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Preparation of transparent non-crystalline stoichiometric magnesium aluminate gel-monolith by the sol–gel process

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Transparent non-crystalline stoichiometric magnesium aluminate gel-monolith was prepared by chemical polymerization reaction between aluminium alkoxide and magnesium salt. The reaction mechanisms of gel formation are discussed. The oven-dried gel was freed from residual organics by chemical treatment with hydrogen peroxide solution. X-ray analysis of organic-free gel powder after heat treatment for 4 h at 2000° C did not show any indication of phase separation. It is suggested that the use of sol–gel-derived powders could largely eliminate most of the problems associated with the conventional method of fabrication of optically transparent stoichiometric magnesium aluminate spinel.

1. Introduction

Optically transparent magnesium aluminium spinel, $MgAl_2O_4$, has long been recognized as an excellent optical material by virtue of its intrinsic infrared transmission characteristics. Moreover, it possesses excellent mechanical and thermal shock resistance properties and chemical durability. These attractive properties make this material suitable for such applications as infrared windows and missile domes. Another potential application of stoichiometric $MgAl_2O_4$ (single crystals) could be as insulating substrates for metal-oxide semiconductor (MOS) devices [1]. A number of fabrication techniques [1–6] have been used by different investigators for producing spinels in both single-crystal [1–4] and polycrystalline forms [5, 6]. Generally, high-purity aluminium oxide, Al_2O_3, and magnesium oxide, MgO, are used as the starting raw materials. The powder components are intimately mixed, pressed into pellets, calcined and then melted in iridium or molybdenum containers under a protective environment. It is reported [1] that calcination of the pressed pellet (for complete reaction of the oxides to form $MgAl_2O_4$) is a critical step for controlling the composition of the melt. The loss of MgO (due to its higher vapour pressure relative to $MgAl_2O_4$ or Al_2O_3) causes phase separation (α-Al_2O_3) during solidification of the melt and, as a consequence, cracks develop in the spinel body due to differences in the thermal expansion coefficients of the phases. On the other hand, the presence of free MgO is believed to cause oxygen deficiency and metallic inclusion in the spinel due to its reaction with the container material. Moreover, the presence of the bubbles or voids often found in the transparent spinel body is believed to be related to the chemical nature of the starting material [1] and the melting temperature [6]. It was thought that the above problems could be largely avoided if, instead of using a physical mixture of MgO and Al_2O_3 powders, $MgAl_2O_4$ powders synthesized at a lower temperature could be used for the fabrication of transparent spinel. The main objective of the present investigation was to synthesize $MgAl_2O_4$ (spinel) material at low temperature by the sol–gel process [7] and to examine its crystallization behaviour at high temperatures. The chemistry

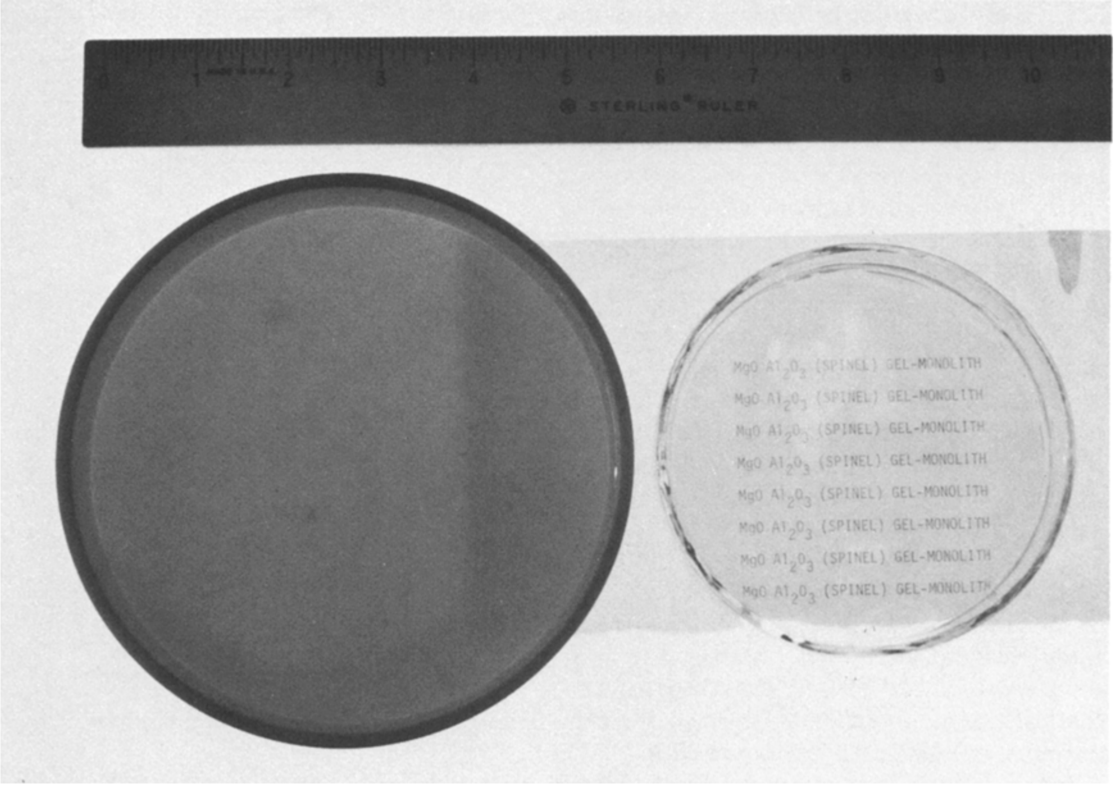

Figure 1 Transparent magnesium aluminate gel-monoliths. The scale is in inches (25.4 mm = 1 in.).

of the sol–gel synthesis of $MgAl_2O_4$ spinel has been reported by Dislich [7]. However, the chemistry of the sol–gel process of the present investigation was different from that reported by Dislich.

2. Experimental procedure

2.1. Gel preparation

Commercially available reagent-quality chemicals were used for gel preparation. In a plastic beaker 182.71 g of 95% aluminium secondary butoxide, $Al(OC_4H_9)_3$, was combined with 280 ml i-butanol, C_4H_9OH, and the required amount of acetylacetone, $CH_2(COCH_3)_2$. The above mixture was stirred with a teflon-coated magnetic stirrer at room temperature. A clear yellow solution was obtained. In another plastic beaker, 75.562 g magnesium acetate tetrahydrate, $Mg(OOCCH_3)_2 \cdot 4H_2O$, was dissolved in a solution mixture containing 100 ml i-butanol, 400 ml anhydrous ethanol, C_2H_5OH, 80 ml distilled water and 8 drops concentrated nitric acid, HNO_3. The solution of magnesium acetate was quickly added to the solution of aluminium secondary butoxide with vigorous stirring. The solution mixture (pH 6.8) was poured into teflon and fused-silica petri dishes. The petri dishes were placed in a plastic container and covered with plastic wrap. The viscosity of the solution increased rapidly to form transparent (almost colourless, with slightly yellowish tint) gel-monoliths (Fig. 1) in less than 5 min.

2.2. Removal of organics

The gel was initially dried in an air oven at 110° C overnight. Subsequently, the dried gel was placed in a plastic beaker and treated with commercially available 30% hydrogen peroxide (H_2O_2) solution. The exothermic oxidative reactions were carried out by incremental additions of hydrogen peroxide and vigorous stirring. The reactions were assumed to be complete when no more effervescence occurred. The milky-white, thick slurry obtained after the above chemical treatment was dried in an air oven at 110° C for 48 h. The organic-free gel particulates were ground in an agate mortar to fine powders.

2.3. Heat treatment of organic-free gel

Two different heat-treatment procedures were followed. In one experiment, about 1 g powder was taken in a small platinum crucible and heated at 1000° C for 2 h in an electrically heated tube furnace provided with a microprocessor controller. The heat treatment was performed in the ambient atmosphere. The heating rate was $50°\,C\,h^{-1}$. After 2 h holding at 1000° C, the furnace was allowed to cool naturally. In the second experiment, cold gel in rod form isostatically pressed at 50 000 psi (345 MPa) was used. The gel rod was placed in a molybdenum tubular container and covered with a molybdenum cap. Heat treatment was conducted in a manually controlled tungsten resistant furnace (marketed by Richard D. Brew and Company, New Hampshire) having a temperature capability of about 2100° C in nitrogen/argon. The gel specimen was heated at 2000° C for 4 h in an argon atmosphere. The heating rate was approximately $300°\,C\,h^{-1}$. The furnace temperature was monitored by a tungsten–rhenium thermocouple. After 4 h holding at 2000° C, the furnace was allowed to cool naturally by switching off the power source. The flow of argon was continued until the end of the experiment. The sintered rod was cut into about 1.0 mm thick wafers for characterization.

2.4. Characterization of gels

X-ray analyses were performed on as-prepared gel after drying at 110° C and on the heat-treated samples to examine their crystallinity using a Siemens X-ray diffractometer (Model Kristalloflex 4) which was calibrated against a silicon powder standard. Cu$K\alpha$ radiation and a nickel filter were used. Dried gel powder and 1000° C heat-treated powder were loaded on a "double-stick" tape laid on a microscope slide and the 2000° C heat-treated specimen in the form of a wafer was loaded after mounting it on a microscope slide. Relative intensities of the diffraction peaks were determined by measuring their heights relative to the strongest diffraction peak (relative intensity = 100).

TABLE I X-ray diffraction data for heat-treated gel-derived $MgAl_2O_4$ (Cu$K\alpha$ radiation)

1000° C, 2 h		2000° C, 4 h	
d (nm)	I/I_1	d (nm)	I/I_1
0.468	25	0.457	10
0.286	40	0.282	14
		0.2673	2
0.243 7	100	0.2414	100
0.233 6	< 3	–	–
0.202	63	0.2002	18
0.165 2	10	0.1642	7
0.155 7	38	0.1546	18
0.143 0	63	0.1423	14
		0.1420	12
0.136 7	4	0.1361	< 2
0.127 8	4	0.1272	< 2
0.122 9	8	0.1228	< 2
0.121 0	5	–	–
0.166 6	6	0.1163	< 2
0.111 2	2	0.1128	< 2
0.108 3	3	0.1077	2
0.103 6	4	0.1049	6
0.101 2	8	0.1009	2
0.097 51	6	0.1005	< 2
0.090 68	6		

3. Results

The dried gel powder was amorphous to X-ray. The results of X-ray analyses on samples after heat treatment at 1000° C for 2 h and 2000° C for 4 h are shown in Table I. The gel powder after heat treatments at 1000 and 2000° C both showed the presence of only $MgAl_2O_4$ (synthetic spinel). The diffraction pattern of 1000° C heat-treated powder showed minor divergence from the standard pattern in the high index lines. Moreover, some intensity anomalies of minor degree were observed. Also, the diffraction pattern of the 2000° C heat-treated specimen showed some divergence from the standard pattern and, more significantly, in intensities. Moreover, it showed an absence of two index lines at 0.2335 and 0.121 87 nm. The two additional small peaks at 0.2673 and 0.1420 nm could not be assigned. The divergences in X-ray pattern of the 2000° C heat-treated specimen may be related to preferred orientation, preferred growth rate, the presence of impurities leading to substitution of ions and/or lattice defects.

4. Discussion

The formation of a stoichiometric magnesium aluminate spinel in solution depends upon carefully controlled hydrolysis and condensation reactions between aluminium secondary butoxide and magnesium acetate. Since aluminium secondary butoxide is rapidly hydrolysed by water to produce mono- or trihydroxide [8], it was necessary to stabilize aluminium secondary butoxide using a tautomerically reacting compound (namely, acetylacetone) to form a soluble aluminium chelate,

$$(CH_3COCHCOCH_3) \cdot Al(OC_4H_9)_2.$$

It was found that the conditions of reactions for the formation of the aluminium complex are critical for the synthesis of stoichiometric magnesium aluminate gel. If the reaction conditions are not properly controlled, a precipitate may be obtained. Presumably, the formation of the precipitate may be due to either homocondensation reactions between the molecules of the aluminium complex to form a coordination polymer containing an aluminium–oxygen backbone [9], or disproportionation reactions to form an aluminium complex having more than one molecule of chelating agent per molecule of aluminium alkoxide [10], or both.

Stoichiometric magnesium aluminate gel is formed by a complex sequence of reactions involving the formation of an aluminium complex and hydrolytic polycondensation reactions between the aluminium complex and magnesium salt in the presence of water. The reaction mechanisms are not clearly understood. However, the sol formation and gelation may be represented by the following simplified reactions:

$$\begin{aligned} &x\,Al(OC_4H_9)_3 + y(CH_3COCH_2COCH_3)\\ &\quad\rightarrow x\,Al(OC_4H_9)_2 \cdot y(CH_3COCH\ COCH_3)\\ &\qquad + x\,C_4H_9OH \qquad (1)\end{aligned}$$

$$\begin{aligned} &2[x\,Al(OC_4H_9)_2 \cdot y(CH_3COCH\ COCH_3)]\\ &\quad + x\,Mg(OOCCH_3)_2 + 6x\,H_2O\\ &\rightarrow x\left\{Mg\left[Al(OH)_3 \cdot \frac{y}{x}\left(CH_3COCH\ COCH_3\right)\right]_2\right\}\\ &\quad + 4x\,C_4H_9OH + 2x\,CH_3COOH \qquad (2)\end{aligned}$$

$$\begin{aligned} &x\left\{Mg\left[Al(OH)_3 \cdot \frac{y}{x}\left(CH_3COCH\ COCH_3\right)\right]_2\right\}\\ &\rightarrow x\left\{Mg\left[-O\,Al \cdot \frac{y}{x}\left(CH_3COCH\,COCH_3\right) \cdot O-\right]_2\right\}\\ &\qquad + 3H_2O\\ &\rightarrow \left\{Mg\left[-O\,Al \cdot \frac{y}{x}\left(CH_3COCH\ COCH_3\right) \cdot O-\right]_2\right\}_\eta \\ &\qquad\qquad (3)\end{aligned}$$

It is speculated that the coordination complex in Equation 2 forms complicated multiple bridging of aluminium atoms by condensation reactions as well as extensive association [9] leading to the formation of the gel.

Residual organics of the gel were removed by oxidative reactions with hydrogen peroxide solution. Here the objective was to examine the hydrolytic stability of $MgAl_2O_4$ gel. X-ray analyses of 1000 and 2000° C heat-treated samples (which received treatment with hydrogen peroxide prior to heat treatment) did not show the presence of either MgO or free Al_2O_3. This indicates that the hydrolytic stability of $MgAl_2O_4$ gel was good. Moreover, the absence of a second phase at a temperature as high as 2000° C indicates that the problems associated with the conventional method of fabrication of optically transparent stoichiometric spinel could be avoided by using $MgAl_2O_4$ gel as the starting material. However, systematic studies would be required to fully establish the process.

5. Conclusions

1. Transparent non-crystalline stoichiometric magnesium aluminate gel-monolith can be prepared by chemical polymerization reactions between aluminium secondary butoxide and magnesium acetate.
2. Magnesium aliminate gel can be freed from residual organics by chemical treatment with hydrogen peroxide solution.
3. Gel-derived $MgAl_2O_4$ powder did not show any evidence of phase separation after heat treatment at 2000° C for 4 h.
4. Use of gel-derived $MgAl_2O_4$ powder can offer the potential advantage to greatly reduce or eliminate the problems associated with the conventional method of fabrication of optically transparent stoichiometric spinel material.

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References

1. D. VIECHNICKI, F. SCHMID and J. W. McCAULEY, *J. Appl. Phys.* **43** (1972) 4508.

2. R. A. WICKERSHEIM and R. A. LEFEVER, *J. Opt. Soc. Amer.* **50** (1960) 831.
3. B. COCKAYNE and M. CHESSWAS, *J. Mater. Sci.* **2** (1967) 498.
4. P. F. BECHER, *Amer. Ceram. Soc. Bull.* **56** (1977) 1015.
5. D. W. ROY, Final Technical Report No. AFWAL–TR–81–4005 (March 1981).
6. R. L. GENTILMAN, *Amer. Ceram. Soc. Bull.* **60** (1981) 906.
7. H. DISLICH, *Angew. Chem.* (*Int. Edn. Engl.*) **10** (1971) 363.
8. B. E. YOLDAS, *J. Appl. Chem. Biotechnol.* **23** (1973) 803.
9. B. P. BLOCK, "Inorganic Polymers", edited by F. G. A. Stone and W. A. G. Graham (Academic, New York, 1962) p. 447.
10. T. R. PATTERSON, F. J. PAVLIK, A. A. BALDONI and R. L. FRANK, *Organ. Biol. Chem.* **81** (1959) 4213.

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