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Zirconia-spinel composites. Part I: synthesis of powders and dense materials

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Abstract

MgAl₂O₄ and x wt% ZrO₂-MgAl₂O₄ ($1 \leq x \leq 30$) composite powders were prepared by the urea combustion route. The powders were further ground by either ball milling or attrition to refine the grain size. Zirconia was found solely in the tetragonal form. Dense materials were prepared by hot pressing. The spinel matrix grains were submicronic in size. The ZrO₂ particles were homogeneously dispersed at the grain junctions of the matrix, and their average size increased from less than 0.20 μm to ca. 0.45 μm with increasing content of ZrO₂. The formation of monoclinic ZrO₂ particles proceeded accordingly, being easier in materials with a finer matrix grain size (ex-attrition). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Oxides; A. Composites; B. Chemical synthesis; C. Electron microscopy; D. Microstructure

1. Introduction

The spinel MgAl₂O₄ has many interesting properties, including a high melting point, a low thermal expansion coefficient, low dielectric losses, and excellent resistance to acid and alkali, but its poor mechanical properties at room temperature limit its field of applications. A well-known method for the enhancement of the mechanical properties of ceramics is the dispersion of micrometric ZrO₂ particles as a discrete second phase. However, most studies have dealt with ZrO₂-Al₂O₃ composites (see Wang and Stevens [1] for a review), and only

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a few with $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites [2–6]. The synthesis and microstructure of the latter materials are reviewed in the following.

Claussen and Rühle [2] prepared 25 wt% $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites by mixing Al_2O_3 and MgO powders with zirconium acetate, which decomposes to form ZrO_2 during a heat treatment. Both the metastable tetragonal form (t- ZrO_2) and the monoclinic form (m- ZrO_2) of ZrO_2 are detected after either hot pressing (60% t- ZrO_2) or conventional sintering (20% t- ZrO_2). Fujita et al. [3] prepared powders of spinel and of a 24 wt% ZrO_2 -spinel composite by the powder mixing and alkoxides routes. In these materials, the spinel was alumina rich ($\text{MgO}:\text{Al}_2\text{O}_3 = 3:4$). Dense specimens (relative density $\geq 95\%$) were prepared by conventional sintering or hot pressing. The matrix grain size was close to 2 μm in the sintered (ex-alkoxide) spinel and ZrO_2 -spinel materials, and the average size of the ZrO_2 particles was 0.5 μm . For the hot-pressed (expowder mixing) materials, the matrix grain size was close to 4–5 μm in the spinel, and much smaller (1.2 μm) in the composite. The proportion of t- ZrO_2 in the as-prepared dense materials was higher than 95%, but it was much lower in the polished specimens (ca. 80%). Oudjedi et al. [4] prepared dense $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites (relative density $\geq 98\%$) by conventional sintering of composite powders synthesized by the sol-gel method. They reported that ZrO_2 favors sinterability and that the dense materials exhibit a very fine microstructure without exaggerated spinel grain growth. The ZrO_2 particles and the MgAl_2O_4 grains were found to be in the 0.05–0.2 μm and 0.5–1 μm size ranges, respectively. The ZrO_2 particles were finely dispersed, and they were found entirely as t- ZrO_2 , up to a total content of ZrO_2 equal to 20 wt%. Suzuki et al. [5] prepared composite powders of yttria-stabilized ZrO_2 and MgAl_2O_4 by double nozzle ultrasonic spray pyrolysis. The particles were in the form of needles and spheres, some of which were hollow. The average diameter of the spherical MgAl_2O_4 and ZrO_2 particles was 0.47 and 0.60 μm , respectively, but the size distribution was fairly large. The powders were wet milled and cold-isostatically pressed prior to sintering in air (1700°C, 10 h). They claimed that a powder containing 6.64 mol% yttria-stabilized ZrO_2 has an excellent sinterability because the relative density is equal to 97.6%, while a composite with a higher ZrO_2 content (24.49 mol%) presents a much poorer sinterability. Upon sintering, the ZrO_2 particles and the MgAl_2O_4 grains grow to sizes close to 3 and 20 μm , respectively, and consequently, some ZrO_2 particles are entrapped in the spinel grains. Hyun and Song [6] prepared a 20 wt% ZrO_2 -spinel composite powder by the emulsion-hot kerosene route. The sintered material (relative density = 97.8%) consisted of a spinel matrix (grain size = 1.5–2 μm) containing 1–2 μm cubic ZrO_2 (c- ZrO_2) agglomerates made up of much smaller primary grains.

The aims of this work were, first, to investigate the direct synthesis of $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composite powders with different ZrO_2 contents, and second, to study the microstructure of dense specimens prepared by hot pressing. The combustion synthesis method [7] was chosen because it is simple and cost effective, and allows large quantities of powders to be produced quickly. In particular, MgAl_2O_4 [7,8] and $\text{ZrO}_2\text{-Al}_2\text{O}_3$ composite powders [7] have been prepared by this method. The mechanical properties of the present $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites are reported in a companion paper [9].

2. Experimental

MgAl₂O₄ and x wt% ZrO₂-MgAl₂O₄ (x = 1, 5, 10, 20, and 30) composite powders were prepared by the combustion route. The appropriate amounts of the desired metal nitrates were mixed in stoichiometric proportions with urea and dissolved in the minimum amount of water in a Pyrex vessel. The quantities were calculated so that a combustion batch yields about 6 g of oxide powder. The stoichiometric composition of the redox mixtures was calculated using the total oxidizing and reducing valency of the metal nitrates (oxidizer) and urea (fuel), which serves as numerical coefficient for the stoichiometric balance, so that the equivalence ratio is equal to unity [7]. The vessel containing the solution was inserted into a furnace preheated to 600°C. The solution immediately started to boil and undergo dehydration. The decomposition of the metal nitrates was accompanied by a large release of gases (oxides of nitrogen and ammonia). The obtained paste frothed and formed a foam, which swelled and then ignited. A white flame occurred with the production of a material that swelled to the capacity of the Pyrex vessel. The total combustion process took place in less than 5 min.

Elemental analysis confirmed that the combustion products contained the desired proportions of magnesium, aluminum, and zirconium, the observed differences being smaller than the standard deviation of the analysis method ($\pm 2\%$). For each composition, the so-obtained powders were separated into two parts, which were ground using different methods. Some specimens were ball milled for 1 h in ethanol using zirconia balls and vessel. These powders will hereafter be denoted as BM0, BM1, BM5, BM10, BM20, and BM30, the number reflecting the ZrO₂ weight percentage. The other powders were attrition milled for 40 min in an aqueous solution of dispersant (Duramax D-3005) using alumina balls smaller than 2 mm in diameter and a rotor and a vessel both made of nylon. A calcination in air (500°C, 15 min) was performed to burn the carbon contamination originating from nylon erosion and from the dispersant. These powders will be denoted as A0, A1, ..., A30 in the following sections.

The BM and A powders were uniaxially hot pressed in graphite dies at 1500°C in a primary vacuum. The hot-pressed specimens (20 mm in diameter and 2 mm thick) were ground with diamond suspensions to a finish finer than 6 μm , and a final polish was made using "colloidal" silica (0.05 μm). Relative densities were calculated from the mass and dimensions of the hot-pressed composites. For the sake of brevity, the compounds issued from the hot pressing of ball-milled and attrited powders are denoted as BM and A specimens, respectively.

Phase detection and identification was performed with X-ray diffraction (XRD) pattern analysis (Co K α , $\lambda = 0.17902$ nm) on powders and silica-polished dense specimens. The relative amounts of tetragonal and monoclinic zirconia (t-ZrO₂ and m-ZrO₂, respectively) were calculated from the XRD patterns using the Garvie-Nicholson equation [10]. The powders and dense specimens were also studied by scanning and transmission electron microscopy (SEM and TEM, respectively). To reveal the grain boundaries of the matrix, the dense materials were etched in boiling H₃PO₄ (12 mol liter⁻¹). The average size of the spinel grains was obtained by the linear intercept method.

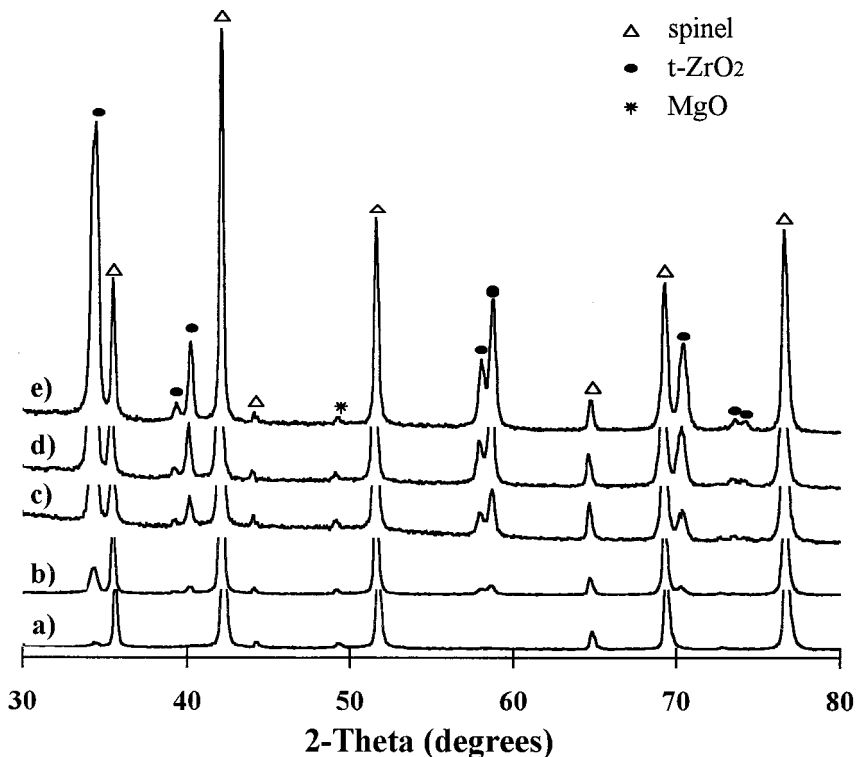


Fig. 1. XRD patterns of the ball-milled $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites (a) BM1, (b) BM5, (c) BM10, (d) BM20, and (e) BM30.

3. Results and discussion

3.1. Powders

Analysis of the XRD patterns of the BM powders (Fig. 1) shows, in addition to the spinel and ZrO_2 phases, the presence of a small amount of MgO. The relative intensity of the (200) MgO peak is similar whatever the ZrO_2 content. It was previously shown [8] that the spinel prepared by the present method is not the stoichiometric MgAl_2O_4 compound, but, rather, a slightly nonstoichiometric $\text{Mg}_{1-3x}\square_x\text{Al}_{2+2x}\text{O}_4$ (\square : vacancy) spinel with x less than 0.02. The lattice parameter of the present spinel phase is 0.8083 nm, showing no deviation, compared with that reported for stoichiometric MgAl_2O_4 [11]. Only the tetragonal form of ZrO_2 is detected in the XRD patterns whatever the ZrO_2 content. The same result was obtained from XRD patterns of the powders prior to any grinding (not shown). These results could indicate that the combustion route in the present experimental conditions produces ZrO_2 particles small enough to allow the suppression of the tetragonal-to-monoclinic ($t \rightarrow m$) phase transformation during the rapid cooling from the flame temperature to the furnace temperature. This is supported by comparing with the work of Kingsley and Patil [7] reporting the combustion synthesis of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ composite powders, in which all the ZrO_2

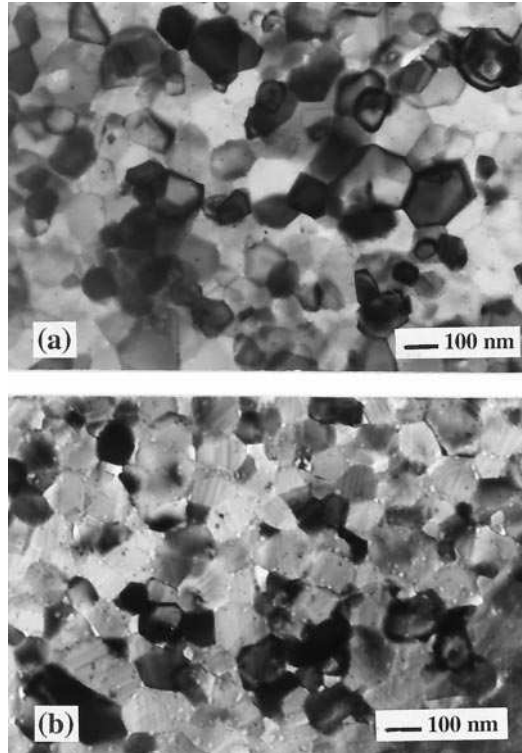


Fig. 2. TEM images of the ball-milled powders (a) BM0 and (b) BM5.

particles are tetragonal and have a size close to 30 nm. Similar features are observed in the XRD patterns of the A powders, but a small proportion of α - Al_2O_3 is also detected, resulting from the erosion of the balls used for attrition. The relative intensity of the most intense α - Al_2O_3 peak is similar for all A powders, and elemental analysis indicates that the amount of α - Al_2O_3 is close to 5 wt% (ca. 6 mol%).

SEM observations of the as-prepared (unground) ZrO_2 - MgAl_2O_4 powders reveals a microstructure similar to that previously observed for pure MgAl_2O_4 [8]. The grains are platelet-like and their surface shows holes resulting from the escaping of the gases during the combustion process. For powder BM0, the agglomerate size distribution measured by sedimentation granulometry in ethanol is fairly large (1–18 μm) with a flat peak close to 6 μm . For powder A0, the agglomerate size distribution is narrow (0.5–3.5 μm) with a peak close to 1.5 μm . These results are in agreement with the SEM observations conducted on the BM and A powders, respectively. TEM examinations of the MgAl_2O_4 powders revealed that the grains are made up of polyhedral crystallites, the size of which ranges between 20 and 200 nm (Fig. 2a). The ZrO_2 - MgAl_2O_4 composite powders appear to be very similar to the MgAl_2O_4 ones. Indeed, the ZrO_2 particles appear as dark areas on the TEM images (Fig. 2b), and are not easily distinguished from the spinel crystallites, because some MgAl_2O_4 crystallites in the Bragg position can also appear as dark areas. In situ energy dispersive X-ray analysis is essential to discriminate between them. Owing to these difficulties, we did not

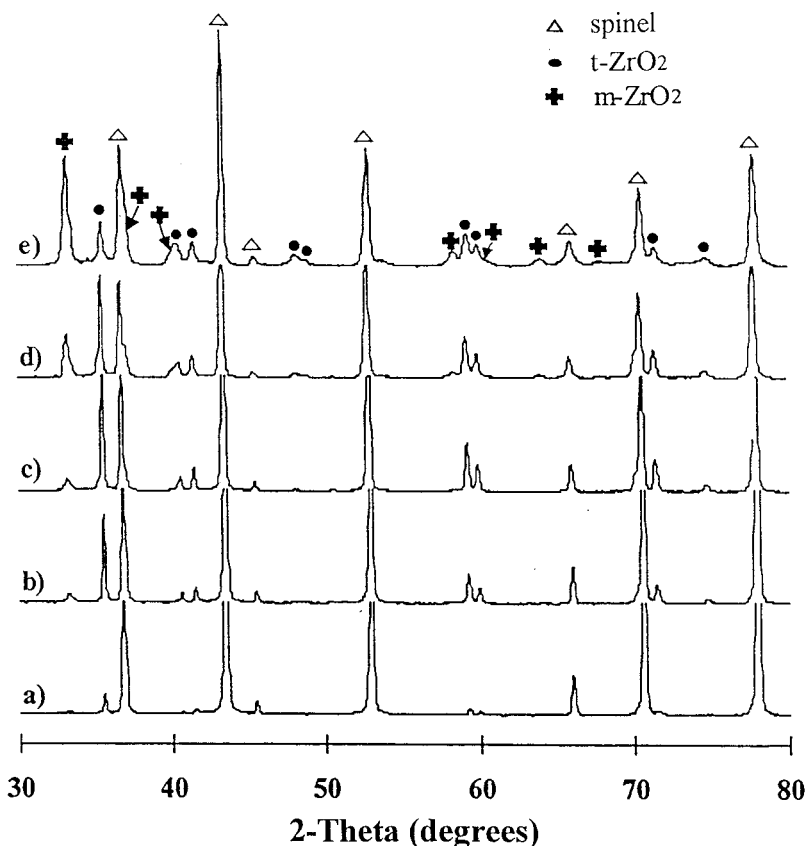


Fig. 3. XRD patterns of the hot-pressed $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites (A specimens) (a) A1, (b) A5, (c) A10, (d) A20, and (e) A30.

attempt to evaluate the average size and size distribution of the ZrO_2 particles in the powders. It seems that no ZrO_2 particles are dispersed in the intragranular position in the matrix.

3.2. Hot-pressed composites

Analysis of the XRD patterns of the BM specimens reveals that the only detected phases are the spinel, t-ZrO_2 , and m-ZrO_2 . MgO is no longer present, indicating that the Mg^{2+} ions have reintegrated with the spinel lattice during hot pressing. Thus, the matrix of the BM dense specimens is the stoichiometric spinel. Al_2O_3 is not detected in the XRD patterns of the A compounds (Fig. 3), indicating that the Al^{3+} ions have diffused into the spinel lattice during hot pressing. The resulting oxide matrix is thus an aluminum-rich spinel, the formula of which is $\text{Mg}_{1-3y}\square_y\text{Al}_{2+2y}\text{O}_4$. According to the elemental analysis performed on the A0 powder (ca. 6 mol% excess Al_2O_3), one can estimate that y is close to 0.03, leading to the formula $\text{Mg}_{0.91}\square_{0.03}\text{Al}_{2.06}\text{O}_4$. In contrast to what has been observed for the powders, both t-ZrO_2 and m-ZrO_2 are present in the hot-pressed materials, except for BM1 and A1, in which only t-ZrO_2 was detected. The proportion of t-ZrO_2 (Table 1) slightly decreased to a

Table 1
Some characteristics of the $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ hot-pressed specimens

Specimen ^a	d_r	t-ZrO ₂	\varnothing_s	\varnothing_z
BM0	96.2	—	1.4	—
BM1	96.5	100	0.8	n-m ^b
BM5	95.7	84	0.8	0.19
BM10	98.3	89	0.8	0.25
BM20	96.9	87	0.8	0.36
BM30	96.7	48	0.8	0.44
A0	95.5	—	0.3	—
A1	95.7	100	0.3	n-m
A5	96.6	88	0.3	0.35
A10	95.8	89	n-m	0.37
A20	96.4	60	0.2	0.42
A30	94.8	19	n-m	0.44

d_r : relative density; t-ZrO₂: proportion (%) of tetragonal zirconia with respect to the total amount of ZrO₂; \varnothing_s and \varnothing_z : average size (μm) of the spinel grains and of the ZrO₂ particles, respectively.

^a BM and A denote specimens issued from hot-pressing of ball-milled and attrited powders, respectively, and the number indicates the ZrO₂ content in wt%.

^b n-m: not measured.

value close to 85% for BM5, BM10, and BM20, and sharply decreased upon further addition of ZrO₂ (48% for BM30). A similar evolution is observed for the A composites, but it is noteworthy that the sharp decrease of the t-ZrO₂ proportion takes place for a lower ZrO₂ content (60% for A20). The m-ZrO₂ particles are formed owing to the t \rightarrow m phase transformation occurring for the larger ZrO₂ particles upon cooling from the hot-pressing temperature. Thus, the increasing proportion of m-ZrO₂ upon the increase in the total amount of ZrO₂ reflects the growth of the ZrO₂ particles. Their gathering at the matrix grain junctions is easier when these grains are smaller (A specimens). The hypothesis that polishing could have provoked the t \rightarrow m phase transformation of ZrO₂ particles located at the surface of the materials was ruled out, because it has been checked that the proportion of m-ZrO₂ is similar in the unground, 6 μm ground, and silica-polished specimens.

The main characteristics of the hot-pressed materials are presented in Table 1. The relative density (d_r) ranges between 94.8 and 98.3. In contrast to other results [4,5], which indicate that the densification of MgAl₂O₄ is favored by the addition of ZrO₂, there is no correlation between d_r and the total ZrO₂ content. However, the present specimens were hot pressed, giving similar relative densities for the spinels and the ZrO₂-MgAl₂O₄ composites ($d_r > 94.8\%$), whereas the spinel sintered in air without applying a charge [4,5] were poorly densified ($d_r < 85\%$), the more so when it is aluminum-rich [12]. Except for BM10, which has a higher d_r than any other present specimen (98.3%), there are no significant differences in d_r between the BM and A materials.

The SEM images of the etched surfaces (Fig. 4) show that the spinel grain size (\varnothing_s in Table 1) is larger in the BM composites (ca. 0.8 μm) than in the A specimen (0.3 μm). This reflects the difference in grain size in the corresponding powders. These images also confirm that the ZrO₂ particles are located at the grain boundaries or grain junctions of the matrix (Fig. 4a). The average grain size of the spinel grains (\varnothing_s) is smaller for the BM composites

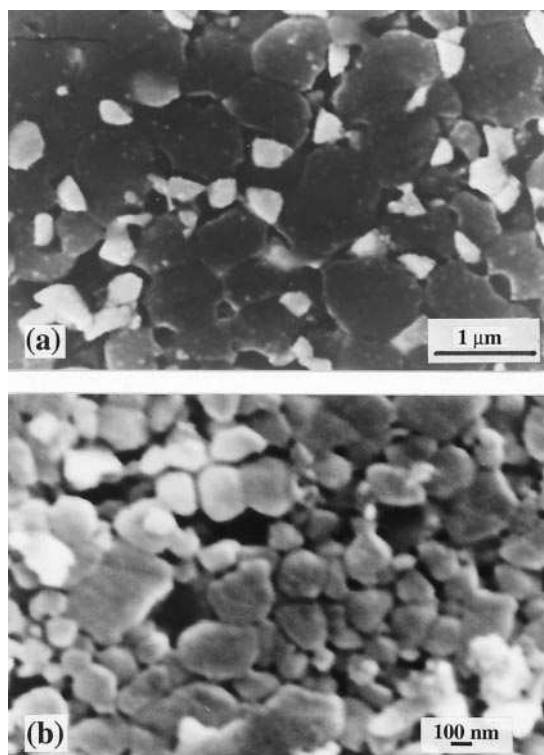


Fig. 4. SEM images of the etched surface of some hot-pressed $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ composites (a) BM20, and (b) A5.

(ca. $0.8\ \mu\text{m}$) than for BM0 ($1.4\ \mu\text{m}$), showing that the presence of ZrO_2 particles inhibits the growth of the matrix grains upon hot pressing. On the contrary, the presence of ZrO_2 particles has no or very little influence on the average size of the spinel grains ($0.2\text{--}0.3\ \mu\text{m}$) for the A specimens. One may note that it has been difficult to reveal the grain boundaries of the A specimens. A treatment in H_3PO_4 that is too long leads to the destruction of the smaller matrix grains ($<0.1\ \mu\text{m}$), whereas a treatment that is too short does not enable one to reveal the grain boundaries. Numerous tests performed on A10 using different durations failed and thus \varnothing_s has not been measured for this composite.

The SEM backscattered images (BEI) of the polished surface of the composites (Fig. 5) show the ZrO_2 particles (appearing as white areas on a dark background) dispersed at the grain boundaries and grain junctions of the spinel matrix. Very few ZrO_2 particles are observed in BM1. In BM5 (Fig. 5a) and BM10, the dispersion of the ZrO_2 particles is homogeneous and their shape is quite isotropic. Similar results have been obtained for A5 (Fig. 5d) and A10 specimens. For BM20 and BM30 (Fig. 5b and c), it is observed that some gathering at spinel grain boundaries produces ZrO_2 particles with anisotropic shapes. In contrast, more ZrO_2 particles have kept an isotropic shape in A20 and A30 (Fig. 5e and f), but they are larger than in BM20. The size distribution of the ZrO_2 particles in the BM and A composites (Fig. 6) was obtained from the measurement of at least 300 particles on the SEM negatives. The average size (\varnothing_z) of the ZrO_2 particles increases from 0.18 to $0.44\ \mu\text{m}$ in the BM materials and from 0.35 to $0.45\ \mu\text{m}$ in the A composites with an increasing total

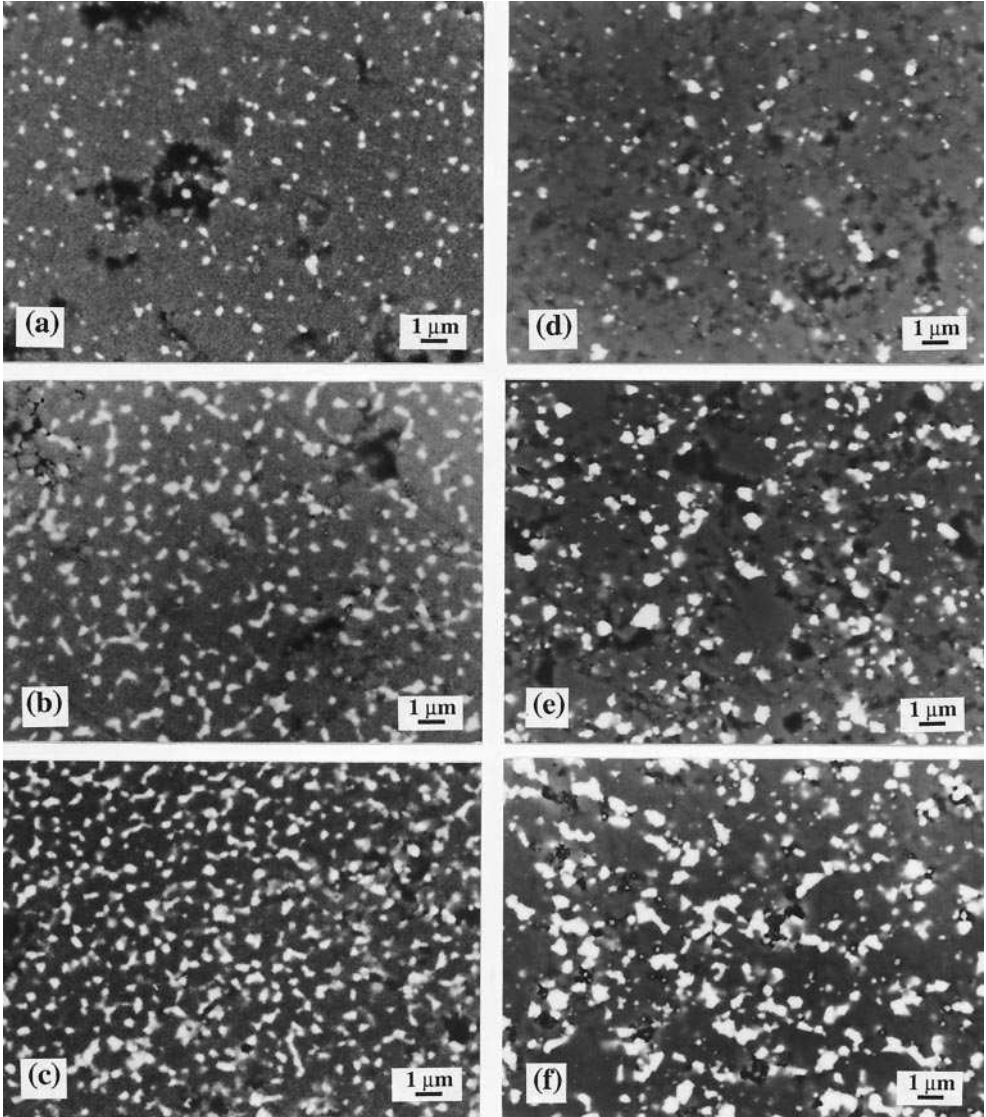


Fig. 5. SEM back-scattered images (BEI) of the polished surface of the hot-pressed ZrO_2 - MgAl_2O_4 composites (a) BM5, (b) BM20, (c) BM30, (d) A5, (e) A20, and (f) A30.

amount of ZrO_2 from 5 to 30 wt% (Table 1). For a given ZrO_2 content, the size relative to the maximum of the distribution profile is similar in both cases, but \varnothing_z is higher for the A composites. Indeed, a shoulder appears on the high-size side of the distribution profile, indicating the presence of larger ZrO_2 particles ($>0.5 \mu\text{m}$), which results in a higher average particle size. The presence of such large particles arises from the gathering of some ZrO_2 particles at spinel grain junctions. Indeed, this phenomenon is more pronounced in the A composites than in the BM composites, because the spinel grains are much smaller (\varnothing_s in Table 1) in the former. These results are in good qualitative agreement with the evolution of

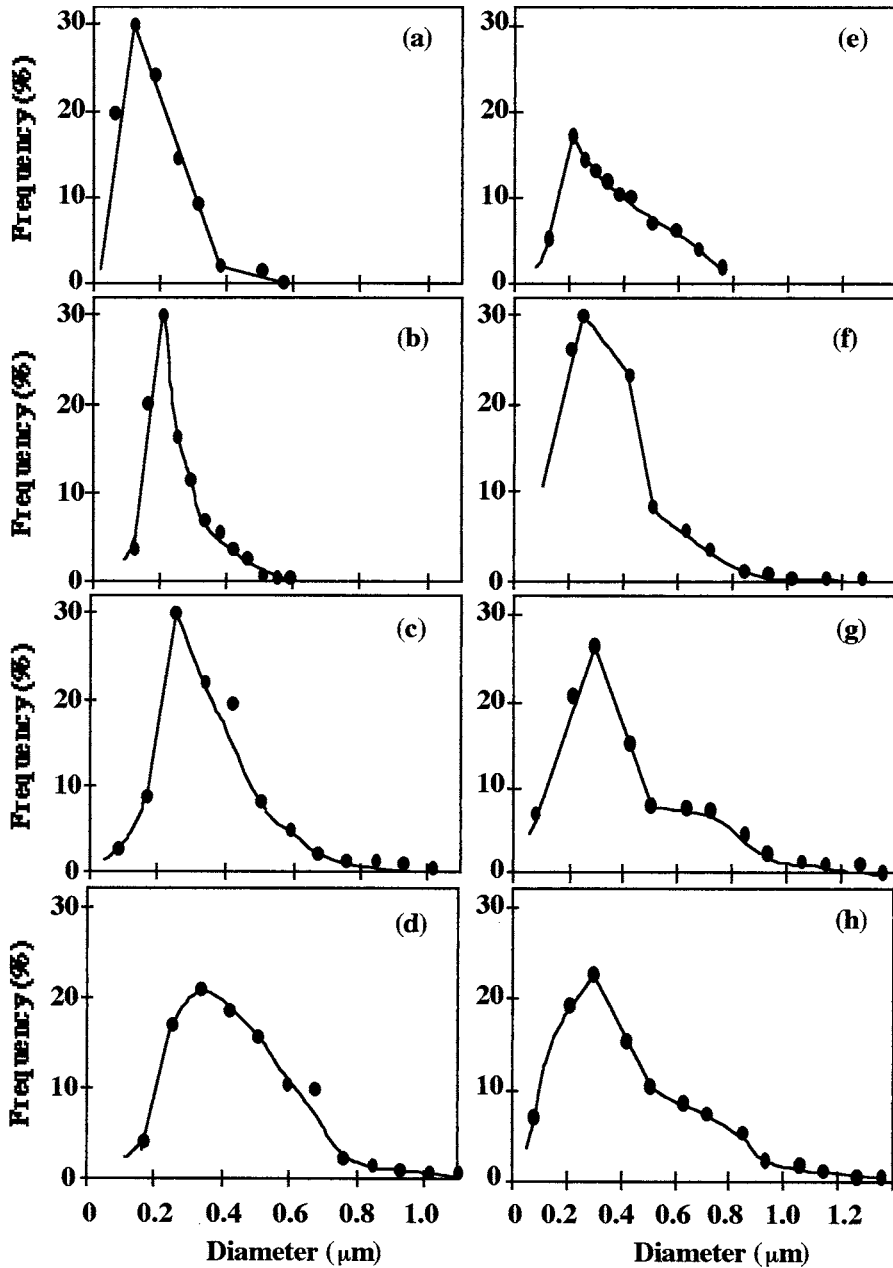


Fig. 6. Size distribution (in number) of the ZrO_2 particles in the hot-pressed ZrO_2 - $MgAl_2O_4$ composites (a) BM5, (b) BM10, (c) BM20, (d) BM30, (e) A5, (f) A10, (g) A20, and (h) A30. The solid lines are guides for the eye.

the proportion of m - ZrO_2 as deduced from the X-ray diagrams. SEM images of polished materials at a lower magnification also showed some differences in the residual porosity between BM and A specimens. In the BM ones, the pores are generally larger, less numerous, and often with more isotropic shapes than those of the A specimens. Indeed, in the latter

composites, the anisotropic pores are located between agglomerates, which, being too hard, are probably insufficiently crushed upon hot pressing.

4. Conclusions

It has been shown that MgAl_2O_4 and x wt% ZrO_2 - MgAl_2O_4 ($1 \leq x \leq 30$) composite powders can be readily prepared by the urea combustion route. This method is cost effective and suitable for scaling up. The powders are further ground by either ball milling or attrition to refine the grain size. The ZrO_2 particles are small enough to retain the tetragonal form. In dense materials prepared by hot pressing, the spinel matrix grains are submicronic in size. The ZrO_2 particles are homogeneously dispersed at the grain junctions of the matrix and their average size increases from less than $0.20 \mu\text{m}$ to ca. $0.45 \mu\text{m}$ upon increasing the content of ZrO_2 . The formation of monoclinic ZrO_2 particles (0.2 – $0.45 \mu\text{m}$) proceeds accordingly, being easier in the materials with the finer matrix grain size (ex-attrition). Such ZrO_2 - MgAl_2O_4 composites may be of interest for superplastic forming, and present improved mechanical characteristics compared to pure MgAl_2O_4 .

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