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Preparation and Characterization of a Dispersion Toughened Ceramic for Thermomechanical Uses (ZTA). Part I: Material Preparation. Characterization of Microstructure

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Abstract

Zirconia toughened alumina (ZTA) materials containing increasing amounts of zirconia (5–45 vol.%) and yttria (0–3 mol% zirconia) were prepared from commercial ceramic powders by different techniques of homogenization, shaping and sintering. The powder mixtures were homogenized by a chemical method (addition of dispersing agents at fixed pH), by a mechanical method (attrition milling) and by combining the two methods. The materials were formed and sintered following two ways:

(i) Shaping by isostatic pressing or slip casting, followed by pressureless sintering.
(ii) Hot uniaxial pressing.

The physical, crystallographical and microstructural properties of the materials prepared following these different techniques are compared.

Aluminiumoxidwerkstoffe, die mit Zirkonoxidpartikeln (5–45 Vol.%) oder Zirkonoxid–Yttriumoxidpartikeln (bis 3 mol% Yttriumoxid) verstärkt sind (ZTA), wurden ausgehend von handelsüblichen Keramikpulvern mittels unterschiedlicher Misch-, Form- und Sintertechniken hergestellt. Die Pulvermischungen wurden entweder mit einem chemischen Verfahren (Zugabe eines Dispersionsmittels bei konstantem pH-Wert) oder einem mechanischen Verfahren (Attritormahlung) oder einer Kombination aus beiden Verfahren hergestellt. Die Werkstoffe wurden dann auf zwei unterschiedlichen Wegen geformt und gesintert:

(i) Isostatisches Pressen oder Schlickerguß und druckloses Sintern.
(ii) Heißpressen.

Die physikalischen, kristallografischen und mikrostrukturellen Eigenschaften dieser Werkstoffe, die mit den unterschiedlichen Herstellungsverfahren produziert wurden, werden miteinander verglichen.

Des alumines renforcées par des particules de zircone (ZTA) (de 5 à 45% en volume) stabilisée à l'oxyde d'yttrium ou non ont été préparées à partir de poudres commerciales par différentes techniques de mélange, de mise en forme et de frittage. Les mélanges de poudre ont été homogénéisés par une méthode chimique (addition d'agents dispersants à pH donné), une méthode mécanique (broyage par attrition) ou par une combinaison des deux méthodes. Les

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matériaux ont été mis en forme et frittés selon deux processus:

(i) Pressage isostatique ou coulage en barbotine et frittage sans pression.

(ii) Pressage uniaxial à chaud.

Les propriétés physiques, cristallographiques et microstructurales des matériaux obtenus à l'aide des différentes techniques sont comparées.

1 Introduction

Among the different works devoted to the enhancement of the mechanical properties and reliability of high-performance ceramic materials, the most promising results are obtained by the synthesis of composite materials made of a ceramic matrix and a second phase: long or short fibers, whiskers, particles.[1] Dispersion of fibers can lead to considerably improved fracture energy values according to the nature of the fibers and the composition of the interface between the fibers and the matrix,[2] but these materials are most often not isotropic and are difficult to sinter without any damage to the fibers. The use of short fibers or whiskers is a promising alternative, and extensive work is being done today on the effect of whiskers content, aspect ratio and interface characteristics.[3] Polyphase materials containing dispersed ductile or brittle particles can be obtained from powder technology. It is found that the important strength-controlling factors include the thermal expansion coefficient of the two phases, the elastic properties of the two phases, and the volume fraction and the particle size of the dispersed phase.[4] Best results are obtained with metastable particles which exhibit some phase transformation: ZrO_2, HfO_2, quartz; in the case of ZrO_2 particles (or precipitates) in ceramic matrices improved fracture properties, especially fracture toughness (K_{Ic}), can be observed.[5,6]

However, previous work shows that significant strengthening can be achieved only by optimized dispersion of the second phase and a close control of the zirconia particle size, which must be maintained close to the critical transformation size.[7,8]

The objective of this study was to develop a processing method adapted to the fabrication of high-performance zirconia toughened alumina (ZTA) materials. The first part of this paper is devoted to the material preparation: powder mixing, shaping, sintering, physical and microstructural characterization of sintered materials. The second part is concerned with mechanical characterization and the study of toughening mechanisms.

2 Experimental Procedure

The mixing of alumina (RC172DBM, The Reynolds Company, USA, mean diameter = 0·5 μm), zirconia (UPH 'V', Criceram, France, mean diameter = 0·4 μm) and yttria (Ceramic Grade, Rhône-Poulenc, France, mean diameter = 2 μm after attrition milling) powders in order to allow the production of the fine and homogeneous zirconia dispersion was performed using three methods.

(a) A vigorous mechanical milling leading to the breakage of agglomerates. Compositions of up to 45 vol.% ZrO_2 (unstabilized or stabilized by 3 mol% Y_2O_3) were prepared by attrition milling in water using zirconia balls and a PVC vessel. The grinding time varied up to 18 h (typically 4·5 h). PVA was added as a binder to the suspensions before spray drying. Part of the resulting granulated powder was isostatically pressed (400 MPa) to a green density of 60%, debinded and pressureless sintered in air at 1600°C for 2 h. The other part was uniaxially pressed (400 MPa) into pellets which were debinded and hot pressed (30 MPa) in graphite dies at 1500°C for 15 min under vacuum.

(b) Giving to each particle the same surface charge, sufficiently high to avoid agglomeration due to Van der Waals attraction so that moderate stirring leads to a good dispersion.[9] Al_2O_3, ZrO_2 and Y_2O_3 slurries were prepared at different pH values. The deflocculation of the suspensions was studied by the measurement of the agglomeration (Sedigraph technique) as well as the electrokinetic potential (Riddick's zetameter or electrophoresis mass transfer analyser, EMTA). As an example, sedimentation curves of zirconia at different pH, zeta potential of alumina (EMTA) and yttria (zetameter) as a function of pH are given in Figs 1, 2 and 3, respectively.

The EMTA method consists of adding a powder suspension to a small cell with a small hole and placing it in a larger cell also filled with the same powder suspension. After applying an electrical field between two electrodes located inside the internal and external cells, the weight gain or loss of the small cell is measured and related to the surface charge of migrating particles. This method allows the measurement of the zeta potential of suspensions with high dry matter content (~60–70 wt%).

In contrast, Riddick's zetameter method does not

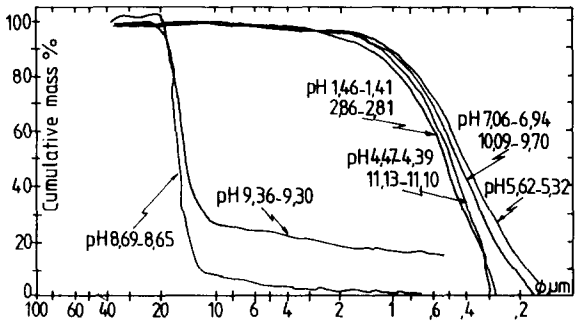

Fig. 1. Sedimentation curves of UPH 'V' zirconia at different pH.

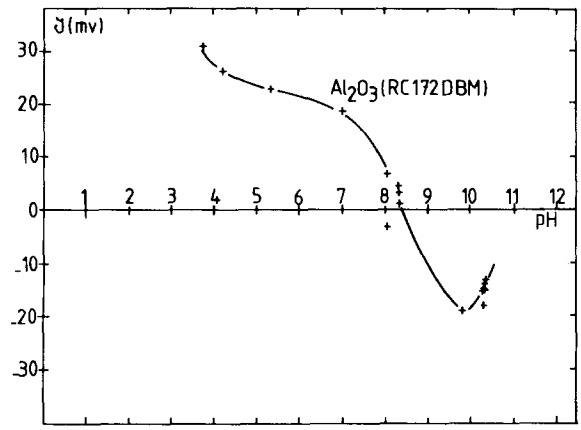

Fig. 2. Potential of RC172DBM alumina as a function of pH (EMTA).

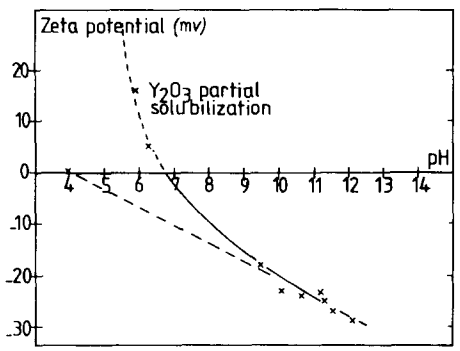

Fig. 3. Potential of yttria (Rhône-Poulenc) as a function of pH (zetameter).

enable work to be done with highly concentrated suspensions. The measurement principle consists of determining the migration rate of particles in suspension through a narrow glass tube during application of an electrical field. This last method allows the measurement of the particle mobility for a very small amount of powder and was used for the study of high cost powders (zirconia and yttria).

Figure 4 shows pH values at which good deflocculation is reached for the different powders as a function of the described test techniques (dashed lines correspond to de-agglomerated suspensions (sedigraph method) or suspensions for which the

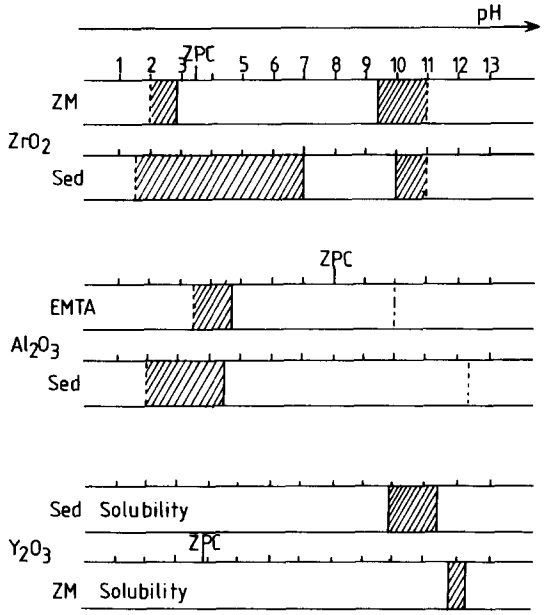

Fig. 4. Deflocculation pH values of Al_2O_3, ZrO_2 and Y_2O_3 slips as a function of different techniques.

repulsion potentials $[\zeta] > 30\,mV$ (zetameter or EMTA methods).

It can be noted that two pH regions seem favorable for zirconia powder dispersion: acid and basic pH. The alumina powder is better dispersed in acid whereas yttria powder presents a nonnegligible solubility. Therefore, it seems preferable to prepare slurries of basic pH (10–11) and to increase the surface charge of suspended alumina grains at this pH value by adding some complexing agents.

The optimum amount of Al complexing agent was determined according to the ζ potential, the agglomerate dispersion, and the rheological (viscosity, Bingham flow limit) and electrochemical properties of the slurry (resistance to polarization, amount of free O_2). Unfortunately, the electrokinetic potential of the alumina suspension was too low for it to have a stable slurry. For this reason, an optimum amount of a surfactant determined by the same procedure as previously was used in addition to the complexing agent. The good deflocculation of zirconia and yttria slurries was confirmed after the addition of the same amount of surfactant.

Al_2O_3, ZrO_2 and Y_2O_3 slurries containing respectively 75, 40 and 50% dry matter were prepared separately in the determined conditions. After stabilization, they were mixed together in the required weight fractions in order to obtain the desired compositions: up to 15 vol.% unstabilized ZrO_2, 10 and 15 vol.% of ZrO_2 stabilized with 1 to 3 mol% Y_2O_3, respectively. Then, they were vibro-energetically milled using alumina cylinders and plastic vessels and slip cast in plaster molds. The

green products were dried for several days. A portion of each was pressureless sintered in air at 1550°C for 2 h, and the other part was dry milled. The resulting powders were sieved and hot pressed (30 MPa) in graphite dies at 1500°C for 15 min under vacuum.

(c) A combination of these two dispersion routes. The powder dispersion procedure included two steps: firstly, preparation of separate slips, showing the same rheological behavior; secondly, mixing and vigorous attrition milling for 6 h. After slip casting or compaction of spray-dried powders, pressureless sintering (1550°C, 2 h) and hot pressing (1500°C, 15 min, 30 MPa) were performed. The compositions prepared by slip casting contained increasing zirconia up to 15 vol.%, and, different stabilizer amounts up to 3 mol% were added to the 15 vol.% zirconia composition. The spray-dried isostatically pressed materials contain up to 20 vol.% of unstabilized zirconia, and 1–3 mol% of yttria was added to this composition. A 45 vol.% zirconia (stabilized with 3 mol% Y_2O_3) composition was also prepared.

3 Results

3.1 Physical and crystallographic characterization

The densification level expressed by the percentage of theoretical density ($\%\rho_{th}$) and the relative tetragonal zirconia ratio (T_r) for all the prepared materials are presented in Table 1. The bulk density was measured by Archimedes' method and the relative tetragonal zirconia ratio was determined by X-ray diffraction following the corrected Porter & Heuer's relation (eqn 1):[10]

$$T_r = 1 - \frac{2{\cdot}315 I_{(11\bar{1})}}{I_{(111)t} + 2{\cdot}315 I_{(11\bar{1})m}} \quad (1)$$

where $I_{(11\bar{1})m}$ and $I_{(11\bar{1})t}$ are respectively the intensities of monoclinic $(11\bar{1})$ and tetragonal $(11\bar{1})$ lines.

It can be noted about the densification level that:

(i) The slip-cast materials generally present a lower densification level than ones prepared by isostatic pressing.

Table 1. Physical and crystallographic characteristics of various sintered materials

A. Mechanical homogenization — *isostatic pressing*

Composition	*Milling time (h)*	*Pressureless sintering*		*Hot pressing*	
		ρ_{th} (%)	T_r (%)	ρ_{th} (%)	T_r (%)
A10Z3Y	4·5	98·8	99	98·8	99
A15Z3Y	2·25	99·3	99	99·3	99
A15Z3Y	4·5	99·8	99	99·8	99
A15Z3Y	9	100	99	100	99
A15Z3Y	18	100	99	100	99
A20Z3Y	4·5	99·8	99	99·8	99
A45Z3Y	4·5	100	100	100	100

B. Electrochemical repulsion — *slip casting*

Composition	*Pressureless sintering*		*Hot pressing*	
	ρ_{th} (%)	T_r (%)	ρ_{th} (%)	T_r (%)
A5Z	98·3	95	99·8	94
A10Z	98·6	57	100	76
A15Z	99·5	19	100	58
A10Z1Y	93·5	82	100	100
A10Z2Y	90·4	92	100	100
A10Z3Y	95·4	95	100	100
A15Z1Y	96·7	64	100	79
A15Z2Y	95·8	93	100	96
A15Z3Y	96·0	96	100	97

C. Combined dispersion method

(a) slip casting

Composition	*Pressureless sintering*		*Hot pressing*	
	ρ_{th} (%)	T_r (%)	ρ_{th} (%)	T_r (%)
A5Z	98·3	96	99·8	100
A10Z	98·3	50	100	88
A15Z	99·1	27	100	40
A15Z1Y	99·3	41	100	65
A15Z2Y	98·4	74	100	100
A15Z3Y	98·6	89	100	100

(b) isostatic pressing

Composition	*Pressureless sintering*		*Hot pressing*	
	ρ_{th} (%)	T_r (%)	ρ_{th} (%)	T_r (%)
A5Z	99·0	98	100	96
A10Z	98·8	48	100	82
A15Z	99·3	20	100	23
A20Z	100	15	100	7
A20Z1Y	99·5	33	100	30
A20Z2Y	99·5	95	100	97
A20Z3Y	99·1	98	100	100
A45Z3Y	99·6	96	100	99

(ii) The combined dispersion method allows an increase of the densification level of slip-cast materials.

(iii) All the hot-pressed materials present a high densification level which is close to the theoretical density (ρ_{th}).

It can be noted about the relative tetragonal zirconia content that:

(i) The relative tetragonal ratio (T_r) is close to 100% for all the mechanically homogenized compositions prepared by isostatic pressing, whereas the relative tetragonal ratio (T_r) depends on the zirconia and yttria content for the other materials.

(ii) For these latter materials, the addition of yttria allow an increase of the zirconia content (up to 45 vol.%) without a decrease of the relative tetragonal zirconia ratio occurring. The retention of tetragonal phase is maximum for 3 mol%.

3.2 Microstructural and thermal characterization

The microstructural characterization was only carried out on the materials homogenized by the combined dispersion method. Moreover, a dilatometric analysis (Netzsch dilatometer type 402 ED) was also performed on the pressureless sintered materials (specimen size: $20 \times 8 \times 8\,mm^3$). The dilatometric curves are presented in Fig. 5. The thermal and microstructural characteristics are listed in Table 2.

The dilatometric analysis cycle was as follows: a soaking time of 1 h at 1300°C with a rise and drop rate of 5°/min. For the four tested compositions, a shrinkage due to the monoclinic→tetragonal zirconia transformation was observed. The final transformation temperature (A_f) is in the same range for the four materials, whereas the starting inverse transformation (t→m) temperature (M_s) decreases

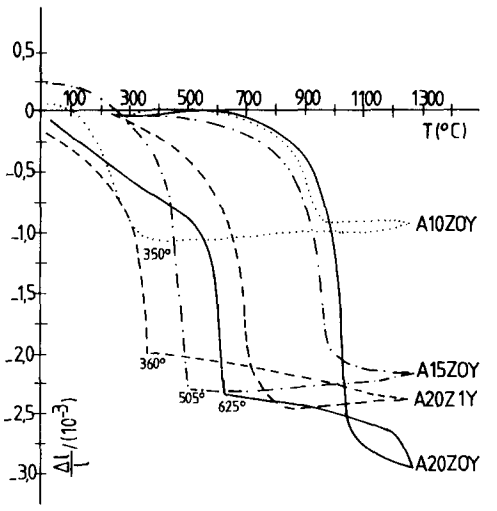

Fig. 5. Shrinkage of various ZTA materials versus temperature.

when the zirconia content decreases because of the grain size reduction and when a stabilizer (yttria) is added.

The microstructural analysis was carried out on SEM pictures of polished and thermally etched surfaces. Examples of typical microstructures obtained for pressureless sintered and hot-pressed materials are presented in Figs 6–9. The determination of the grain size distribution expressed in volume (about 1000 grains) has allowed the deduction of the average diameters (D) of zirconia and alumina grains and the critical transformation diameter (d_c), as the relative tetragonal zirconia ratio (T_r) is known. The evolution of grain diameter values for the pressureless sintered (PS) and hot-pressed (HP) materials versus the zirconia and yttria content is presented in Figs 10 and 11.

It can be noted that, except for the hot-pressed materials A20Z, the alumina grain size decreases with zirconia content increase, which is a secondary effect of particle toughening in a matrix, as has been reported by Lange[11] and should contribute to enhanced mechanical properties. Simultaneously,

Table 2. Thermal and microstructural characteristics of materials prepared from spray-dried powders

Composition	*Isostatic pressed and pressureless sintered materials*					*Hot pressed materials*		
	M_s (°C)	A_f (°C)	$\bar{D}_{Al_2O_3}$ (μm)	$\bar{D}_{ZrO_2}$ (μm)	d_c (μm)	$\bar{D}_{Al_2O_3}$ (μm)	$\bar{D}_{ZrO_2}$ (μm)	d_c (μm)
A5Z	—	—	1·9	0·6	1·0	1·6	0·6	1·0
A10Z	350	970	1·6	0·7	0·7	1·2	0·6	0·8
A15Z	505	1 000	1·3	0·8	0·6	1·0	0·6	0·5
A20Z	625	1 050	1·3	0·9	0·6	1·3	0·9	0·6
A20Z1Y	360	800	1·2	0·7	0·6	1·0	0·7	0·6
A20Z2Y	—	—	1·2	0·6	0·9	0·9	0·5	0·9
A20Z3Y	—	—	1·2	0·6	0·9	0·9	0·6	—
A45Z3Y	—	—	1·0	0·7	1·1	0·8	0·7	1·2

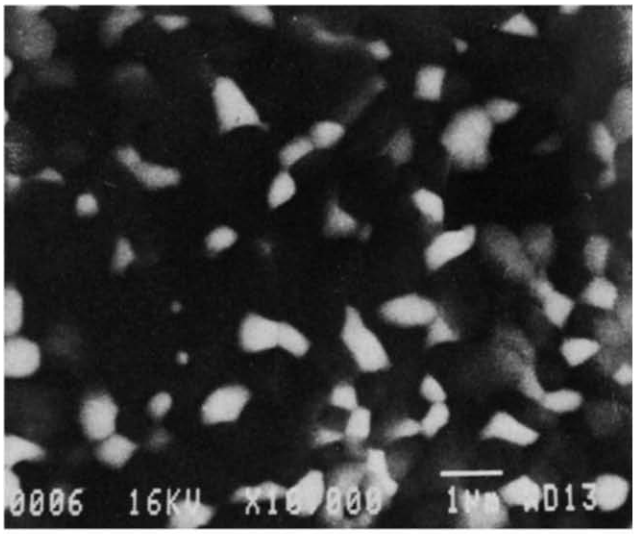

Fig. 6. Typical microstructure of pressureless sintered material containing 15 vol.% of zirconia (A15Z-PS).

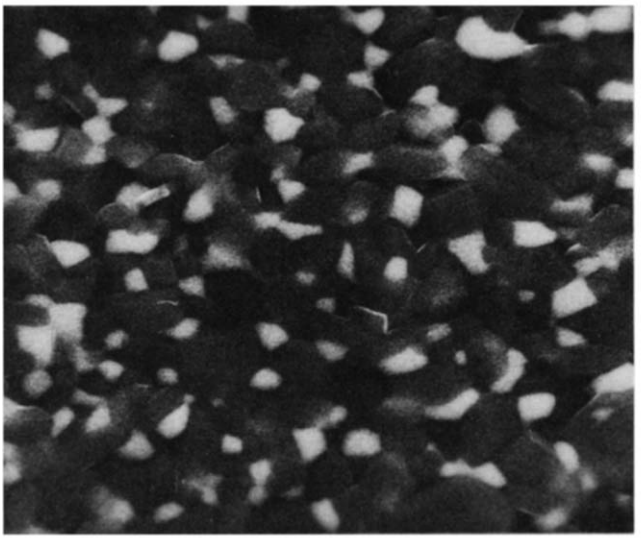

Fig. 7. Typical microstructure of hot-pressed materials containing 15 vol.% zirconia (A15Z-HP).

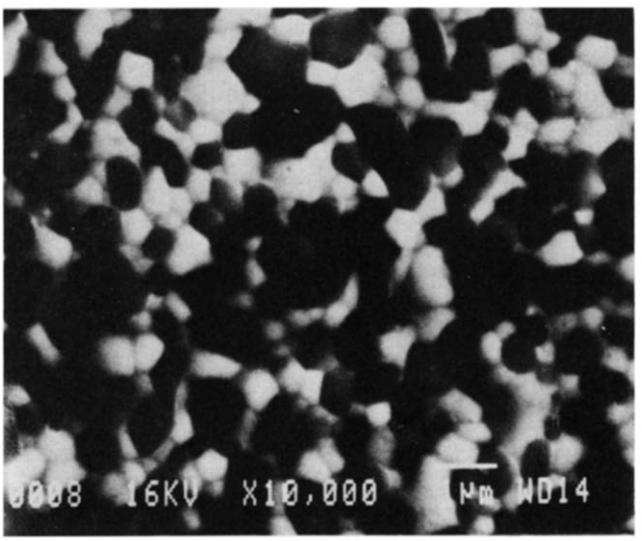

Fig. 8. Typical microstructure of pressureless sintered materials containing 45 vol.% of zirconia with 3 mol% Y_2O_3 (A45Z3Y-PS).

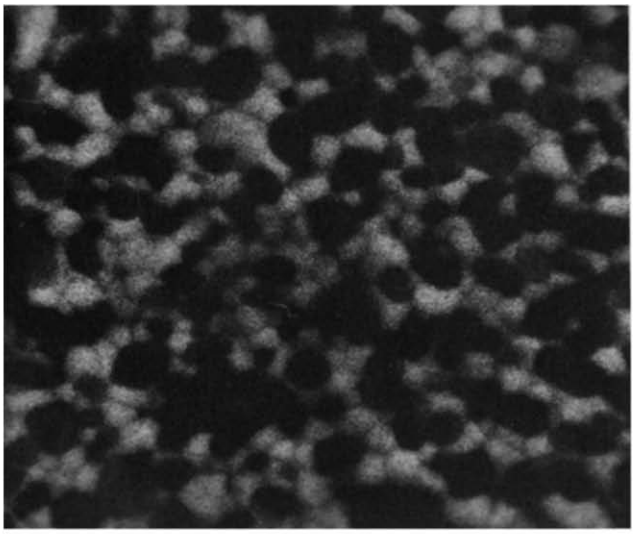

Fig. 9. Typical microstructure of hot-pressed materials containing 45 vol.% of zirconia with 3 mol Y_2O_3 (A45Z3Y-HP).

the zirconia grain size of PS materials increases, which involves a reduction of the relative tetragonal zirconia ratio. For the hot-pressed materials, this zirconia grain growth appears only for the composition containing 20 vol.% zirconia (Fig. 10).

The addition of Y_2O_3 allows the obtention of very high T_r values (up to 100% for 3 mol% Y_2O_3) because of an increase of the critical transformation size but also because of the decrease of the zirconia grain size. Concerning the alumina mean particle size, the addition of the stabilizer leads to a decrease of this parameter mainly for hot-pressed materials (Fig. 11).

When the microstructural parameters for PS and

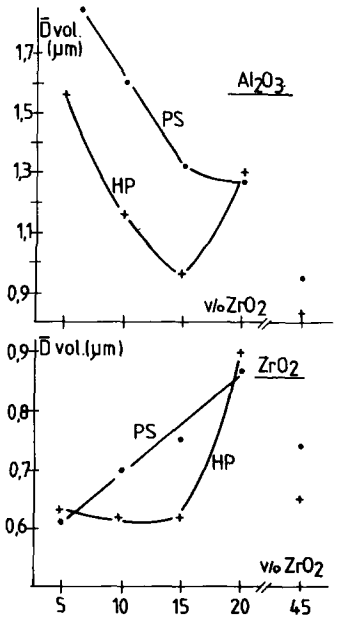

Fig. 10. Mean diameters of alumina and zirconia grains for pressureless sintered and hot-pressed materials versus zirconia content.

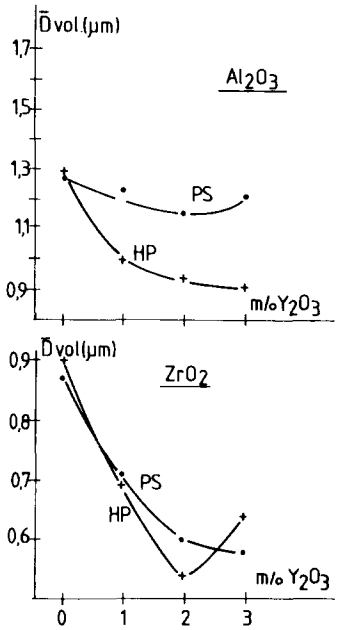

Fig. 11. Mean diameter of alumina and zirconia grain for pressureless sintered and hot-pressed materials versus yttria content.

HP materials are compared, it can be seen that, as expected, the hot-pressing technique allows reduction of the alumina and zirconia grain size (the zirconia agglomerate size in the green mixture being of about 0·6 μm). The critical transformation diameter (d_c) appears to be minimum for A15Z, this has to be correlated to the decrease of Young's modulus with zirconia addition together with a shape change of the embedded particles.

The homogeneity of the zirconia grain dispersion in the alumina matrix was evaluated for the pressureless sintered and hot-pressed material microstructures by an original method.[12] In few words, the method consists of measuring the distance between all zirconia grains and in classifying these values in what is called an interdistance matrix. Then, for a given inspection distance $(DI)_i$, this matrix is examined. When the interparticle distance is inferior to the inspection distance $(DI)_i$, the particles can be considered as forming an agglomerate, the diameter of which is computed (DA_i). The ratio of agglomerate diameter to inspection distance (RD_i), defined as the agglomeration factor, is calculated. Then, the inspection distance is increased and the analysis occurs again. This iterative mathematical procedure is illustrated in Fig. 12. The agglomerate presence is revealed from a maximum value of agglomeration factor versus inspection distance.

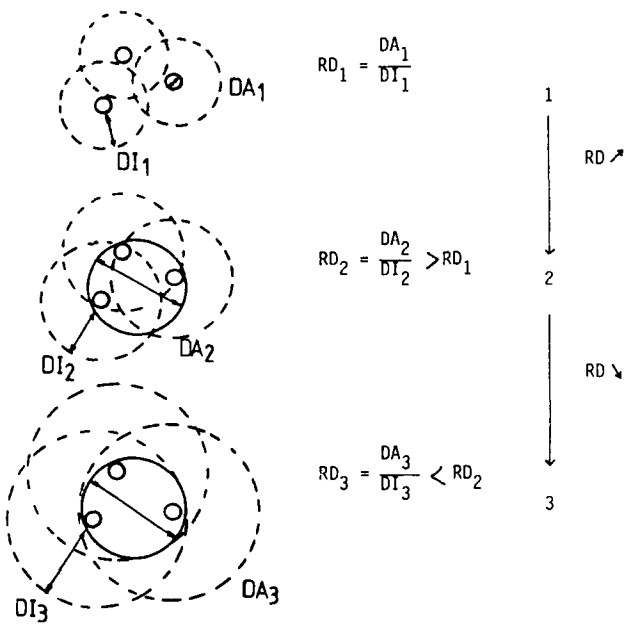

Fig. 12. Schematic presentation of the agglomerate revealing method.

Figures 13 and 14 present the values of the agglomeration factor versus the increasing inspection distance (DI) for various PS and HP materials respectively. The results show that clusters of particles occur when zirconia volume or yttria content increases (for the minimum inspection

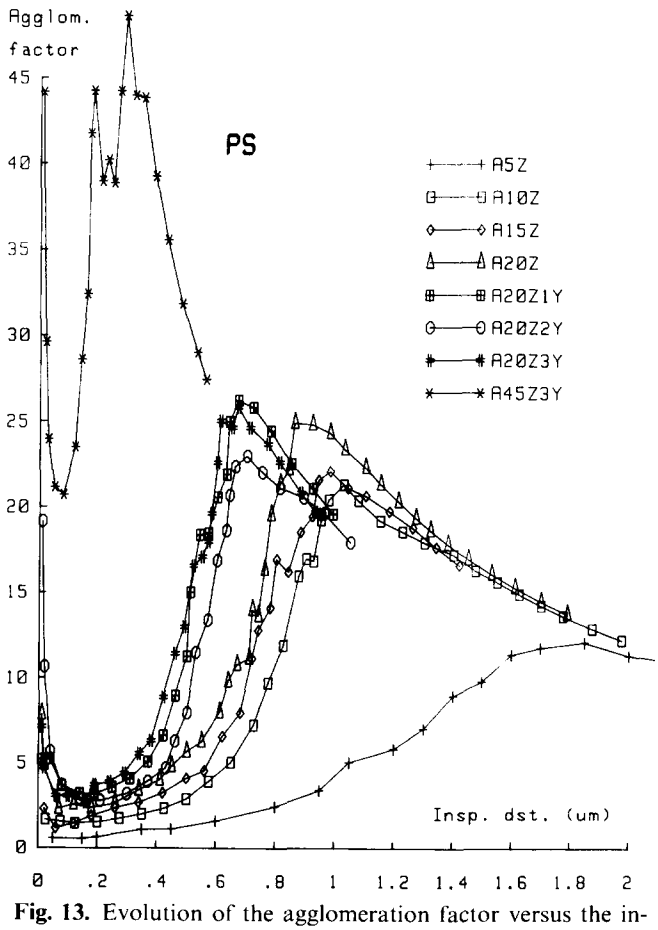

Fig. 13. Evolution of the agglomeration factor versus the inspection distance for various materials prepared by pressureless sintering.

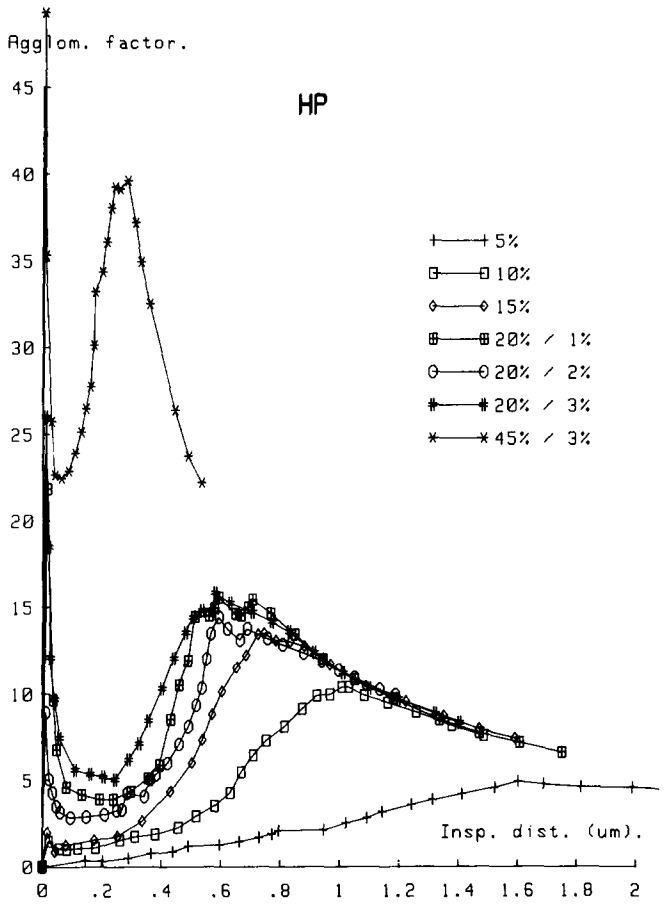

Fig. 14. Evolution of the agglomeration factor versus the inspection distance for various materials prepared by hot pressing.

distance: 0·01 μm). It must be noted that for HP materials, interparticle distance distributions are larger and the mean particle distances are smaller. Moreover, the agglomeration factor value (first peak at 0·01 μm) is generally higher for hot-pressed materials which implies higher agglomerate sizes.

From the microstructural examinations of the various prepared ZTA materials, it appears that a compromise has to be found concerning zirconia volume, in order to keep both the alumina and the dispersed phase particle sizes as low as possible. Moreover, the zirconia volume increase induces a tetragonal zirconia ratio decrease. However, a large tetragonal zirconia ratio can be obtained by yttria addition, which is favorable to the reduction of the zirconia grain growth.

4 Conclusion

A combined electrochemical and mechanical dispersion method leads to the fabrication of dense zirconia toughened alumina composites presenting a fine and homogeneous zirconia dispersion required for effective toughening of the alumina matrix. The addition of 3 mol% of yttria allows maintenance of a high tetragonal zirconia content because of a chemical stabilization of tetragonal zirconia and of a decrease of zirconia grain size.

As the hot-pressing technique impedes the grain coarsening, the hot-pressed materials present the finest microstructure mainly for the compositions with less than 20 vol.% of zirconia. The zirconia and alumina grain size vary from 0·5 to 0·9 μm and from 0·9 to 1·6 μm respectively following the composition. However, pressureless sintered materials also present a fine microstructure with submicronic zirconia grains (0·6 μm to 0·9 μm) and micronic alumina grains (1·0 to 1·9 μm).

In conclusion, these ZTA materials present all the microstructural characteristics necessary to obtain high mechanical performances. The addition of 3 mol% of yttria allows an increase of the zirconia content (up to 45 vol.%) without a decrease of the relative tetragonal zirconia ratio (T_r) occurring.

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