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Aluminum Magnesium Oxynitride: A New Transparent Spinel Ceramic

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Abstract

A pure and dense spinel solid solution can be obtained by reaction-sintering between alumina–magnesia or aluminate of magnesium and aluminum nitride or oxynitride. The influence of post isostatic pressing on density, microstructure and transmittance (visible-IR) is studied for different starting materials. Transmittances of 65 and 80% are obtained for a 6 mm thick sample in visible and infra-red spectra, respectively.

1 Introduction

New technologies need optical materials with the best mechanical properties. Initially monocrystalline ceramics as quartz or sapphire were developed, and more recently polycrystalline ceramics like $MgAl_2O_4$[1–3] and γAlON[4–8] have been studied. Indeed these spinel solid solutions can be obtained transparent in the range 0·1–6 μm. The aluminate of magnesium is more easily sintered than γAlON (sintering temperature 1600–1700°C against 1850–1900°C for γAlON), but γAlON exhibits good mechanical properties: MOR = 500 MPa[8] instead of 400 MPa for $MgAl_2O_4$.[3]

The present paper describes the preparation of a new transparent polycrystalline oxynitride spinel phase, MgAlON (Fig. 1). A pure solid-solution containing Al–Mg–O and N could be prepared by reaction sintering between Al_2O_3–AlN–MgO or Al_2O_3–$MgAl_2O_4$–AlN. Jack[9] observed at 1800°C a large field of homogeneity of this solid-solution. Later, Weiss *et al.*[10] at 1750°C and Sun *et al.*[11] at 1600°C specified this field. Weiss *et al.*[10] remarked that the magnesium aluminate was an intermediate phase before obtaining the MgAlON phase during the Al_2O_3–AlN–MgO reaction. Laurent-Fievez[12] observed MgAlON at 1350°C and this result has been confirmed by Willems.[8] Previous papers have described the reactivity[13] and the sintering-reaction[14] of MgAlON whose main results were: (i) the control of the parasite reaction between AlN–MgO and AlN–$MgAl_2O_4$; (ii) the role of cationic vacancies of the intermediate aluminate of magnesium phase; and (iii) the morphology role of the starting materials.

2 Experiments

Six compositions (A to F) with different starting materials (Table 1) were studied: alumina (α + γ and γ crystallographic forms), magnesium oxide or aluminate of magnesium, aluminum nitride (commercial powder or obtained by nitridation of boehmite[15]), aluminum oxynitride (also obtained by nitridation of boehmite[16]) and MgAlON powder prepared in the laboratory.

Starting powders (samples A to E) were milled with highly pure alumina balls in anhydrous ethyl alcohol with phosphoric ester as dispersant agent (1·5 wt%). After drying under vacuum, the powders were sieved at 200 μm. In one case (D), polyvinyl butyral (PVB) and polyethylene glycol (PEG) were used as binder and plasticizer (1·5 wt%/dry powder). The slurry was then spray-dried.

Samples F were prepared in a different way. First, pellets with α-alumina, MgO and AlN (Starck) powders were heated at 1550°C for 6 h to perform the reaction. Then the pellets were crushed in an Aurec grinder and ball milled for 24 h with 1 wt% of MgO, 0·5 wt% PVB and 1 wt% PEG. Finally the slurry was spray-dried.

The pellets for samples A to F (about 25 × 25 × 10 mm) were obtained by isostatic pressing in plastic mold under 400 MPa; if necessary a debonding cycle was carried out to remove organic binder (samples D and F).

The reaction sintering (samples A to E), like the sintering (sample F), took place in a graphite furnace at 1675°C for 6 h in a powder bed made of 50 wt% AlN and 50 wt% MgO under a nitrogen atmosphere (0·1 MPa).

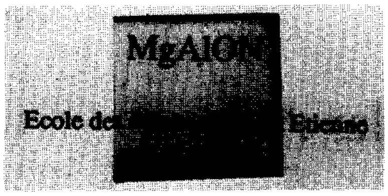


Fig. 1. MgAlON transparent piece (25 × 25 × 6 mm).

All the samples were post-hipped in the temperature range 1675–1810°C for 1 or 1·5 h under 155 MPa of nitrogen. (HIP treatments were performed by National Forge Europe (B).)

Samples were characterized by density (by the Archimede's method in water), X-ray control, microstructure analysis (SEM after thermal etching in N2 atmosphere at about 1600°C, 1 min, rate ramp: 15°C/min TEM), transmittance in visible (Perkin-Elmer Lambda 2) and infra-red (Biorad FTS40) spectra after polishing down to 1 μm diamond.

3 Results

The given compositions (Table 1) have been determined previously[13,14] to obtain pure and sintered (without open porosity) MgAlON samples at low temperature (1550°C). For each composition (A to F) the ratio between chemical elements was the same and corresponding to 21 mol% MgO, 13 mol% AlN, 66 mol% Al_2O_3.

After a treatment at 1675°C for 6 h, each sample was monophased but due to parasite reactions between AlN–MgO or AlN–$MgAl_2O_4$[13] which induce a loss of Mg and N, the spinel solid compositions differ. Each sample contained 3–3·5 wt% of nitrogen determined by complete oxidation.[13]

3.1 HIP effects on chemical composition

Monophased MgAlON samples obtained from the compositions A to F by reaction-sintering or sintering at 1675°C for 6 h, preserved the same lattice parameter after post-hipping whatever the HIP temperature was. For all the samples, lattice parameters measured after sintering were between 0·7992 and 0·8009 nm and were between 0·7994 and 0·8004 nm after HIP treatments. These values are within the accuracy of measurement (0·005 nm).

3.2 HIP effects on densification

Results are given in Table 2. As the relative accuracy of the density determination was 0·1%, HIP treatments had a significant effect at 1675°C (the same temperature as those of the sintering cycle): +3·3% for A and +0·5% for other samples (B to E). Higher HIP temperatures had no effect on the densification.

After reaction-sintering, samples A could have some very fine open porosity, not detected by measurement (in water), so HIP treatment was inefficient for these samples.

Only one HIP treatment was performed at 1810°C for 1 h, it induced an increase of densification (1·7%).

3.3 Microstructural effects of HIP treatments

Before hipping, sample microstructures could be arranged in three classes:

(i) homogeneous and fine grain size (2–3 μm) for B, C, D samples (see Fig. 2)
(ii) homogeneous and coarse grain size (about 10–15 μm) for A, E and F samples (see Fig. 3).
(iii) inhomogeneous for D with binder or D annealed above 1750°C (see Fig. 4).

A TEM observation of D with binder had shown that the fine intergranular porosity disappeared by hipping at 1675°C with a light grain growth (Fig. 5). This was also observed by SEM analysis for B and C samples up to 1810°C HIP treatment and for D up to 1765°C HIP treatment.

Table 1. Studied compositions (mol%)

Composition	Al_2O_3 (%)	AlN (%)	MgO (%)	$MgAl_2O_4$ (%)	γAlON (%)	MgAlON (%)
A	$\gamma Al_2O_3{}^a$ 53	7^b		40^c		
B	$\alpha Al_2O_3{}^d$ 46 $\alpha Al_2O_3{}^e$ 20	13^f	21^g			
C	$\alpha Al_2O_3{}^d$ 55 $\gamma + \alpha$ $Al_2O_3{}^h$ 11	13^f	21^g			
D	$\gamma + \alpha$ $Al_2O_3{}^h$ 66	13^b	21^g			
E			11^g		89^i	
F			1 wt%			99^j

[a] CR125 Baïkowski Chimie.
[b] Starck grade C.
[c] S30 Baïkowski Chimie.
[d] Residue of nitridation.
[e] SM8 Baïkowski Chimie.
[f] Nitridation of boehmite.
[g] Rhône Poulenc.
[h] CR30 Baïkowski Chimie.
[i] Nitridation of boehmite.
[j] Laboratory prepared.

Table 2. Specific mass (g cm^{-3}) evolution by HIP-treatments (relative accuracy 0·1%)

	A	B	C	D	D(with binder)	E	F
Before post-hipping 1675°C, 6 h	$3{\cdot}48_5$	$3{\cdot}60_2$	$3{\cdot}58_7$	$3{\cdot}57_5$	$3{\cdot}60_0$	$3{\cdot}55_5$	$3{\cdot}50_3$
HIP 1675°C, 1 h	$3{\cdot}60_5$	$3{\cdot}62_9$	$3{\cdot}60_0$	$3{\cdot}60_1$	$3{\cdot}62_5$	—	—
HIP 1720°C, 1 h 30	$3{\cdot}49_9$	$3{\cdot}63_3$	$3{\cdot}61_5$	$3{\cdot}60_3$	$3{\cdot}62_9$	—	—
HIP 1765°C, 1 h	$3{\cdot}56_5$	$3{\cdot}62_8$	$3{\cdot}60_5$	$3{\cdot}60_2$	$3{\cdot}62_6$	—	—
HIP 1810°C, 1 h	—	$3{\cdot}62_7$	$3{\cdot}61_5$	$3{\cdot}60_5$	$3{\cdot}62_8$	$3{\cdot}60_2$	$3{\cdot}56_0$

Fig. 2. Microstructures of B, C and D samples sintered at T = 1675°C, 6 h.

Fig. 3. Microstructure of A, F samples sintered at T = 1675°C, 6 h.

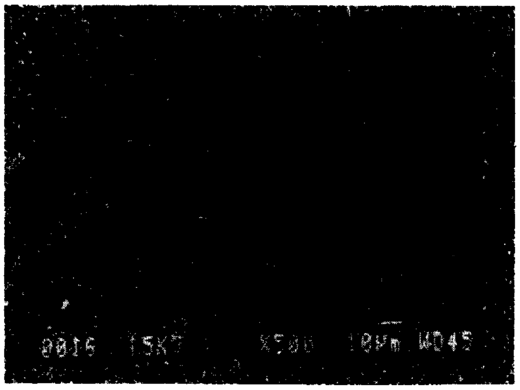
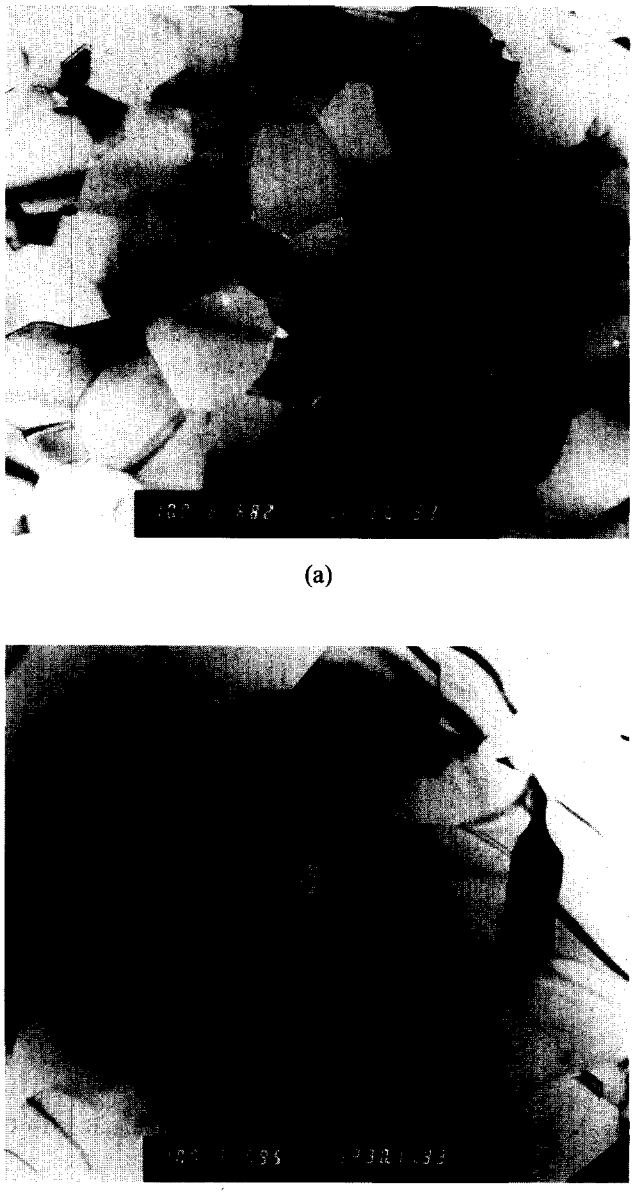


Fig. 4. Microstructure of D (with binder or annealed) sintered at T = 1675°C, 6 h.



(a)

(b)

Fig. 5. TEM observations (a) before HIP, (b) after HIP.

For homogeneous but coarse grain size (A,E,F samples) the grain size did not change, as shown in Fig. 6, and up to 1765°C, intergranular porosity still remained. At 1810°C, E samples presented large grains (2–300 μm) with intragranular porosity (Fig. 7) whereas F samples had a homogeneous grain size (50 μm) without porosity (Fig. 8).

When initial samples presented some heterogeneity (some large grains) as D with binder or D annealed samples, HIP treatment preserved this microstructure up to 1765°C (Fig. 9) but above this temperature the grain size became bimodal (see Fig. 10).

The post-hip treatment can be considered as an annealing treatment under pressure. To analyse the pressure effect, homogeneous samples were annealed for several hours under 0·1 MPa of N_2. Up to 1750°C a homogeneous microstructure had remained but at 1750°C the grain growth and

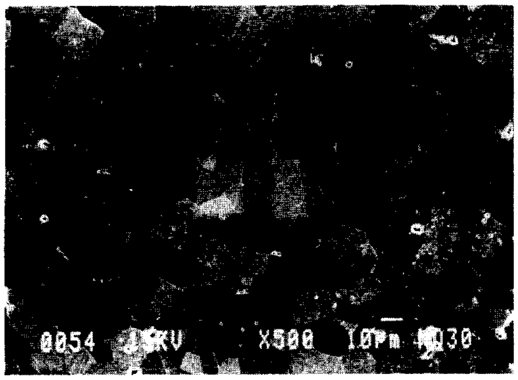


Fig. 6. Microstructures of A, E and F samples after hipping at 1765°C, 155 MPa.

Fig. 7. Microstructure of E samples after hipping at 1810°C, 155 MPa.

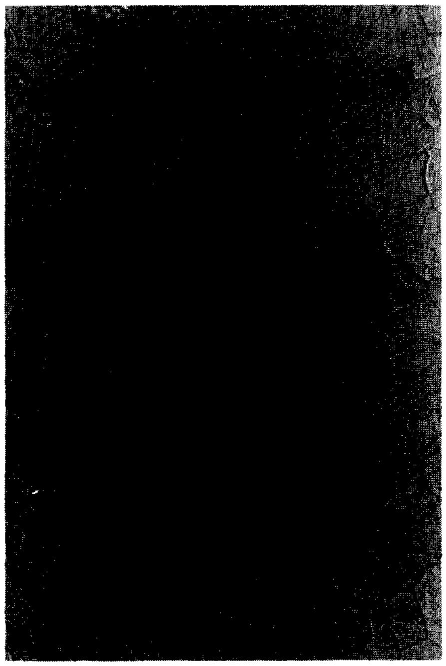


Fig. 8. Microstructure of F samples after hipping at 1810°C, 155 MPa.

porosity appeared (Fig. 11). So the pressure delays the grain growth during the HIP treatment. Nevertheless this delay depends on the HIP temperature and the initial kind of microstructure. For C and D samples grain growth occurred at 1810°C HIP treatment; conversely in samples A the microstructure remained almost identical whatever the HIP treatment (between 1675 and 1810°C).

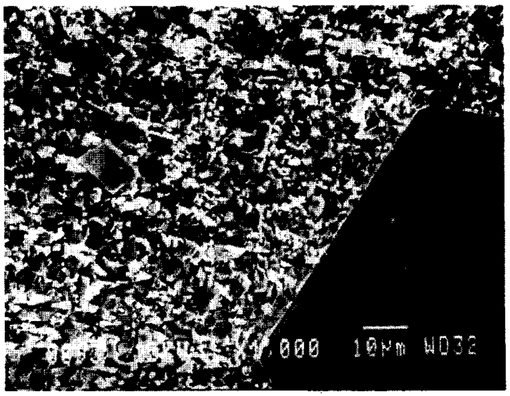


Fig. 9. Microstructure of D (with binder or annealed) after hipping up to 1765°C, 155 MPa.

Fig. 10. Microstructure of D (with binder or annealed) after hipping up to 1810°C, 155 MPa.

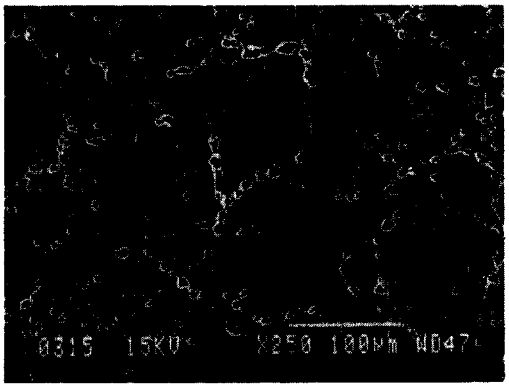


Fig. 11. Effect on grain size by annealing treatment without pressure ($T < 1750$°C).

The microstructure evolution of hipped samples was linked to the initial state of the sample and also to the HIP treatment conditions.

3.4 Optical effects of HIP treatments

Table 3 reports transmittance results (%) in visible wavelength for different HIP treatments.

Samples A and E were impervious to visible waves because of the fine intragranular porosity which has been previously observed. For B, C and D (without binder) samples, although a maximum density was reached from 1675°C, the transmit-

Table 3. Transmittance in line (%) in visible spectrum versus HIP treatments at 500 and 700 nm (thickness of the sample in mm)

	A		B		C		D (with binder)		D (without binder)		E		F	
λ (nm)	500	700	500	700	500	700	500	700	500	700	500	700	500	700
1675°C, 1 h	opaque		0 (5,4)	10 (5,4)	3 (4)	18 (4)	3 (6,3)	20 (6,3)	0 (6)	0 (6)	—	—	—	—
1720°C, 1·5 h	—		50 (6,2)	60 (6,2)	5 (5,2)	20 (5,2)	10 (6,2)	20 (6,3)	5 (7,6)	15 (7,6)	—	—	—	—
1765°C, 1 h	translucent		10 (5)	30 (5)	10 (5)	25 (5)	35 (6)	50 (6)	15 (7,3)	30 (7,3)	—	—	—	—
1810°C, 1·5 h	—		50 (6)	65 (6)	35 (4)	45 (4)	18 (6)	25 (6)	15 (4,5)	30 (4,5)	opaque	white	5 (3)	5 (3)

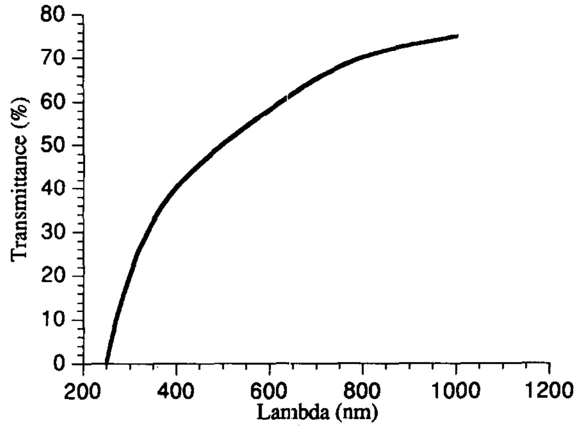


Fig. 12. Visible spectrum of B samples (thickness 6 mm).

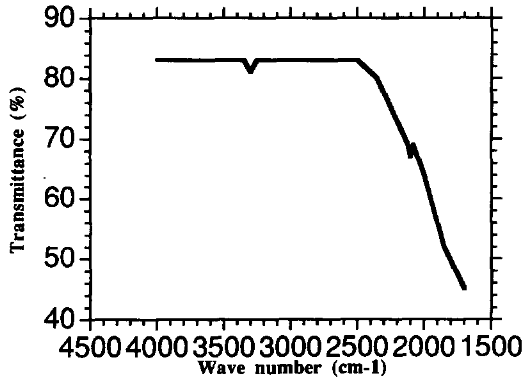


Fig. 13. Infra-red spectrum of B samples (thickness 6 mm).

tance increased above this HIP temperature (65% for B sample at 1810°C, Fig 12). For D samples the binder effect was significant on densification but when the grain size was bimodal the transmittance decreased (at 1810°C) as shown in Table 3. For F samples despite a regular grain size and no porosity, the transmittance for a thickness of about 3 mm in the visible spectrum is very poor (5%).

Unfortunately the samples were often coloured perhaps by carbon or metallic oxide pollution. Only B samples were not coloured, the nitridation could increase the purity of powders.

The I-R spectrum is shown in Fig. 13. A weak peak of OH or NH absorption can be seen. The transmittance was 80% up to 2500 cm^{-1} and the cut off appeared at 1700 cm^{-1}. This spectrum is very close to those of γAlON and $MgAl_2O_4$.

4 Conclusion

γAlON has very good mechanical properties but it is difficult to obtain it transparent with a sufficient thickness. The magnesium aluminate ($MgAl_2O_4$) is easier to sinter but its intrinsic mechanical properties are lower than those of γAlON.

It has been shown in this study that it is possible to obtain a new transparent solid solution spinel: a MgAlON spinel phase sample has been made transparent (Fig. 1) in visible (60%) and infra-red spectra (80%) for a 6 mm thickness with a very fine grain size 5–7 μm and about 3 wt% of nitrogen. The choice of the starting powders and the choice of the reaction-sintering cycle linked to a HIP temperature are the predominant parameters which allow the attainment of transparent samples with a homogeneous microstructure.

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