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Alumina–γ-AlON Composites: Chemical and Microstructural Effects of Sintering Y_2O_3 Additions

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Abstract

A small amount of yttria (0·04 mol%) is sufficient to obtain fully dense alumina-γ-AlON composite ceramic when the initial AlN content is greater than 7 mol%, but the microstructure is modified in comparison with the material without Y_2O_3. The γ-AlON formation is delayed and the decomposition of this metastable spinel phase is increased especially under pressure. Y_2O_3 (3 mol%) delays the beginning of the shrinkage and gives a yttrogarnet phase.

Geringe Mengen zugegebenen Yttriumdioxids (0·04 mol%) reichen aus, um Aluminiumdioxid–γ-AlON-Verbundkeramiken vollständig zu verdichten, wenn der Ausgangsgehalt an AlN oberhalb 7 mol% liegt. Im Vergleich zu einem Material ohne Y_2O_3-Zusatz entwickelt sich jedoch ein verändertes Gefüge. Die Bildung von γ-AlON ist verschoben, wobei die Zersetzung dieser metastabilen Spinell-Phase, insbesondere durch Druckanwendung gefördert wird. Y_2O_3 (3 mol%) führt zu einer Verlagerung des Schrumpfungsbeginns und stabilisiert eine Yttrogranat-Phase.

Une quantité faible d'oxyde d'yttrium (0·04% en mole) est suffisante pour densifier complètement une céramique composite alumine–AlON-γ, lorsque la teneur initiale en AlN est supérieure à 7% en mole. Cependant, la microstructure obtenue est différente de celle du même matériau fritté sans Y_2O_3. Dans ces conditions expérimentales, la formation de l'AlON-γ est retardée et la décomposition de cette phase spinelle métastable est accélérée, spécialement sous l'effet de la pression. Y_2O_3 (3% en mole) retarde le début de la densification et conduit à l'obtention d'une phase grenat d'yttrium.

1 Introduction

The sintering (starting from Al_2O_3–AlN powder mixtures) and the properties of Al_2O_3–γ-AlON composites have been described elsewhere.[1–3] Aluminium nitride inhibits the composite sintering in comparison with pure alumina; therefore some densification aids (Y_2O_3, MgO) may be used to obtain fully dense materials. The present paper deals with the effect of yttria on the reactivity of this system (shrinkage, phases, etc.) and the composition microstructures (SEM, TEM).

Yttria is used to densify alumina materials.[4–11] Although it leads to a densification rate decrease, such materials present a higher density than pure alumina. An addition of 0·5 mol% is optimal, but Hubner & Hausner[8] have found an alumina grain coarsening in this case. Yttria is also used to densify AlN material.[12–15] Gauthier *et al.*[12] have shown that the densification is optimal for 0·05 mol% Y_2O_3. Komeya and co-workers[13–15] have found the yttrogarnet (YAG) or yttroalumite (YAM) formation depends on the composition and elaboration conditions, but they have not proved the presence of nitrogen in substitution of oxygen in these phases.

2 Experimental Methods

The three powders (Al_2O_3, Criceram, France; AlN, grade C, Starck, FRG; Y_2O_3, Rhône-Poulenc, France) are mixed by ball-milling in anhydrous ethyl alcohol. The mixture is dried under vacuum and sieved (200 μm). The compositions studied are given in Table 1.

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Table 1. Initial powders contents for composites Z and Y (mol%)

Composites	Al_2O_3	*AlN*	Y_2O_3
Z1	92·58	7·41	—
Z2	92·54	7·41	0·04
Z3	89·49	7·17	3·33
Y1	89·68	10·31	—
Y2	89·64	10·31	0·04
Y3	86·74	9·97	3·28

range 1500–1750°C, either under 0–150 MPa or without pressure, under a nitrogen atmosphere. During pressureless sintering (PS) samples are protected by a powder bed of the same composition. Uniaxial pressure is used during hot-pressing up to 40 MPa in graphite dies and some samples after initial pressureless sintering are HIPed between 1550 and 1700°C under 150 MPa of nitrogen.

The shrinkage is followed by dilatometry during both pressureless sintering (Adamel TI24) up to 1575°C (heating rate 5°C/min) and hot-pressing (heating rate 30°C/min).

Samples are characterized by X-ray diffraction, pycnometric measurements in water for specific density, microstructure analyses by SEM after etching in air and by TEM (200 kV). Some micro-analyses are carried out on thin foils.

3 Results

3.1 Dilatometric analyses

The studied compositions are reported in Table 1 and denoted Y1, Y2 and Y3. The shrinkage and its rate versus temperature are shown in Figs 1 and 2 (pressureless), and Figs 3 and 4 (hot-pressing under 10 and 40 MPa).

The beginning of the shrinkage is nearly 1100°C for Y1 and Y2, and 1300°C for Y3, in both pressureless and hot-pressure sintering.

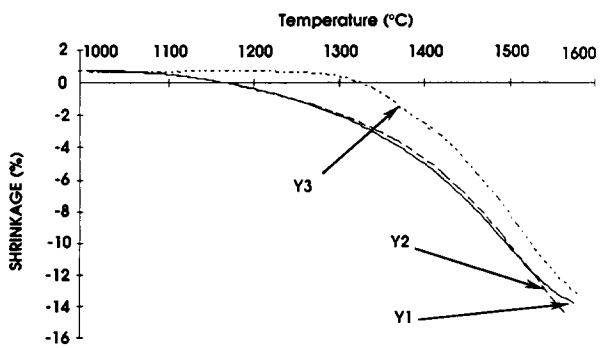


Fig. 1. Dilatometric curves in pressureless sintering.

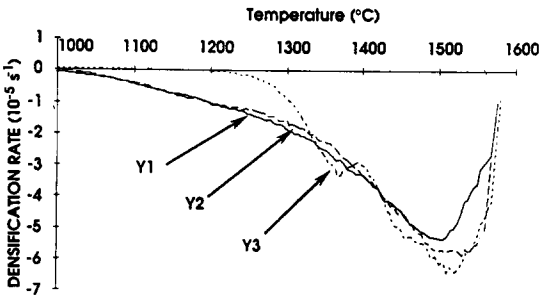


Fig. 2. Densification rate versus temperature in pressureless sintering.

In hot-pressing generally three peaks corresponding to three maximum densification rates exist at about 1150, 1350 and 1475°C. The first one (1150°C) takes place only under pressure for all the compositions. The second one (1350°C) is present for Y3 in pressureless sintering and for all the compositions under pressure at a temperature not affected by the composition. The third one (1475°C) exists in all the cases and it is independent of the Y_2O_3 content, but it is shifted towards the lower temperatures when the pressure increases (Fig. 4). Above 1600°C a maximum of shrinkage is reached (Figs 1–2) that has been explained elsewhere.[16] This maximum takes place at 1650°C for Y1 and Y3, and 1620°C for Y2 under 10 MPa, whereas it is at about 1550°C under 40 MPa.

3.2 X-Ray diffraction

Above 1600°C AlN reacts with Al_2O_3 to form a spinel phase γ-AlON.[17] The ratio R_1 determines the

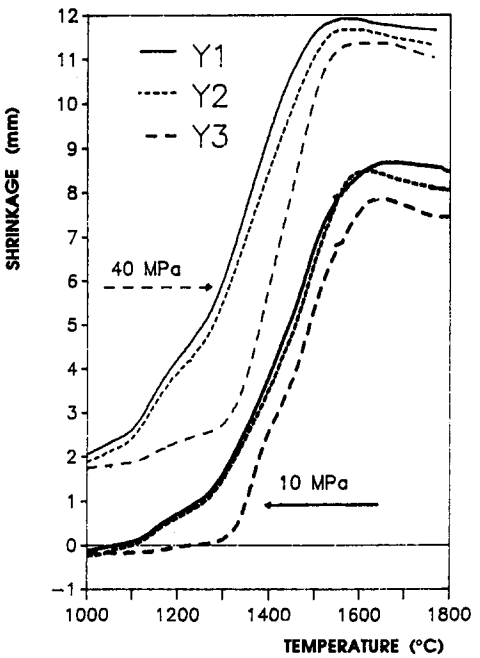


Fig. 3. Dilatometric curves in hot-pressing.

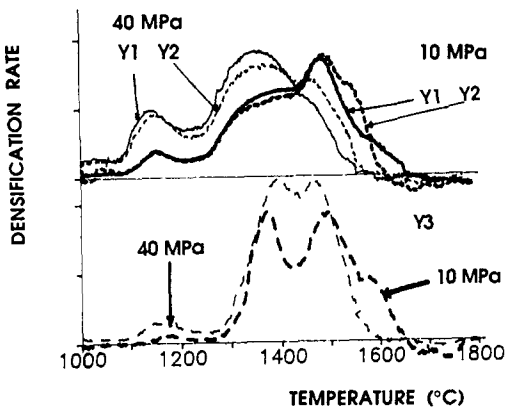


Fig. 4. Densification rate versus temperature in hot-pressing.

γ-AlON content in the composites:

$$R_1 = \frac{I^{\gamma\text{-AlON}}_{[400]}}{I^{\alpha\text{-}Al_2O_3}_{[113]} + I^{\gamma\text{-AlON}}_{[400]}} \times 100$$

and R_2 the content of YAG ($Y_3Al_5O_{12}$) due to the reaction between Al_2O_3 and Y_2O_3:

$$R_2 = \frac{I^{YAG}_{[420]}}{I^{\alpha\text{-}Al_2O_3}_{[113]} + I^{YAG}_{[420]}} \times 100$$

Table 2 shows R_1, R_2 and the γ-AlON unit cell parameter versus the sintering temperature. The γ-AlON content (R_1) increases with the temperature by alumina dissolution[16] and the spinel unit cell parameter decreases. More alumina is dissolved under pressure than during pressureless sintering. A small amount of Y_2O_3 (Y2) is not favourable to this dissolution (Table 2).

The yttrogarnet phase ($Y_3Al_5O_{12}$) is not detected by X-ray analysis of 0·04 mol% Y_2O_3 (Y2). The content and the unit cell parameter of YAG are constant between 1600 and 1650°C for Y3. Above 1700°C a liquid phase appears and is expelled out of the matrix, so R_2 drops (Y3).

HIPed samples have also been analysed (Table 3). Pressureless sintering is carried out in the temperature range where γ-AlON can be obtained (i.e. 1650°C). Whatever the temperatures are, HIP treatments lead to:

—An important R_1 decrease and the formation of AlN (not given in Table 3), especially at 1550°C and when samples contain yttria (0·04 mol%).
—A slight γ-AlON unit cell parameter increase.

The amount of YAG does not really change; because R_1 is decreasing, so the concentration of Al_2O_3 increases, leading to an apparent R_2 decrease.

If pressureless sintering is carried out in the temperature range ($T \approx 1500$°C) where no γ-AlON is formed, after HIPing (1700°C) of these samples, the expected ratio of γ-AlON is obtained (Table 3).

3.3 Specific density

γ-AlON is a non-stoichiometric phase which can dissolve a lot of alumina versus the temperature.[16] So it is impossible to determine the theoretical density of samples. Specific density is reported but never the ratio of densification of materials.

Table 4 correlated the densities, the temperature and the Y_2O_3 contents. Samples with ≈7 mol% AlN (Z) are almost fully dense during hot-pressing or pressureless sintering. With ≈10 mol% AlN (Y) it is necessary to use a small amount of Y_2O_3 (0·04 mol%) to close open porosity and to obtain a complete densification. For 3·3 mol% Y_2O_3 above 1700°C open porosity appears because a liquid phase is present.

HIPed samples compositions change during HIPing treatments so their theoretical densities evolve. HIP treatments are very efficient if initial sintering temperatures are low (1500°C). But for sintering treatments above 1650°C, samples with yttria are nearly dense and HIP treatments do not change their densification (Table 3).

3.4 Microstructures

Micrographs (Fig. 5) show the evolution of the microstructure between 1500 and 1750°C when no Y_2O_3 is added. The γ-AlON appears at grain boundaries then extends to the triple junction; γ-AlON grain coarsening occurs at high temperature. The presence of γ-AlON limits the grain growth of the alumina matrix. When a small amount of

Table 2. Influence of sintering parameters on the composites properties

	Y1			*Y2*			*Y3*		
	R_1	R_2	*pm (nm)*	R_1	R_2	*pm (nm)*	R_1	R_2	*pm (nm)*
1600°C–10 MPa	20	0	0·794 7	15	0	0·794 4	23	40	0·794 2
1650°C–10 MPa	25	0	0·794 1	24	0	0·794 2	27	40	0·793 9
1700°C–10 MPa	29	0	0·794 0	23	0	0·794 1	29	15	0·793 8
1750°C–10 MPa	33	0	0·793 7	29	0	0·793 4	Fusion	Fusion	Fusion
1650°C–0 MPa	34	0	0·793 8	27	0	0·793 8	34	43	0·793 7

Table 3. Influence of HIP treatments

			Y1		
	PS–1500°C	*PS–1500°C HIP–1700°C*	*PS–1650°C*	*PS–1650°C HIP–1650°C*	*PS–1650°C HIP–1550°C*
Density (g/cm^3)		3·63	3·83	3·87	3·89
R_1	0	28	35	29	13
Unit cell parameter (nm)		0·793 8	0·793 5	0·794 0	0·794 1
R_2	0	0	0	0	0
			Y2		
	PS–1500°C	*PS–1500°C HIP–1700°C*	*PS–1650°C*	*PS–1650°C HIP–1650°C*	*PS–1650°C HIP–1550°C*
Density (g/cm^3)		3·89	3·86	3·87	3·9
R_1	0	24	30	25	5
Unit cell parameter (nm)		0·793 8	0·793 5	0·794 1	0·794 9
R_2	0	0	0	0	0
			Y3		
	PS–1500°C	*PS–1500°C HIP–1700°C*	*PS–1650°C*	*PS–1650°C HIP–1650°C*	*PS–1650°C HIP–1550°C*
Density (g/cm^3)		3·96	3·89	3·93	3·97
R_1	0	17	28	33	16
Unit cell parameter (nm)		0·793 9	0·793 8	0·793 8	0·793 9
R_2		36	41	39	36

Y_2O_3 (0·04 mol%) is used, γ-AlON disappears from the grain boundaries but precipitates in a non-uniform dispersion of nodules that leads to the alumina grain coarsening (Z2) (Fig. 6(b)). For a higher Y_2O_3 content (3·3 mol%), γ-AlON has the same behaviour but YAG formation occurs and inhibits the alumina grain growth (Z3 and Y3) (Figs 6(c) and 7(c)).

The coarsening of the matrix grains depends on the γ-AlON content and is more important after hot-pressing (Fig. 6) than after pressureless sintering (Fig. 7).

A small amount of Y_2O_3 (0·04 mol%) in Y (10·3 mol% AlN) samples permits fully dense material to be obtained when γ-AlON is above 20 vol.% (Fig. 7(a) and (b)).

The HIP effects on the microstructure depend on the treatment temperature (Figs 8 and 9). If this temperature is in the range where the spinel phase is stable, the microstructure evolution is limited: alumina grains grow slightly with the yttria content. But if the HIPing temperature is below 1600°C (1550°C, for example), γ-AlON disappears in every case (this result agrees with the phases analysis in Table 3). The γ-AlON decomposition is particularly important for samples with 0·04 mol% Y_2O_3 (Fig. 9(b)).

Transmission electronic microscopy (TEM) is carried out on samples (Y) containing 10 mol% AlN and hot-pressed at 1650°C, 10 MPa for 30 min under a nitrogen atmosphere.

A previous paper[16] described the composite alumina–γ-AlON in which γ-AlON grains present a lot of defects corresponding to intragranular precipitates of alumina resulting from a partial solid-solution decomposition (Fig. 10).

The Y2 samples (0·04 mol% Y_2O_3) observation shows γ-AlON grains with a lot of intragranular

Table 4. Specific density versus different treatments

HP	*Z1*	*Z2*	*Z3*	*Y1*	*Y2*	*Y3*
1600°C–10 MPa				3·90	3·92	3·97
1650°C–10 MPa	3·92	3·92	3·99	3·88	3·89	3·95
1700°C–10 MPa				3·88	3·89	3·89
1750°C–10 MPa				3·87	3·86	
1650°C–0 MPa	3·89	3·92	3·99	3·45	3·88	3·94

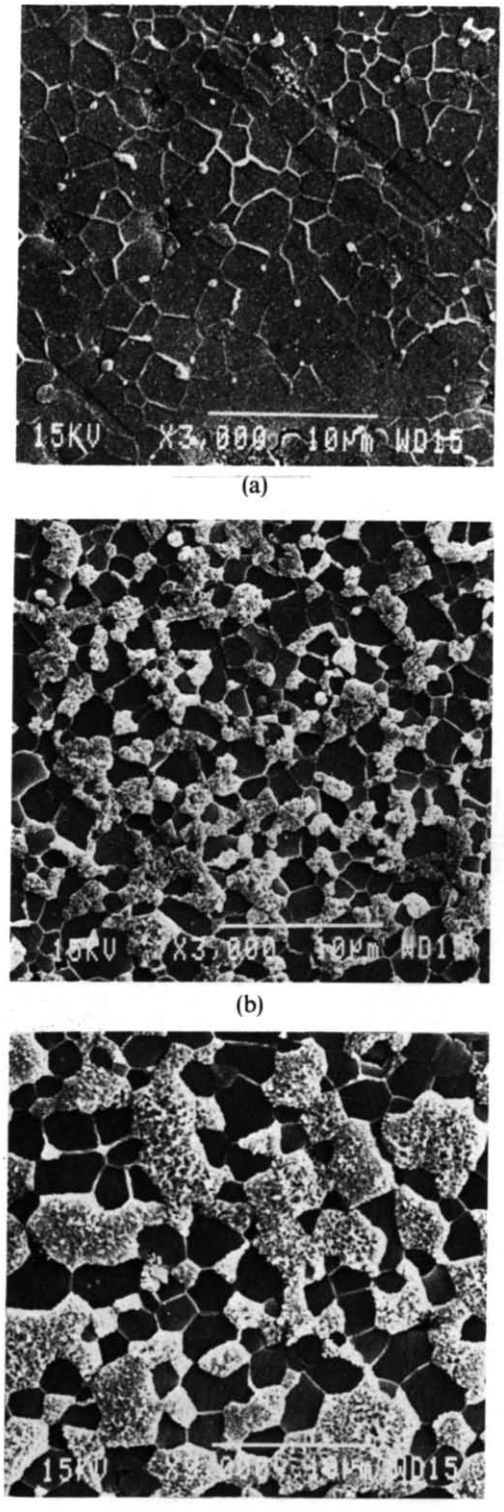


Fig. 5. Influence of temperature on the microstructure for Y samples: (a) 1500°C; (b) 1700°C; (c) >1750°C.

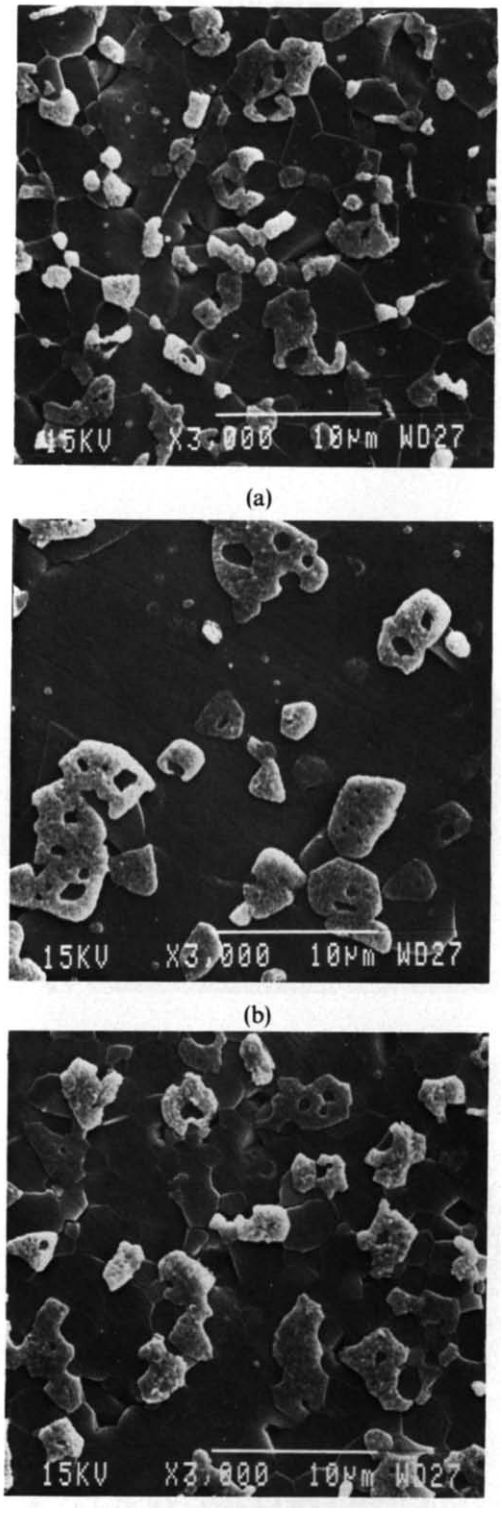
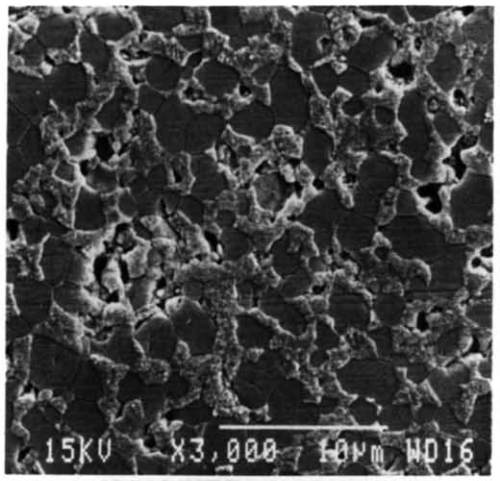


Fig. 6. Influence of Y_2O_3 content on the microstructure in hot-pressing at 1650°C, 10 MPa, 30 min: (a) Z1; (b) Z2; (c) Z3.

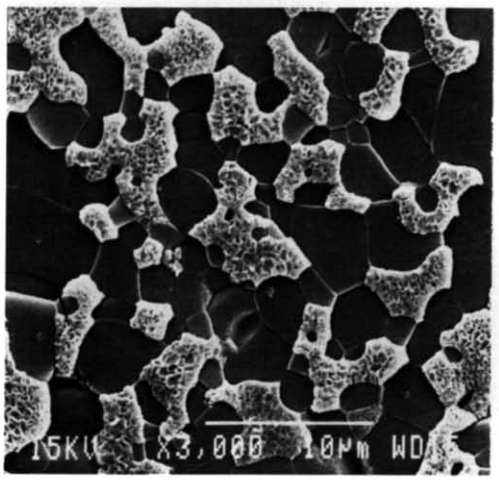
precipitates (platelets) in a more important quantity than in Y1, while all the grains are coarsening (Fig. 11). A vitreous phase containing fine crystallized particles (the composition is not yet determined) is observed at triple junctions (Fig. 12). Elementary analysis shows the simultaneous presence of Y, Si and Al.

For Y3 samples, γ-AlON grains have only a few or no defects; no vitreous phase is detected. YAG grains have two forms, as shown in Figs 13 and 14.

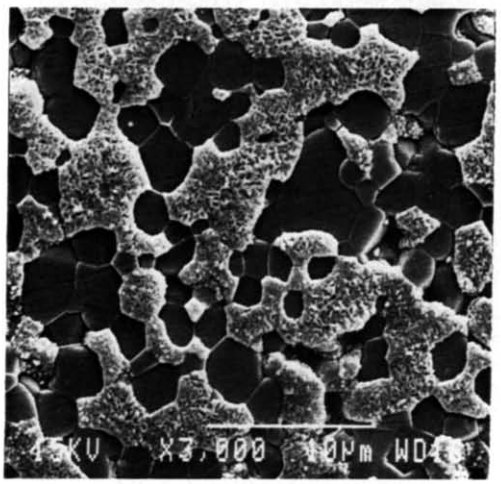
In the present case, the limit of detection of yttrium in an alumina matrix is about 0·5%, so it is impossible to conclude if yttrium is, or is not, present in the grain boundaries or in the γ-AlON phase.



(a)

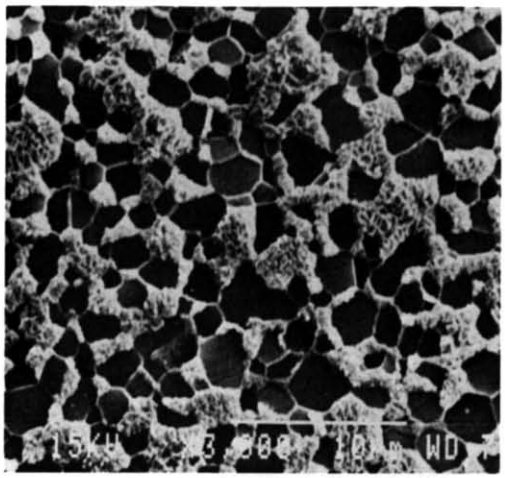


(b)

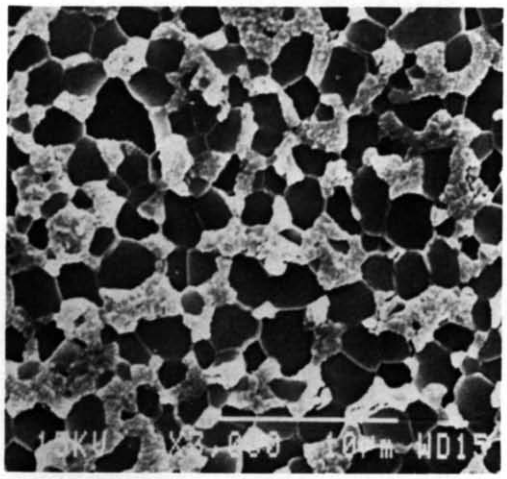


(c)

Fig. 7. Influence of Y_2O_3 content on the microstructure in pressureless sintering at 1650°C, 30 min: (a) Y1; (b) Y2; (c) Y3.



(a)



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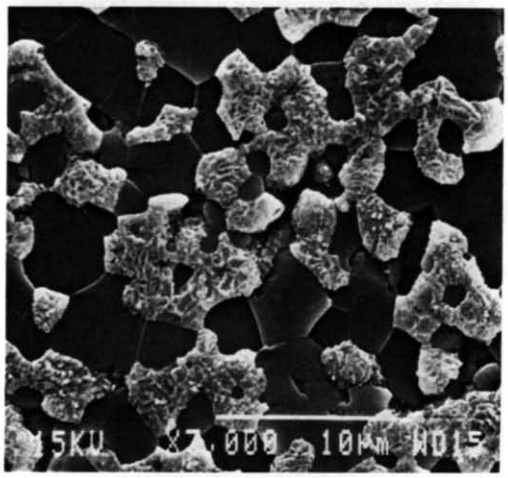
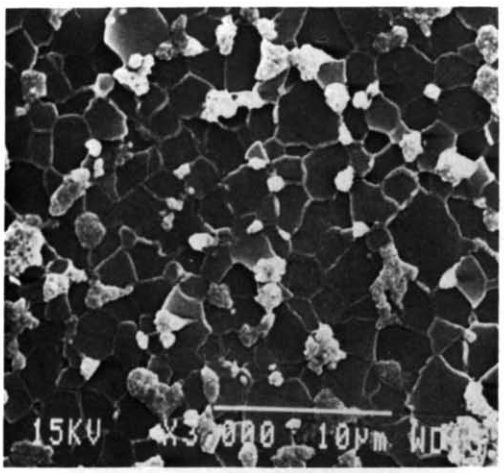


(c)

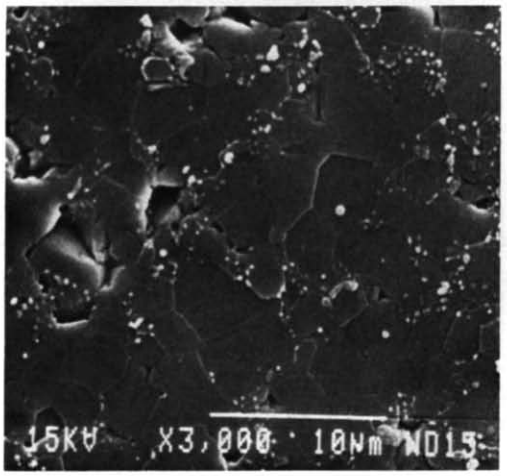
Fig. 8. Effect of HIPing on the microstructure: (a) 0% Y_2O_3 before HIPing; (b) 0% Y_2O_3 after HIPing; (c) 0·04 mol% Y_2O_3 after HIPing. $T_{HIP} = 1650$°C.

4 Discussion

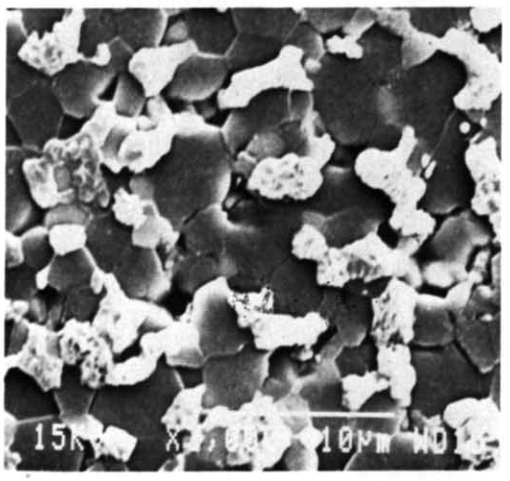
During sintering a reaction takes place between alumina and aluminium nitride; this reaction gives γ-AlON, whose phase volume is larger than that of the initial phase mixture, so a dilatation occurs and the global shrinkage is the result of the two phenomena. This can be modelled to a first approximation for different temperatures of reaction between Al_2O_3 and AlN (Fig. 15). Experimental dilatometric curves of Y1, Y2 and Y3 (Figs 1 and 2) are similar to those denoted respectively f, e and c on



(a)



(b)



(c)

Fig. 9. Effect of HIPing on the microstructure: (a) Y1; (b) Y2; (c) Y3. $T_{HIP} = 1550°C$.

the model. So it can be concluded that the presence of Y_2O_3 delays the γ-AlON formation.

Considering the sintering, Y_2O_3 (3·3 mol%) inhibits the beginning of the shrinkage (Figs 1–4). At low temperature (under 1200°C) a grain rearrangement occurs principally under pressure (Fig. 3).

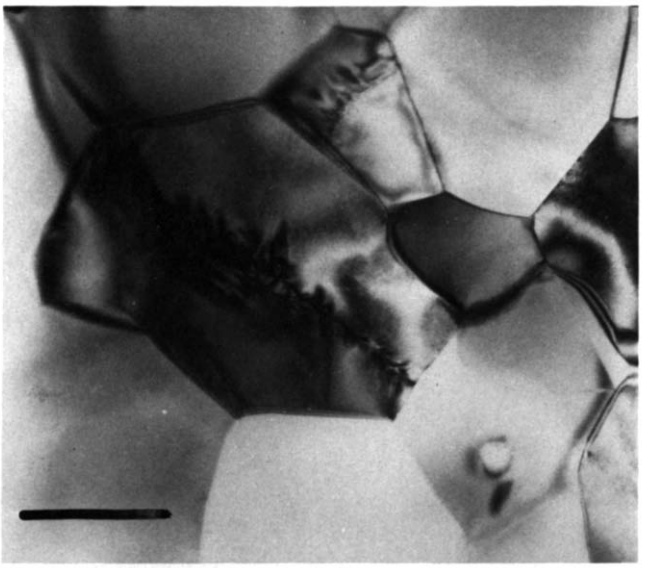


Fig. 10. TEM micrograph of Y1 (bar = 1 μm).

During hot-pressing the shrinkage rate is not affected by Y_2O_3 (Fig. 2). During pressureless sintering the YAG formation leads to an increase of the shrinkage (Fig. 1).

Y_2O_3 is not necessary to densify samples by hot-pressing or for poor AlN ratio by pressureless sintering. For rich AlN ratio (>7 mol%) a small amount (0·04 mol%) of Y_2O_3 permits fully dense materials to be obtained. This result agrees with those of Hubner & Hausner[8] for alumina sintering with Y_2O_3 aid.

For the alumina–yttria system, Nanni *et al.*[4] have shown that for 500 ppm of Y_2O_3 in a small-grained alumina the diffusion in the grain boundaries is very affected by the segregation of yttrium in the grain boundaries; for higher Y_2O_3 content YAG precipitates and yttrium in solid-solution increases the

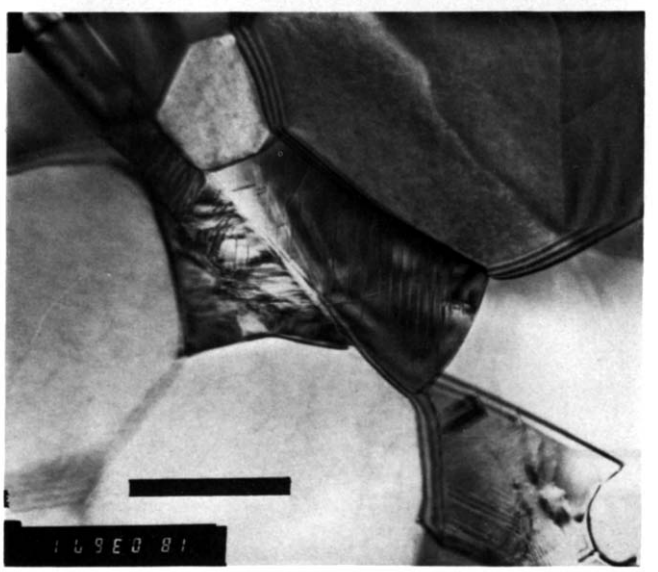


Fig. 11. TEM micrograph of Y2 (bar = 1 μm).

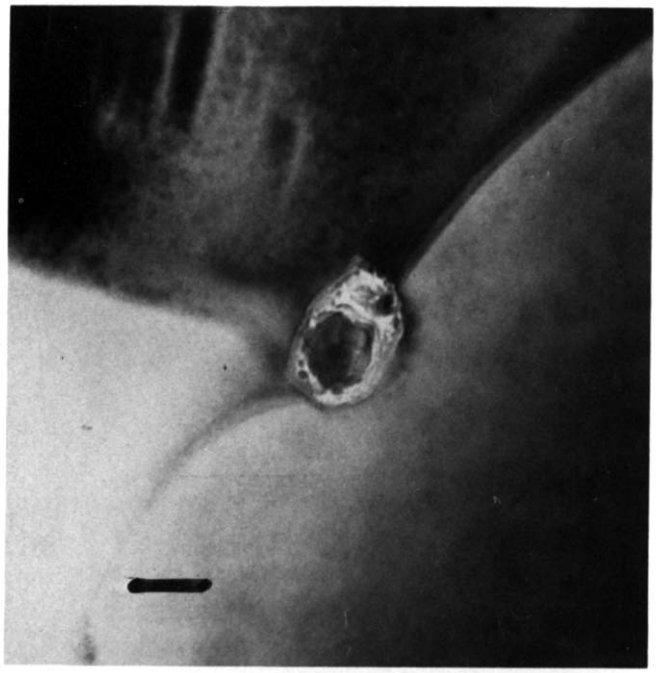


Fig. 12. Vitreous phase at triple junction in Y2 samples (bar = 1 μm).

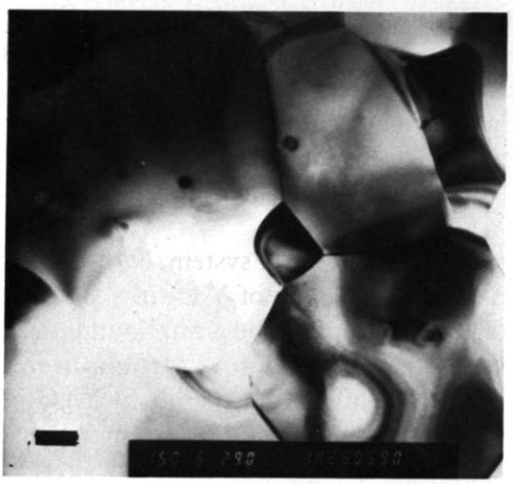


Fig. 13. YAG at triple junction in Y3 (bar = 1 μm).

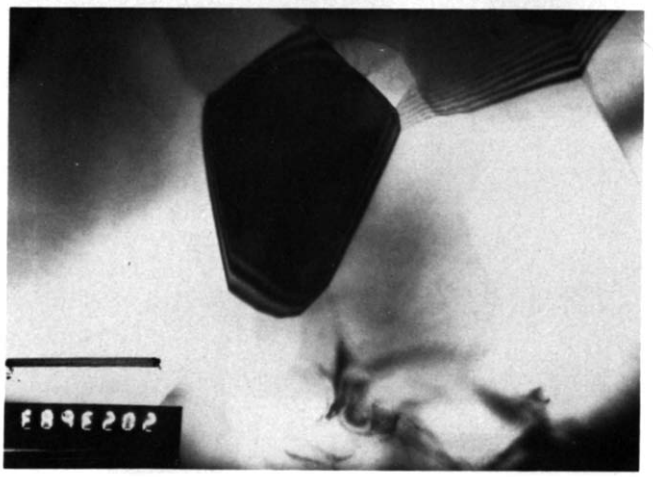


Fig. 14. YAG polyhedral grain in Y3 (bar = 1 μm).

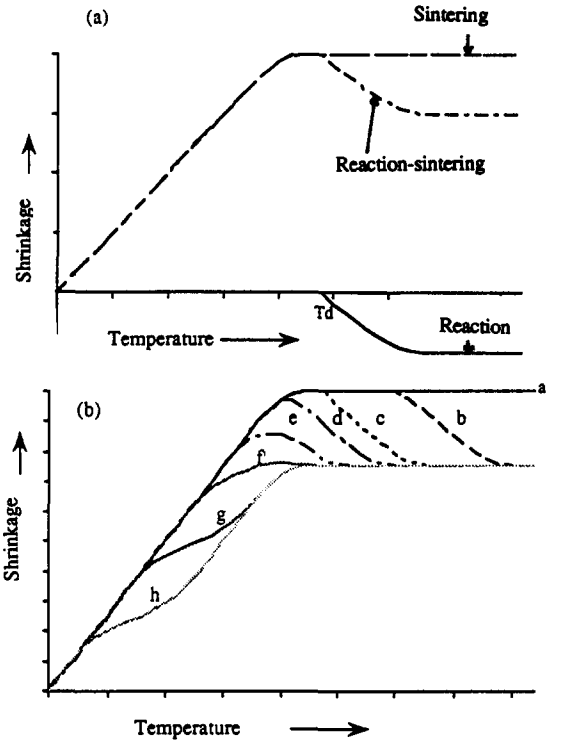


Fig. 15. Modelling of sintering reaction of Al_2O_3–AlN mixture. (a) Theoretical effect of sintering or reaction on shrinkage; (b) theoretical curves versus the temperature of the beginning of reaction (Td).

cationic diffusion coefficients compared to those of undoped alumina.[5] This can explain (i) the final densification of materials containing about 30 vol.% γ-AlON, (ii) the delay of γ-AlON formation and (iii) the typical microstructure which is observed. But how can the decomposition rate increase of the metastable γ-AlON phase when yttria is used be explained? The garnet and the spinel crystallographic structures are not very different. It has been impossible to detect yttrium in the γ-AlON structure. No data exist in the literature. Perhaps some $Y3^+$ in the spinel phase would give a lattice distortion, thus explaining a lower stability of the spinel phase.

5 Conclusion

Yttria addition is not necessary to densify alumina–γ-AlON composites by hot-pressing or by pressureless sintering when the AlN ratio is under 7 mol%. For a higher AlN ratio, a small amount of yttria (0·04 mol%) permits fully dense materials to be obtained. But yttria modifies the microstructure of the material and decreases the γ-AlON stability.

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