent as the single crystal. It has a melting point of 2135° C, high hardness, good thermal shock resistance and high mechanical strength. The processing of the raw materials into suitable spinel powders and the fabrication of translucent polycrystalline spinel by conventional sintering has not been widely reported in the literature although some patents on the fabrication of translucent spinel exist [1, 2]. Recently Bratton [3] reported the sintering of spinel to translucency with calcium oxide additive.

This paper presents some preliminary results on the fabrication of translucent spinel and its compatibility in sodium vapour at elevated temperature.

2. Experimental techniques
2.1. Chemical routes for obtaining spinel powders

Various chemical routes have been tried for obtaining suitable spinel powders by calcination of

TABLE I

Samples	Al$_2$O$_3$ (wt %)	MgO (wt %)	Samples	Al$_2$O$_3$ (wt %)	MgO (wt %)
1	57.70	42.40	4	71.80	28.20
2	65.00	35.00	5	73.40	26.60
3	70.67	29.33			

(1) high purity alumina and magnesia powders in air;

(2) co-precipitates of aluminium and magnesium hydroxide in air. The co-precipitates were prepared from the chlorides and ammonium hydroxide under controlled pH conditions;

(3) fused magnesium nitrate and aluminium ammonium sulphate;

(4) high purity commercial spinel powders with various amounts of excess magnesia.

So far the most promising results have been obtained from fusion and calcination of magnesium nitrate and aluminium ammonium sulphate.

2.2. Preparation of suitable spinel powder

Analar grade magnesium nitrate hexahydrate and ammonium sulphate dodecahydrate were obtained from Fisons Ltd. Thermogravimetric analysis of the salts gave 15.60% magnesium oxide and 12.0% aluminium oxide (wt %) respectively. Several spinel compositions were then formulated as shown in the MgO, Al$_2$O$_3$ equilibrium phase diagram in Fig. 1 and Table I. The appropriate amounts of the salts were fused at about 200° C for 1 h, transferred in a recrystallized alumina crucible and calcined in air. Calcining temperatures between 900 and 1200° and calcining time ranging from
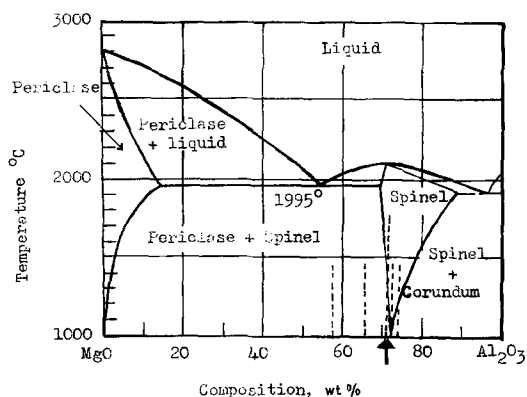

Figure 1 Equilibrium phase diagram in the MgO · Al$_2$O$_3$ system. Dotted vertical lines are compositions studied. The most satisfactory result is achieved from the composition arrowed.

$\frac{1}{2}$ to 5 h were used. The powders were removed after cooling to ambient. The calcination of the fused salts above 1000° C usually gives a homogeneous single-phase spinel composition. The powders were wet milled for several hours with deionized water. It was found that 5 ml water for every gram of powder gave a slurry which could be fairly easily poured. The slurry made with a batch of 25 g powder was dried for approximately 1 h at 200° C. Spherodized powders have also been used to improve the flow characteristics and surface finish of the sintered spinel.

2.3. Sintering schedules

Discs were compacted in a steel die with a pressure of 5 ton in.$^{-2}$ for 2 min. They were placed in a molybdenum boat and covered with a molybdenum foil. The presence of magnesia vapour in the furnace was found to be beneficial in sintering the spinel to translucency. Besides the high purity of the powder, cleanliness of the molybdenum boat is essential. Sintering was performed in a free flowing hydrogen atmosphere in a molybdenum wound furnace. An intermediate sintering at about 1350 to 1400° C for 16 h followed by a soaking period of 6 h at about 1680° C imparts good translucency to the specimen. Spinel tubes were made by wet bag isostatic pressing. Pressure up to 5 ton in.$^{-2}$ was applied and then immediately released. The as-pressed tube was prefired using a heating rate of about 180° C h^{-1} until the temperature reached 1100° C. The furnace was then cooled to ambient. It was found necessary to embed the tubes in magnesia powder during sintering for improved translucency. A molybdenum foil was placed on the top of the tube to prevent excessive loss of magnesia.

2.4. In-line transmission

The percentage in-line transmission was determined with a Perkin Elmer spectrometer SP500 in the range of 0.2 to 1 μm and an SP200 spectrometer was used in the range of 2 to 7 μm. The specimens were polished down to 1 μm surface finish, etched for about 1 min in hot orthophosphoric acid and thoroughly washed in distilled water and methyl alcohol.

2.5. Compatibility of spinel in sodium vapour

A limited study of the compatibility of spinel in sodium vapour was carried out. A piece of
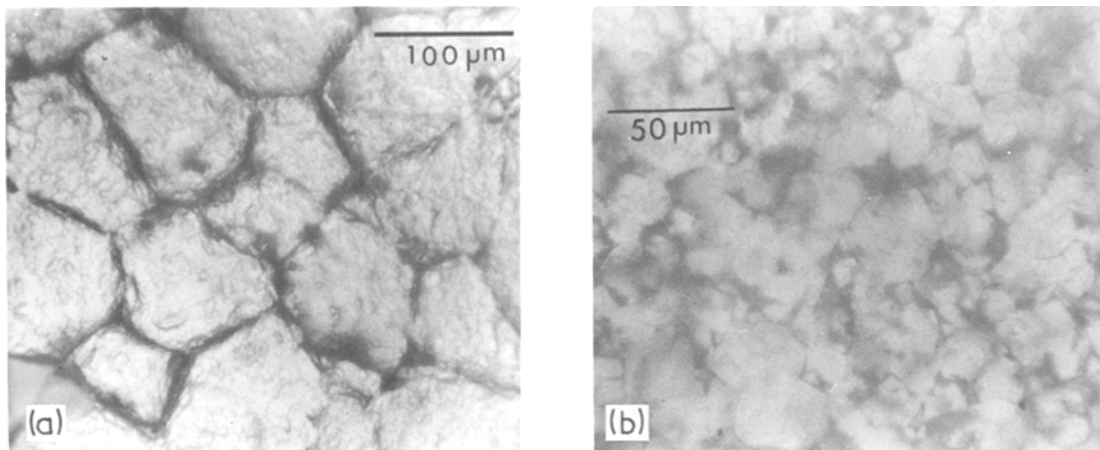
Figure 2 Grain structure of sintered, polished and etched magnesium aluminate spinel in transmission. (a) 29.33% MgO, 70.67% Al₂O₃, (b) 43.30% MgO, 57.80% Al₂O₃. The samples were not embedded in free magnesia during sintering.

Coor's spinel* about 5 mm × 3 mm × 2 mm was introduced inside the 7.5 mm bore alumina arc tube of a 400 W high pressure sodium lamp. The lamp was run for 1200 h in a horizontal position with the spinel sample midway between the electrodes. The tube contained 50 mg sodium and mercury amalgam in the ratio of 1:3 by weight with an initial xenon pressure of 15 Torr. In operation, the sodium developed a pressure of 120 Torr and mercury a pressure of 3 atm. The wall temperature usually exceeded 1000° C in this type of lamp, and the sample was heated to a rather higher temperature since the gas temperature exceeded 4000° K at the axis of the arc.

3. Microstructural observations
3.1. Microstructures of sintered spinel
It was found that spinel with a composition of 70.67% Al₂O₃ and 29.33% magnesia can be sintered to almost theoretical density. Translucent samples between 2 and 3 mm thick have been obtained with a density of 3.56 g cm⁻³ compared with a theoretical density of 3.58 for the stoichiometric spinel with composition 71.80% Al₂O₃ and 28.20% MgO. The specimens have a pinkish coloration indicating possible contamination from the boat. Magnesia-rich spinel with a weight composition of 57.7% Al₂O₃ and 42.30% MgO is difficult to sinter to translucency. The grain size is small and non-uniform. Typical microstructures of the bulk spinel for various spinel compositions are shown in Fig. 2. It is found that the grain size decreases markedly with higher magnesia content.

Spinel tubes with composition 80.67% Al₂O₃ and 29.44% MgO, without any additive, can be sintered to translucency. The translucency is, how-
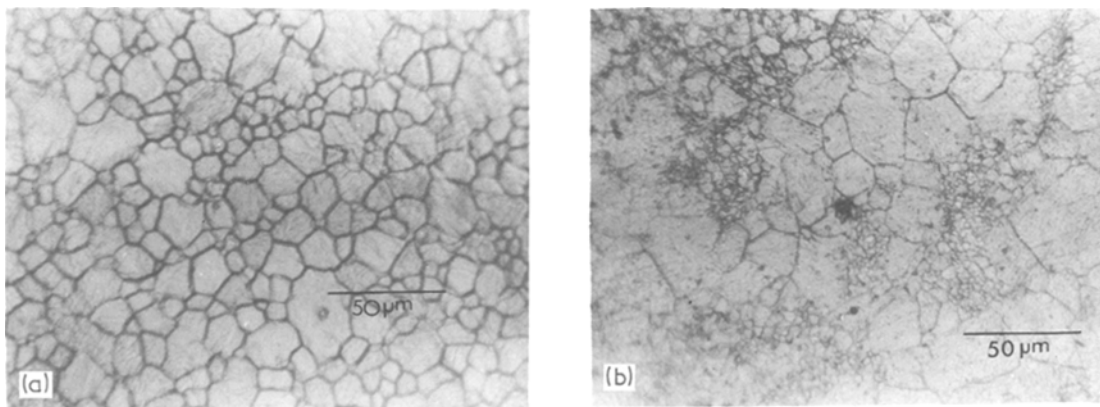
Figure 3 Inner surfaces of sintered magnesium aluminate spinel tube in transmission. (a) 29.33% MgO, 70.67% Al₂O₃, sintered in magnesia vapour, (b) 29.33% MgO, 70.67% Al₂O₃ with 0.3% MgO and 0.3% Y₂O₃.

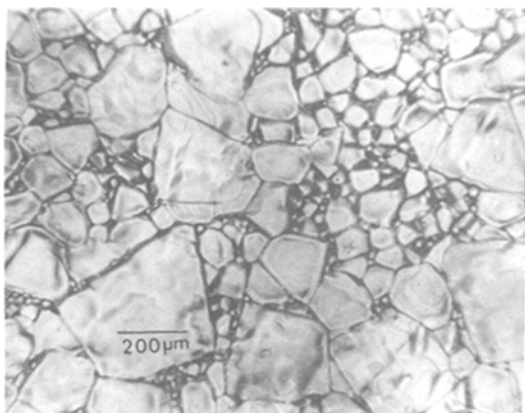* Supplied by Coors Porcelain Company, Golden, Colorado 80401, USA.

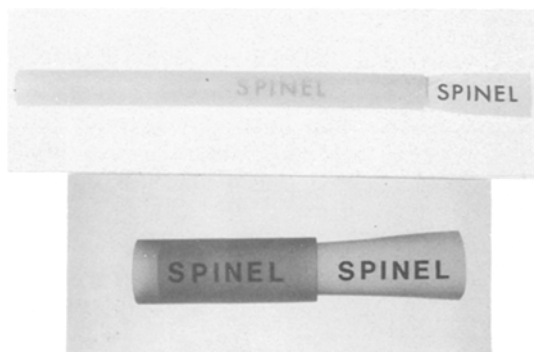*Figure 4* Microstructures of Coor's spinel in transmission showing bimodal structure.

Figure 5 Optical quality of spinel tubes. Top, with fairly uniform medium grains and bimodal structure.

ever considerably improved when the tube is embedded in free magnesia. A typical microstructure is shown in Fig. 3a. Of particular interest is the fairly uniform fine grain structure obtained. The addition of $\sim 0.3\%$ MgO and 0.3% Y_2O_3 as oxides drastically changes the grain structure causing accelerated grain growth, as shown in Fig. 3b. The clusters of small grains in the bimodal structure appeared black in transmission and are largely responsible for the reduction in translucency. The microstructure of Coor's translucent spinel with a composition of 72.40% Al_2O_3, 27.4% MgO, 0.1% CaO, 0.05% Fe_2O_3, 0.05% K_2O and 0.002% TiO_2 has also an essentially bimodal grain structure, with visible grains ~ 0.5 mm diameter (Fig. 4). The grain boundaries, particularly between the small grains are quite wide.

Wet chemical analysis confirms the presence of some LiF which could not be detected by X-ray fluorescence spectroscopy due to the heavy absorption of the X-ray fluorescence wavelengths of these light elements. The optical quality of the spinel tubes is shown in Fig. 5, and the in-line transmission of spinel is illustrated in Fig. 6.

3.2. Microstructures of spinel exposed in sodium vapour

The surface of the Coor's spinel exposed in sodium vapour environment probably above 1000° C, has a lath type phase at the grain boundaries, Fig. 7.

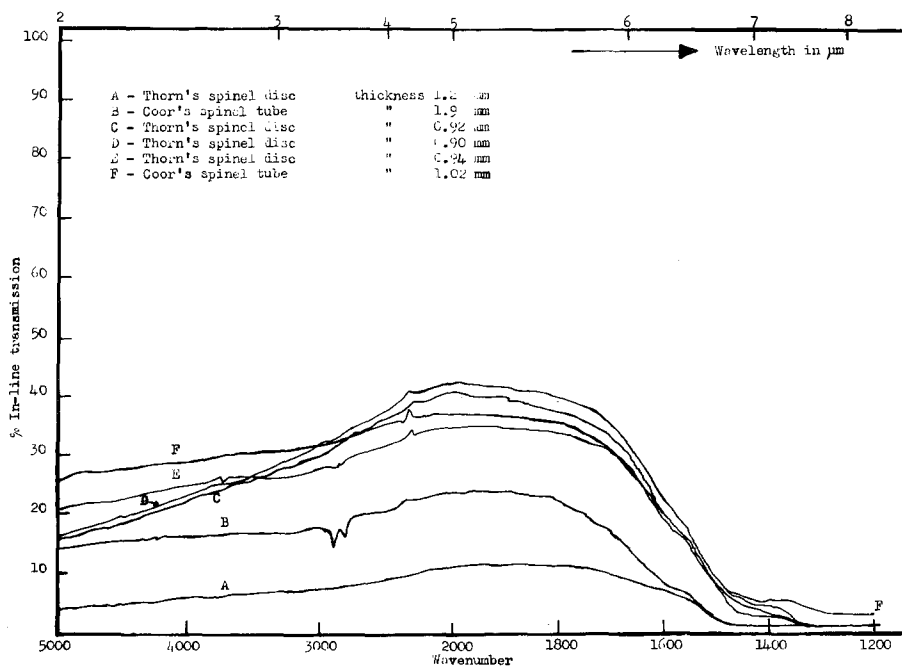*Figure 6* In-line transmission of various spinel at different wavelengths.
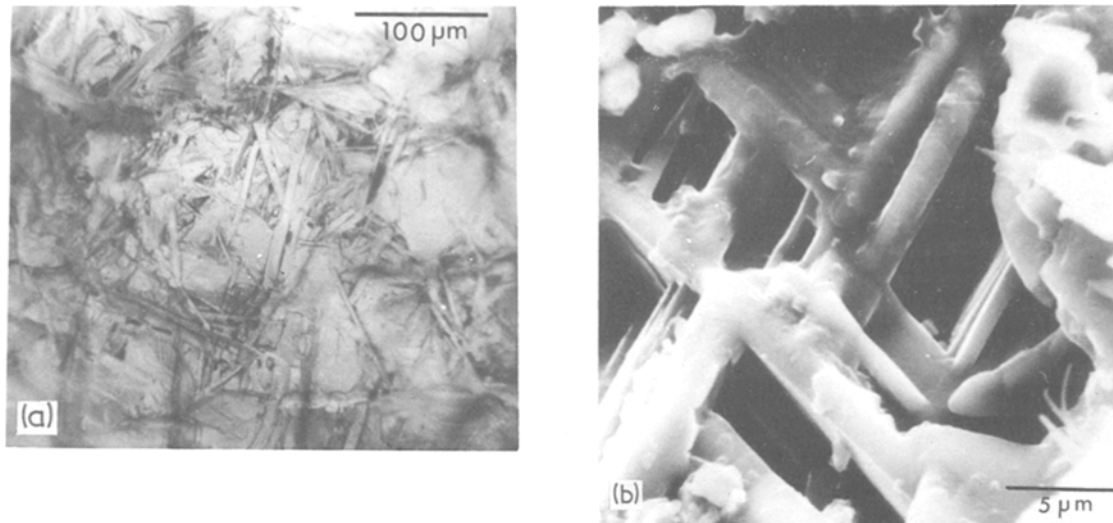
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Figure 7(a) Growth of lath-type phase at clusters of small grains and grain boundaries in Coor's spinel. (b) Enlarged view of growth features. Aged for 1200 h in a high pressure sodium discharge lamp at $\sim 1000°$ C.

The second phase has been identified mainly as $Na_2O \cdot 5Al_2O_3$ with some traces of β-alumina $Na_2O \cdot 11Al_2O_3$ by X-ray powder diffraction (Fig. 8). The formation of the second phase is discussed in Section 4. It is of interest to note that the surface of the spinel grains in contact with the sodium vapour reveals no solid state reaction, although the exposed surface grains have undergone some etching which reveals the extensive twinning in the spinel. Examination of the fracture surface shows that second phases are formed around the grain boundaries and are confined only to the surface grains (Fig. 9). The weakening of the grain boundaries could account for the inter-granular fracture near the surface which changes to an essentially transgranular fracture in the bulk. The cleavage surfaces of the exposed and unex-

posed spinel grains are free from any debris or second phase as shown in Fig. 9. The micro-structural observations indicate that the sodium vapour preferentially attacks the grain boundaries of the surface grains. This is presumably assisted by the higher temperature experienced by the spinel due to the radial temperature distribution of the arc (see Section 4.4) and the segregation of a fair amount of impurities at the spinel grain boundaries. The inner surface of the translucent alumina arc tube exposed to sodium vapour is shown in Fig. 10.

4. Discussion
4.1. Sintering of spinel in excess magnesia
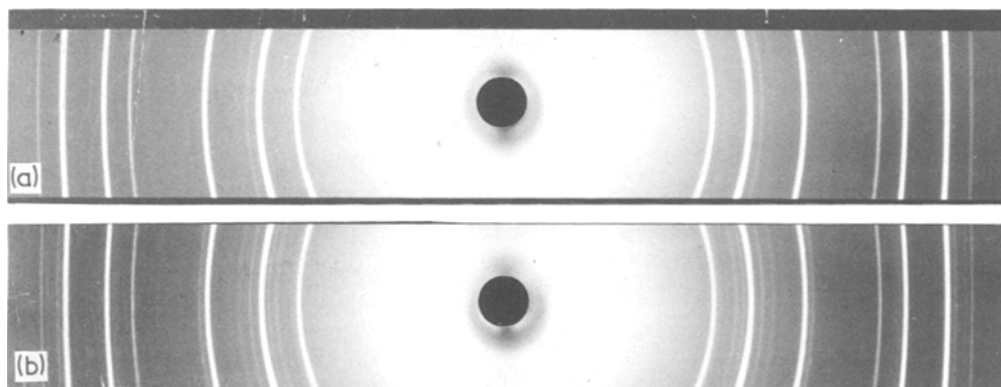Any plausible mechanism to explain the sintering of magnesium aluminate spinel close to stoichio-

Figure 8 Part of X-ray, Debye–Scherrer powder refraction patterns of Coor's spinel (a) unexposed; (b) exposed in sodium vapour after 1200 h in a high pressure sodium discharge lamp at $\sim 1000°$ C.
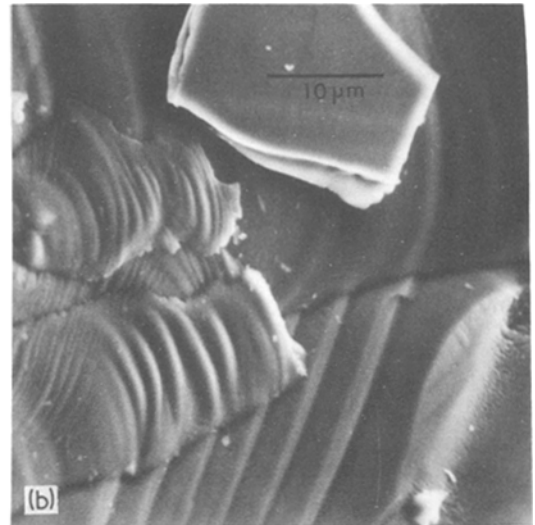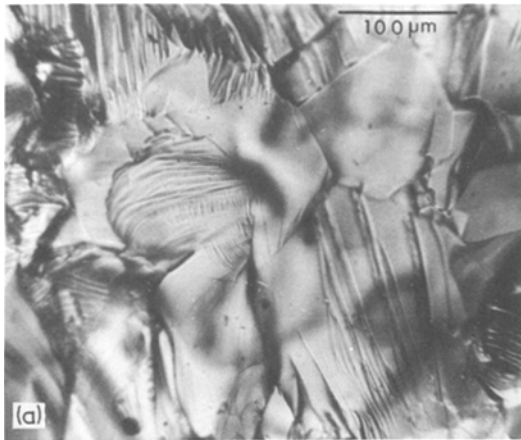
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Figure 9 Surfaces of Coor's spinel (a) unexposed, (b) exposed in sodium vapour after 1200 h above 1000° C. Fracture occurs essentially by cleavage of grains.

metric composition to translucency must take into account the special role of magnesia vapour surrounding the sintered sample. Since magnesia vaporizes at a considerably higher rate than the MgO in the spinel and the vapour pressure of magnesium species above MgO is higher than that of magnesium species above magnesium aluminate at a particular temperature [4], there will be a net flow of magnesium ions which create defects. However, very little is known about the defect structure of spinel containing lanthanide rare-earth ions to advance any explanation.

4.3. Sintering of spinel composition rich in alumina

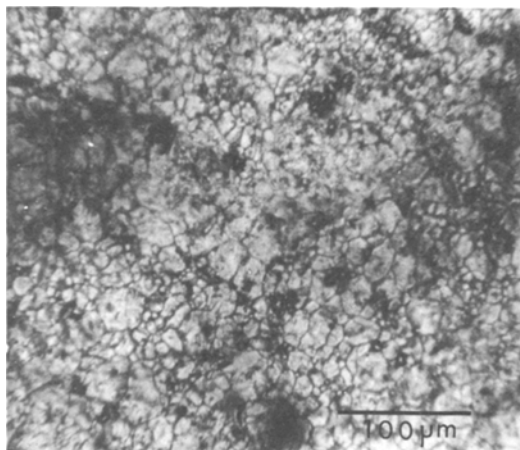It is now well established that a considerable

Figure 10 Microstructure of inner surface polycrystalline alumina arc tube after 1200 h at ~ 1000° C.

amount of alumina can dissolve in the spinel and the solid solution can be written as $MgO \cdot XAl_2O_3$, with $X = 1$ to 7 at 1900° C. The substitution of Mg^{2+} by Al^{3+} creates excess cation vacancies exclusively at the octahedral (aluminium) sites to maintain neutrality [7]. Increasing the amount of Al_2O_3 also decreases the lattice parameter because of increasing concentrations of Al^{3+} on the tetrahedral sites (since atomic radius of Al^{3+} is 0.53 Å and Mg^{2+} is 0.63 Å). It is thought that if the vacancies could be created, and the alumina is retained in solution, this could enhance the sinterability as well as the translucency of the spinel. The fact that spinel with approximately 2% by weight alumina in excess over the stoichiometric composition can be sintered to translucency in about 8 h at 1750° C suggests that the excess vacancies may be responsible for the enhanced densification rate. Unfortunately, the translucent spinel contains a significant amount of white spots. The nature of these white spots has not yet been identified although they are found to be invariably associated with clusters of small grains and grain-boundary pores as shown in Fig. 11.

4.4. The effect of sodium vapour in spinel

The formation of sodium aluminate compounds $Na_2O \cdot XAl_2O_3$ with X mainly 5, and some traces of β alumina compounds $X = 11$ at the grain boundaries when the spinel is exposed to sodium vapour at about 1000° C after 1200 h, suggests that a solid state reaction is involved. Since the spinel used for compatibility experiment has

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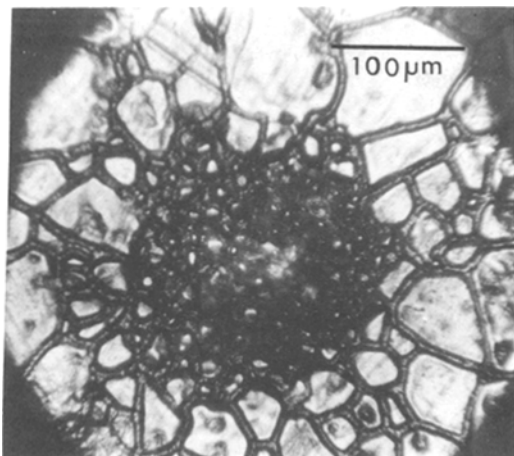
Figure 11 Grain structure of a translucent spinel richer in alumina with composition 73.0% Al_2O_3 and 27.0% MgO in transmission. The spinel contains white spots which cause loss of in-line transmission. Note progressive decrease in grain size around the white spots, probably associated with impurities.

wide grain boundaries, and also contains approximately 1000 ppm of CaO, 500 ppm Fe_2O_3, 500 ppm K_2O and 2 ppm TiO_2, it is quite likely that a fair amount of impurities are segregated at the grain boundaries during grain growth. It is suggested that some β-alumina is first nucleated at the grain boundaries, which is then converted to β'' alumina, possibly through an intermediate β alumina, because of the impurities present. This is not unreasonable since the LiF added to sinter the Coor's spinel to translucency has been reported to segregate at the grain boundaries [8]. The use of Li ions in the stabilizations of β'' alumina ($Na_2O \cdot 5Al_2O_3$) is well known in electro-ceramics technology [9]. Ferric oxide has also been reported to stabilise the β'' alumina [10]. Large grain boundaries, particularly at the clusters of small grains are potential sites for nucleation and growth of second phase. There is quite good expectation that purer sintered spinel with narrow grain boundaries could be less susceptible to the formation of sodium aluminate compounds. Some compatibility experiments on purer sintered spinel with narrow grain boundaries and different grain sizes are being investigated. Because of the lack of phase equilibrium data and sodium diffusivity in the spinel, the $MgO \cdot Al_2O_3 \cdot Na_2O$ system merits further investigation.

However, some care must be exercised in comparing the microstructures of the inner surface of the exposed alumina tube and the spinel samples, because of the radial temperature variation in the arc tube. Since the inner diameter of the arc tube is ~ 0.75 cm and the thickness of the specimens 0.20 cm, the upper surface of the spinel sample is half-way between the axis of this tube and the inner surface of the arc tube. Thus the spinel must have been subjected to a higher temperature than the inner surface of the alumina wall. The work is being extended to investigate the effects of sodium vapour in an actual spinel arc tube.

4.5. In-line transmission

The higher in-line transmission found in the Coor's spinel as shown in Fig. 5 and 6 could be attributed mainly to the absence of second phase scattering as most of the lithium fluoride additive is vaporized during high temperature sintering. On the other hand, the excess magnesia precipitated from the magnesia enriched spinel during sintering, or magnesia freely incorporated during processing of the powder enhances back-scattering in the Mie regime. The addition of a critical amount of magnesia or more volatile species is, therefore, desirable for sintering the spinel to optimum in-line transmission. However, other factors affecting the in-line transmission of sintered polycrystalline ceramics are equally applicable and have been discussed in greater detail by several authors [11–15].

5. Conclusion

Magnesium aluminate spinel on both sides of stoichiometry can be sintered near theoretical density in a hydrogen atmosphere. However, spinel close to stoichiometric composition but slightly enriched in magnesia can be sintered to translucency. The grain size decreases as the magnesia content increases. The addition of 0.3% yttria to the magnesia-enriched spinel produces a pronounced bimodal grain structure without enhancing the in-line transmission. The precipitation of magnesia in the spinel with excess magnesia in solid solution appears to have a marked effect on the sintering behaviour. The in-line transmission is, however, limited by second phase scattering. It is found that $Na_2O \cdot 5Al_2O_3$ and some traces of $Na_2O \cdot 11Al_2O_3$ are formed after prolonged exposure of the spinel in a high temperature sodium vapour environment. The reaction is confined predominantly at the grain boundaries and near the surface of the specimen.

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