JOURNAL OF MATERIALS SCIENCE 24 (1989) 2711-2721

Fabrication and characterization of zirconia-toughened alumina obtained by inorganic and organic precursors

J. P. BACH, F. THEVENOT
Ecole des Mines, 42023 Saint-Etienne Cédex 2, France

In zirconia-toughened alumina (ZTA) the martensitic transformation of zirconia (tetragonal → monoclinic) is at the origin of toughening. If the zirconia particles have a mean grain size less than d_c', they remain tetragonal; if their size is between d_c' and d_c ($d_c > d_c'$), they are stress-induced transformed into the monoclinic form; if their size is larger than d_c, particles are transformed. We prepared ZTA using different precursors and compared their microstructures. The coprecipitation of aluminium and zirconium chlorides gives an hydroxide mixture. Thus the zirconium hydrate is amorphous, and the aluminium hydroxide structure varies with the precipitation temperature and pH values at the end of the neutralization. Alumina is mixed with zirconia obtained by gas-phase reaction. Zirconia is prepared by vaporization of zirconium chloride in an oxygen–hydrogen flame. Alumina powder is impregnated by a zirconium acetate solution. Zirconium acetate is thermally decomposed in a spray-dryer, then by calcination. The cohydrolysis of II Al-butoxide and IV Zr-propoxide was carried out in an alkaline solution. The hydrolysis pH (10 or 12) changes the grain size of the oxide powders. Mechanical property measurements and microstructural analysis allow a comparison of the different composites. The mean grain-size evolution differs according to the preparative route, and may be varied by different elaboration parameters. Fine microstructures were always observed. The mean grain size of dispersed zirconia being very small (near d_c'), we observed a little influence of transformation toughening. We noticed a large increase in rupture strength, while toughness was not noticeably improved.

1. Introduction

A more extensive use of ceramics materials needs a significant increase of their rupture toughness. Thus several solutions have been proposed [1], i.e. toughening by a second phase dispersion. Zirconia-toughened alumina (ZTA) may be used for wear and cutting applications [2]. Owing to the crystallographic properties of zirconia, the martensitic transformation (tetragonal → monoclinic) which takes place with a volume increase (> 3%) during cooling, induces a stress field in the alumina matrix. The resistance to crack growth propagation is favoured by dissipating the rupture energy [3].

Three toughening mechanisms are proposed [4–6].

(1) Microcracking: the crystallographic transformation which takes place only when the zirconia particle size is larger than a critical diameter (d_c), gives rise to microcracks appearing in the matrix, thus absorbing (or deviating) the crack energy.

(2) Stress-induced transformation toughening: at ambient temperature, zirconia particles, with particle size less than d_c, can be retained in the metastable tetragonal form. Most of these particles may be transformed as a crack is propagating: large tensile stresses are generated around the crack, especially ahead of the crack tip; these stresses release the matrix constraint on the tetragonal (t) zirconia particles and if large enough could result in a tensile stress of the particle, which will transform to monoclinic (m) form. The volume expansion developed in the particles creates a resultant compressive strain in the matrix which stops the crack propagation.

(3) Compressive surface layers, due to the t → m transformation of zirconia near the surface, allow an increase of the fracture strength of the ceramic.

In order to reap the benefits of these properties, the ceramic material must have a homogeneous microstructure with well-dispersed zirconia grains. An intimate mixture of the two powders may be obtained either by mechanical (grinding) or electrochemical (with a dispersive agent addition) routes [7].

Our purpose was the production of ZTA composites with the finest microstructures, in order to study the influence of the zirconia particle size on mechanical properties. We synthesized different alumina and zirconia powders, starting from several organic or mineral precursors. After hot-pressing densification, we studied the microstructures and the mechanical properties of the resulting ZTA composites.

0022-2461/89 $03.00 + .12

2. Preparation of metallic oxides from precursors

2.1. Aluminium hydroxide synthesis by halogenide precipitation

The metallic halogenide precipitation using base additions has already been widely studied. Several parameters influence the hydroxide species obtained [8]. The aluminium salt behaviour can only be explained by the presence of specific species in solution (Al^{3+} if $pH < 4$; AlO_2^- for $pH > 12$) [9]. Electrochemical measurements (pH, conductimetry) allow determination of three steps during the metallic hydroxide gel floculation [10]: hydrolysis, an olation mechanism (Al–OH–Al), and an oxolation mechanism (Al–O–Al).

More sophisticated experiments (light diffusion; infrared (IR), Raman and nuclear magnetic resonance (NMR) spectroscopies, etc) have allowed determination of the nature of the species in solution, thus explaining trihydrate formation from a gel with a smaller hydratation degree ($Al\,(H_2O)_6^{3+}$ in acid media;, or $Al(H_2O)_5(OH)^{2+}$ in basic media) [11].

The precipitation pH which depends on the nature and the concentration of the base used, is an important factor that strongly influences the nature and properties of the resulting precipitate [12–14]. Sato [15] has also shown that the base nature plays an important role in gel evolution:

$$\left.\begin{array}{l}\text{new amorphous aluminium}\\ \text{hydroxide gel}\end{array}\right\} \rightarrow \text{pseudo boehmite}$$

$$\rightarrow \left\{\begin{array}{l}\text{bayerite}\\ \text{hydrargillite}\end{array}\right.$$

The transformations occur on ageing of the precipitation solution.

The crystallographic nature of the gel is related to the nature and the content of the remaining impurities [16], which often depend on the solution pH. For low pH values, the positively charged gel is surrounded by foreign anions which are strongly bonded in the structure, thus inhibiting crystallization. For high pH values, the negatively charged gel repulses the rare foreign anions [17]. The crystallization speed of $Al(OH)_3$ is inversely related to the tendancy of the anionic impurity to enter the precipitate structure, i.e. the crystallization speed will be the lower the simpler is structure of the anionic inclusion [16].

2.2. Aluminium hydroxide synthesis from organic precursors

Dense transparent alumina pieces were fabricated by Yoldas [18, 19], and his research formed a basis for ultrafine and pure alumina powder preparation. The hydrolysis of a II-Al butoxide was followed by peptization which allowed a stable dispersion of the precipitate in order to form a sol. The study of the hydrolysis showed different steps of the transformation. Hydrolysis carried out at a temperature higher than 80° C produced boehmite, whereas at ambient temperature an amorphous monohydrate aluminium hydroxide was obtained. During the ageing of the solution, OR radicals are replaced by water, allowing the crystallization to occur. Beyond 80° C, a rapid liberation of OR groups occurs, and the bayerite structure crystallizes. If ageing takes place below 80° C, a slower process of dissolution–recrystallization allows bayerite formation. The alcohol content, present in the mother liquor, also influences the bayerite crystallization.

After stove drying, it is possible to determine the structure, by measuring the weight loss during calcination [20]: 15% weight loss for AlO(OH), 35% weight loss for $Al(OH)_3$.

An original hydrolysis technique allowed the fabrication of amorphous alumina powders, with a mean grain size of 1.5 μm [21]. The II-Al butoxide in alcoholic solution was hydrolysed, not by means of a water addition, but by the water formed by the alcohol dehydratation. This occurred during hypercritical drying autoclaving conditions. The control of gel precipitation in a homogeneous solution gave particles with a 0.1 to 0.2 μm diameter [22]. The thermal treatments which are necessary to the transformation into alumina did not modify the shape, but allowed a precipitate size decrease.

2.3. Sintering of oxides prepared from organic precursors

The nature of the starting hydroxide strongly influences the sintering behaviour of alumina. The trihydrate (bayerite) structure has sintering kinetics higher than that of the monohydrate (amorphous or boehmite). The water content, which is present during hydrolysis, plays an important role in the densification process. For example, if the water quantity is below the reaction stoichiometry, the hydrolysis is incomplete and a total densification cannot be reached [23].

The sintering temperature of alumina may be lowered by 300° C if the preparation conditions are optimized: temperature, hydrolysis pH and reactants content.

Fig. 1 shows the variation in density of pressureless sintered aluminas with sintering temperature, according to the production process (alkoxides) [24–28].

Little work has been carried out on the mechanical characterization of composites. However, Becher and co-workers [29–31] fabricated materials directly after gel elaboration, e.g. fibres, coatings or bulk pieces. A particular way of drying (either by casting in dialysis

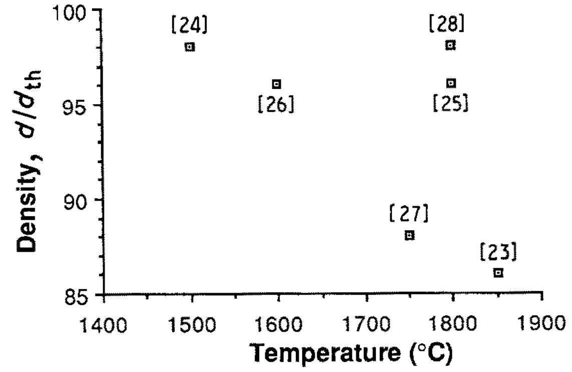


Figure 1 Variation of the densities, *d*, of alumina powders prepared from alkoxides with pressureless sintering temperature (from the literature).

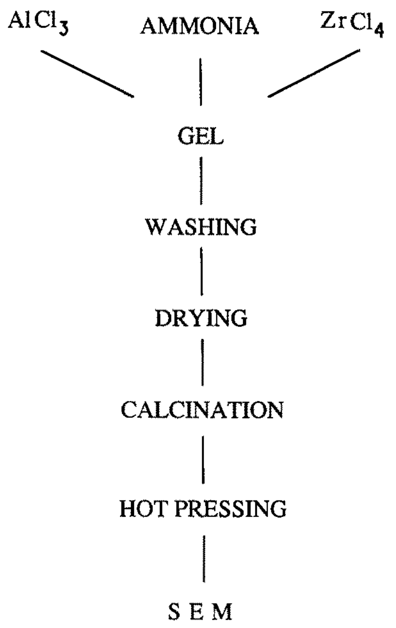


Figure 2 Flow sheet of fabrication of composite from metallic chlorides.

membrane, or into mercury), allows shrinkage-step controle. ZTA composites, with grain sizes of 5 μm for alumina, and less than 1 μm for zirconia, were produced. Powders were prepared by hydrolysis of both aluminium and zirconium alkoxides and then hot-pressed. The ZrO_2 contents were in the range 0.5 to 30 vol %, and depending on the respective composition, the zirconia grain size being included in the limits 0.5 to 2 μm, and that of alumina between 5 and 10 μm. An increase in both rupture energies γ_{IC} (for 10 vol %) has been observed.

3. Experimental procedure

3.1. Fabrication of composites from different precursors

3.1.1. Aluminium and zirconium chlorides

Using the preparation conditions already optimized with a pure alumina powder [32], we produced a mixture of two aluminium and zirconium oxides, starting from both metal chlorides (Fig. 2).

An aqueous solution of aluminium ($AlCl_3$, $6H_2O$; Riedel de Haën) and zirconium ($ZrCl_4$; Merck) chlorides was prepared, in aqueous media, using the following concentrations

$$[AlCl_3] + [ZrCl_4] = 0.6\,\mathrm{mol\,l^{-1}}$$

$$\frac{M_{ZrO_2}}{M_{Al_2O_3} + M_{ZrO_2}} = 0.1$$

The alkaline solution (ammonia, 4M) is used at ambient temperature in order to precipitate both aluminium and zirconium hydroxides. The ammonia addition is continued in order to reach different pH values for the end of neutralization, which correspond to different zeta potential values:

pH 7.5: |30 mV|; pH 10.5: |15 mV|; pH 9: ~0 mV [33]

TABLE I Characteristics of alumina–zirconia powders prepared from chlorides, after drying

	pH at end of neutralization		
	7.5	9	10.5
Structure	Amorphous	Boehmite	Bayerite
% Cl^-	2.2	2.6	1.3

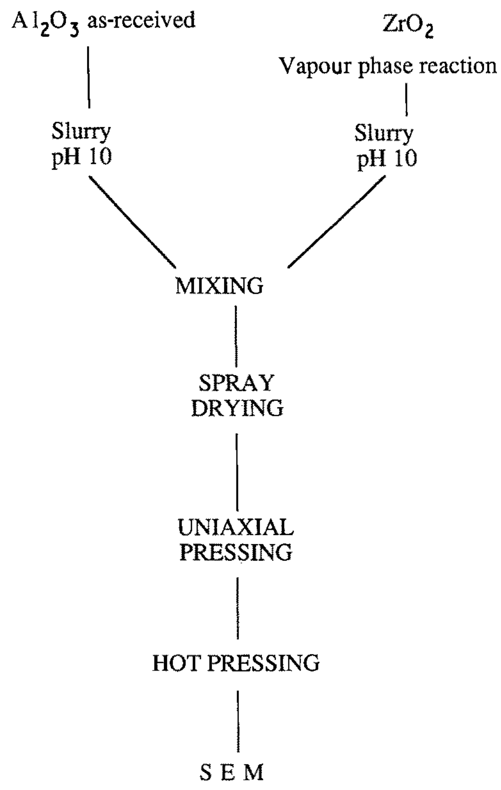


Figure 3 Flow sheet of fabrication of composite from commercial alumina and zirconia prepared by flame reaction.

After ageing the solution (14 h in the mother liquor) the gel was washed on porous glass and then by centrifugation, in order to eliminate the reaction by-products (NH_4Cl, Cl^-).

Table I gives the Cl^- contents after six washing operations, and the X ray phase analysis of the aluminium hydroxide powder obtained after drying (the zirconium hydroxide is amorphous, thus not detected by X-rays).

Differential thermal analysis (DTA) showed that the α alumina formation temperature increases with pH, i.e. a well crystallized hydroxide is transformed in oxide at a higher temperature than that necessary for an amorphous hydroxide. In order to obtain different α alumina contents in composites, powder mixtures were calcinated at the same temperature. Table II gives the α alumina contents in powder mixtures as a function of calcination temperature and end of neutralization pH.

3.1.2. Commercial alumina and gas-phase-prepared zirconia

Starting from an oxide powder mixture, a classical method of ceramic elaboration route was chosen: i.e. spray drying (Fig. 3) [34].

TABLE II α alumina content of alumina–zirconia powders prepared from chlorides, after calcination of the hydroxide mixture

Temperature of calcination (° C)	Time min	pH		
		7.5	9	10.5
1100	30	2	1	0.5
1200	30	93	74	6

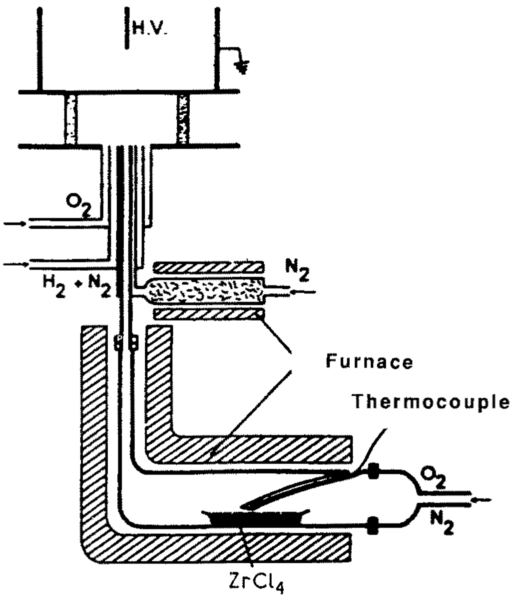


Figure 4 Flame reactor scheme (for zirconia synthesis).

3.1.2.1. Alumina powder. A Bayer powder (RC 172 DBM from Reynolds) was used, and sedigraphic determinations of granulometric repartitions allowed determination of the best electrochemical conditions for which suspensions are optimally dispersed. In order to avoid acidic preparation conditions, a dispersant was needed to obtain good defloculation of the slurry at pH 10.

3.1.2.2. Zirconia powder. Zirconia powder was gas-phase prepared. The method used by the Laboratoire de Catalyse, Lyon I University (France) consisted in the injection of a chloride vapour in a hydrogen–oxygen flame. The precursor was zirconium tetrachloride, it is in a solid state at ambient temperature, and sublimes at 320° C; its vapour pressure is 3.5 torr at 200° C and sharply increases above this temperature.

The vaporization of $ZrCl_4$ is shown in Fig. 4. An amount of chloride is placed in the furnace, the temperature of which determines its partial pressure in the carrier gas. In order to maintain a constant partial pressure of chloride, a continuous introduction system for chloride was built [35].

The reactor used was a torch with coaxial tubes. The chloride vapour is carried by means of an air or oxygen stream in the central tube. Pure hydrogen, or hydrogen diluted with nitrogen, circulating in the third tube is separated from the central tube by a nitrogen screen (in tube 2) which separates or disconnects the flame, which is the reaction zone, and hinders its closure by the resulting oxide deposit. A fourth tube is managed to maintain a slight oxygen excess, with respect to hydrogen, whatever the oxygen stream in the central tube may be.

Both thermodynamic and kinetic parameters of the formation reaction of the oxide may be controlled by varying some experimental parameters.

Electrostatically precipitated zirconia particles are not porous, their size may vary between some nanometres up to 100 nm; phase analysis gives 80% tetragonal and 20% monoclinc. Three different powder batches are used, with respective specific surfaces: 15 to 35 and 60 $m^2 g^{-1}$. Zeta potential and sedigraphic measurements allow determination of the pH regions where the dispersion is optimum: $pH < 3.5$ and $pH > 10$.

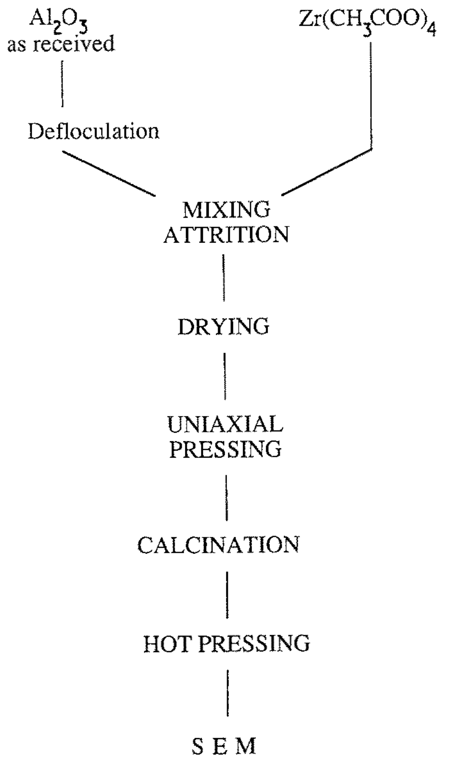


Figure 5 Flow sheet of fabrication of composite from commercial alumina and zirconium acetate.

3.1.2.3. Mixture of the two oxide powders. Alumina and zirconia powders were respectively put in suspensions according to the pH conditions previously determined. Thus two different slurries were prepared at pH 10, where the dispersion was maximum for both powders. The slurry had a 60% dry matter content; after binding agent addition, the mixed slurry was dried by spray-drying, which produces 10 to 30 μm spherical agglomerates.

3.1.3. Commercial alumina and zirconium acetate

Before studying the simultaneous hydrolysis of two organic precursors, we studied the dispersion of a commercially available alumina powder (RC 172 DBM, Reynolds) in a zirconium acetate solution (Magnesium Elektron). Following the slurry (a mixture of alumina and zirconium acetate) homogenization step, a classical fabrication process for technical ceramics was used (Fig. 5) [36].

The initial zirconium acetate solution has a pH near 3, it decomposes giving zirconia during heating. Alumina is well dispersed in a pH 3 slurry. Therefore, alumina powder was slowly added to the zirconium acetate solution. A 6 h attrition milling allowed convenient impregnation of alumina particles by the zirconium salt. The mixture was then spray-dryed, thus transforming the zirconium acetate into a zirconium hydrate; this zirconium hydrate was transformed into zirconia by thermal treatment. Cold-pressed oxides pellets were then heated in air, using a slow rate of temperature increase. This thermal treatment was carried out up to 900° C, samples being consolidated.

3.1.4. *Cohydrolysis of metallic alkoxides*

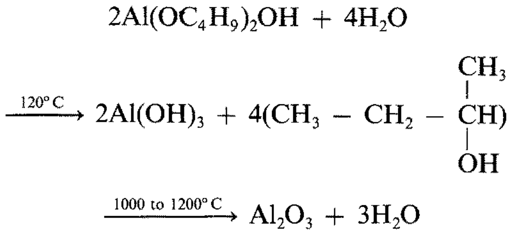
II-Al butoxide and IV-Zr propoxide are dissolved in anhydrous isopropylic alcohol, in the proportions previously described [37]. Hydrolysis was done by addition of ammonia (pH 10 or 12), at ambient temperature, according to the following equations, already proposed by Yoldas [20]

$$\mathrm{Al(OC_4H_9)_3 + H_2O \rightarrow Al(OC_4H_9)_2(OH) + C_4H_9OH}$$

$$\mathrm{Zr(OC_3H_7)_4 + H_2O \rightarrow Zr(OC_3H_7)_3(OH) + C_3H_7OH}$$

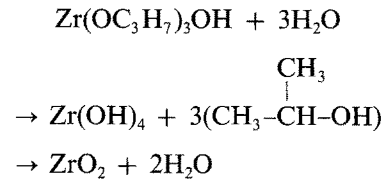
Calcination, under air, at 1000 to 1200° C for 1 h, allowed the transformation of the gel into the oxide.

After hydrolysis, the following reactions occurred in the case of aluminium butoxide:



$$\mathrm{2Al(OC_4H_9)_2OH + 4H_2O} \xrightarrow{120^\circ C} \mathrm{2Al(OH)_3 + 4(CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{CH}})} \xrightarrow{1000\ \text{to}\ 1200^\circ C} \mathrm{Al_2O_3 + 3H_2O}$$

In the same way, the following reactions take place with zirconium propoxide:



$$\mathrm{Zr(OC_3H_7)_3OH + 3H_2O \rightarrow Zr(OH)_4 + 3(CH_3\text{-}\overset{\displaystyle CH_3}{CH}\text{-}OH) \rightarrow ZrO_2 + 2H_2O}$$

Fig. 6 summarizes the different transformation steps in the production of the alumina and zirconia powder mixture.

The transformation "transition alumina" → "α alumina" takes place at lower temperatures with the powder prepared at pH 10. Alumina is completely transformed into the α phase after a calcination at 1200° C. The mean grain size of the powder prepared at pH 10 is very much larger than that of the powder prepared at pH 12. For the powder obtained at pH 10, grinding is necessary to obtain a finer granulometry.

Table III gives the characteristics (specific surface, mean grain size determined by sedigraphy d_{50}) of powders as a function of hydrolysis pH values and calcination temperature.

3.2. Sintering and characterization of materials

All the powders, produced by the different methods, were uniaxially cold pressed under 320 MPa, then hot-pressed sintered (40 MPa, at 1450 to 1600° C for 15 min) in graphite dies (diameter 20 mm) under vacuum. The influence of the thermal sintering cycle on the mechanical properties will be discussed later (Section 5.2.3).

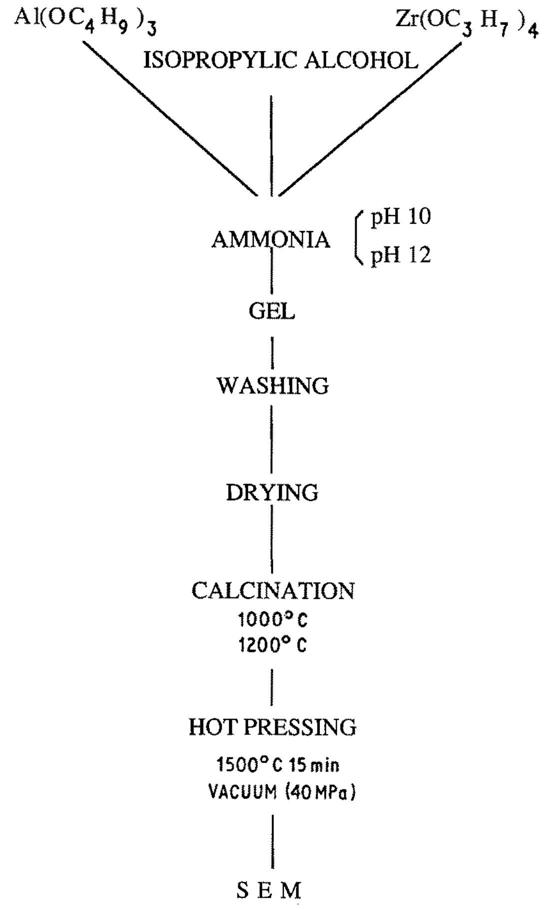


Figure 6 Flow sheet of fabrication of composites from metallic alkoxides.

The dense samples were then characterized. Density was measured by Archimedes' method. The monoclinic or tetragonal phase contents of zirconia were determined by X-ray analysis [38].

Samples (4 mm × 3 mm × 18 mm) used for rupture strength and rupture toughness (single edge notch bend method) were machined using diamond tools.

SEM observations were carried out on polished and then thermally etched samples.

Statistical granulometric determination on micrographs allows determination of granulometric distribution of both alumina and zirconia grains, and then of their mean equivalent diameter (d_{50}).

4. Results

4.1. Physico-chemical and mechanical characteristics

Tables IV to VII give the characteristics of hot-pressed samples prepared from different precursors.

TABLE III Characteristics of alumina and zirconia powders obtained after cohydrolysis of the two alkoxides

	pH of hydrolysis		
	10	12	
Temperature of calcination (° C)	1200	1000	1200
Specific surface, ss (BET) ($\mathrm{m^2\,g^{-1}}$)	8–9	71	30
d_{50} (sedigraph) (μm)	after grinding 2	< 0.2	0.5–0.6

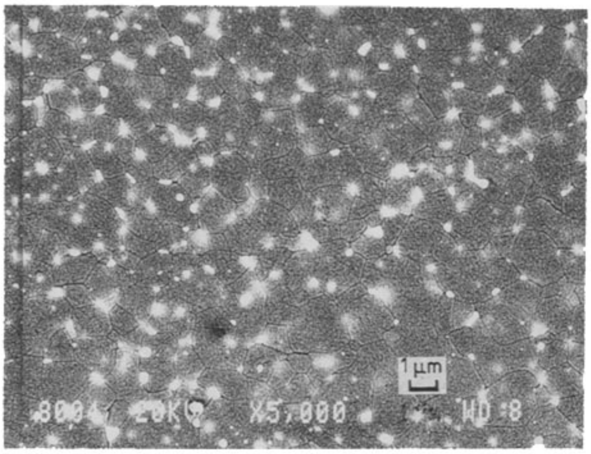


Figure 7 Scanning electron micrograph of a 7.2 vol % zirconia composite prepared by hydrolysis of chlorides at pH 9 (hot-pressed 1600° C for 15 min).

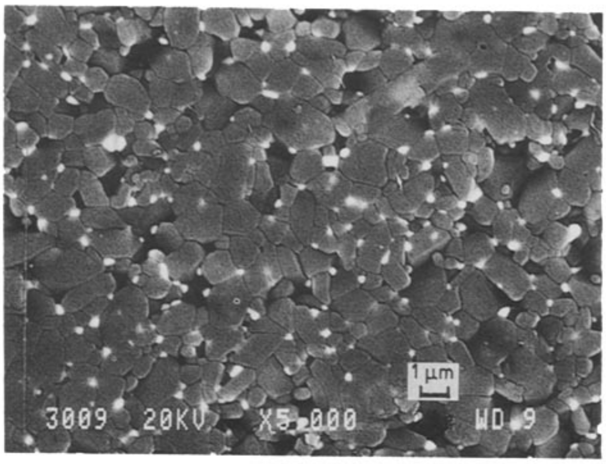


Figure 8 Scanning electron micrograph of a 6.8 vol % zirconia composite prepared from zirconia from flame (SS $35\,m^2\,g^{-1}$) and commercial alumina. Hot-pressed 1500° C for 15 min.

4.2. Microstructures

Figs 7 to 11 are microphotographs of ZTA composites prepared by the different methods.

5. Discussions

5.1. ZTA composites fabricated from aluminium and zirconium chlorides (Table IV)

The best rupture strength values, σ_f, are obtained when densification is carried out at 1600° C, and previous calcination at 1200° C, i.e. powders calcined at 1100° C do not contain enough α alumina before sintering, in order to reach a densification which eliminates open porosities.

The grain size of composites prepared at different pH is quite similar. Fig. 7 shows that a large part of the zirconia is in intragranular positions. In this material type, with an extremely fine microstructure, fracture is generally intergranular, thus intragranular zirconia does not contribute to toughening. Furthermore, the tetragonal zirconia phase analysis shows an almost complete metastabilization of zirconia, hindering microcracking in the material, which may explain the low toughness values.

The zeta potential value and the pH of the solution of the aluminium and zirconium hydrates have really no influence on the nature of the composite microstructure, but they strongly modify the transformation conditions of alumina, thus giving different mechanical properties. In order to obtain optimal densification and best rupture strengths, the α alumina content in the starting powder must be near 6%.

Zirconia produced in the process is too fine in order to improve the material toughness, but by blocking alumina grains, it contributes to the rupture strength increase.

5.2. ZTA composites produced from zirconia prepared by gas-phase reaction (Table V)

5.2.1. Influence of the grain size of the starting zirconia powder

The finest zirconia powder ($60\,m^2\,g^{-1}$) gives rise, after sintering, to grains with a size smaller than that of the other two powders. But, for each zirconia powder, the grain size repartition of alumina is the same after sintering.

The rupture strength is slightly increased when the starting zirconia grain size increases. Toughness, K_{Ic}, is maximum when the finest zirconia powder ($60\,m^2\,g^{-1}$), for 6.8 vol %, is used.

5.2.2. Influence of composition

An increase of the zirconia content induces a decrease in the alumina grain size. This phenomenon, which was previously observed [39], may be explained by a

TABLE IV Physico-chemical characteristics of alumina–zirconia (ZTA) composites prepared from chlorides

pH	Initial phase	ZrO_2 (vol %)	Calcination T (° C)	Al_2O_3 (% α)	sintering T (° C)	t-ZrO_2 (%)	d/d_{th}*	σ_f (MPa)	K_{IC} ($\pm 0.2\,MPa\,m^{1/2}$)	d_{50} (μm)	
										Al_2O_3	ZrO_2
7.5	Amorphous	8.6	1100	2	1600	80	93.5	494 ± 52			
			1200	93	1550	93	94.5	623 ± 75			
			1200	93	1600	100	96.9	731 ± 87	4.5	1.48	0.23
9	Amorphous	7.2	1100	1	1600	15	97.6	434 ± 75			
			1200	74	1550	100	96.6	704 ± 102			
			1200	74	1600	100	98.2	798 ± 48	5.0	1.78	0.29
10.5	Bayerite	6.5	1100	0.5	1600	100	94.2	755 ± 58			
			1200	6	1550	96	98.6	706 ± 95			
			1200	6	1600	97	98.7	841 ± 45	4.8	1.67	0.23

*Ratio of density, d, to theoretical density, d_{th}, × 100.

TABLE V Characteristics of ZTA composites prepared from RC 172 DBM alumina and zirconia from flame (sintering 1500° C, 15 min)

ZrO_2 SS ($m^2 g^{-1}$)	ZrO_2 (vol %)	t-ZrO_2 (%)	d	d/d_{th}	σ_f (MPa)	K_{Ic} (± 0.2 MPa $m^{1/2}$)	d_{50} (μm)	
							Al_2O_3	ZrO_2
15	3.4	100	4.04	98.8	896 ± 97	4.4	1.02	0.42
	6.8	95	4.11	97.5	1000 ± 49	5.0	0.93	0.47
	10.2	77	4.19	97.3	925 ± 92	5.4	0.92	0.52
35	3.4	100	4.09	99.9	775 ± 92	4.6	0.98	0.43
	6.8	92	4.11	98.1	936 ± 80	5.5	0.94	0.49
	13.6	65	4.26	96.7	832 ± 92		0.93	0.54
60	3.4	100	4.03	98.7	853 ± 44	3.9	1.01	0.33
	6.8	98	4.10	97.9	815 ± 73	5.1	0.98	0.39
	10.2	72	4.16	96.7	695 ± 117	4.5	0.87	0.44

blocking of alumina grains by zirconia grains, which are well dispersed in the matrix and tend to coalesce and agglomerate to some extent. A compromise found for alumina and zirconia medium grain size allows the best rupture strengths. In the presence of zirconia, strength is strongly increased, if compared to that of pure alumina. Toughness behaves in almost the same way, the best results being obtained for the largest zirconia grain sizes.

5.2.3. *Influence of sintering temperature*

The hot-pressing temperature was varied between 1450 and 1550° C for 15 min. The optimum sintering temperature which gives the best mechanical resistances (strength, toughness) depends on the composition of the material and the characteristics of the starting powders [32]. A 6.8 vol % zirconia content corresponds to almost the highest strength (~ 1000 MPa).

5.3. ZTA composites fabricated with zirconium acetate

Table VI shows that the alumina grain size decreases when the zirconia content increases. The well-dispersed zirconia hinders coarsening of the alumina grain. The zirconia mean grain size is not changed when the zirconia content increases.

The rupture strength rises to a maximum for 8.7 vol % zirconia, then it decreases slightly up to 14 vol %, and drops sharply for 29 vol %. Toughness behaves in almost the same way for every zirconia content.

For this ZTA composite type, the optimum zirconia content lies in the range 5 to 15 vol %. The wear of the electrofused stabilized zirconia balls during attrition induces a pollution in the slurry. For each composition, 4 to 5 vol % zirconia comes from wear, but that zirconia does not induce either stress-induced transformation toughening or microcracking, i.e. no toughening.

The high strength values are explained by a blocking of alumina grains by the stabilized zirconia introduced by milling, and a slight reinforcement is produced by zirconia fabricated by acetate. The first phenomena seems to be predominant because when the total zirconia content increases, the mechanical properties are reduced. Furthermore, toughness values behave in almost the same way, i.e. the influence of toughening mechanisms is low.

5.4. ZTA composites from alkoxides

Table VII shows the different physico-chemical properties of powders, which result from the fabrication parameters. The three mixed oxide powders have different specific surfaces, ss (BET), thus diverse α alumina contents.

The powder, prepared at pH 10 and then calcined at 1200° C, is completely transformed to α alumina; its particles are strongly agglomerated by a pre-sintering phenomenon, thus it is necessary to grind them before shaping by pressing. The powder, prepared at pH 12 and calcined at 1000° C, contains no α alumina. Hot-pressing gives a complete densification, but the strength values are much more diverse than those of the powders which are calcined at 1200° C.

On sintered materials, the same grain size difference is observed on microstructure as in calcined powders. The zirconia content increase allows zirconia grain coarsening; no noticeable decrease in alumina grain size is observed, and especially for 20 vol % zirconia the zirconia dispersion is no nearer optimum (Table VII).

For the powder prepared at pH 10, the maximum of strength value is observed for the finest alumina microstructure (10 vol % ZrO_2, $d_{50Al_2O_3} = 1.42\,\mu$m).

TABLE VI Characteristics of ZTA composites (from zirconium acetate; 6 h milling; hot-pressed 1500° C, 15 min)

ZrO_2 (vol %)	t-ZrO_2 (%)	d	d/d_{th}	σ_f (MPa)	K_{Ic} (± 0.2 MPa $m^{1/2}$)	d_{50} (μm)	
						Al_2O_3	ZrO_2
4.9	100	4.06	99.5	924 ± 29	5.6	1.08	0.38
8.7	94	4.14	99.5	1067 ± 38	5.4	0.88	0.38
14.0	19	4.22	98.8	889 ± 38	5.7	0.79	0.34
16.1	17	4.24	98.4	602 ± 71	5.0	0.59	0.38
21	8	4.31	99.6	609 ± 83	4.7		
29.3	9	4.45	99.6	463 ± 155	5.7		

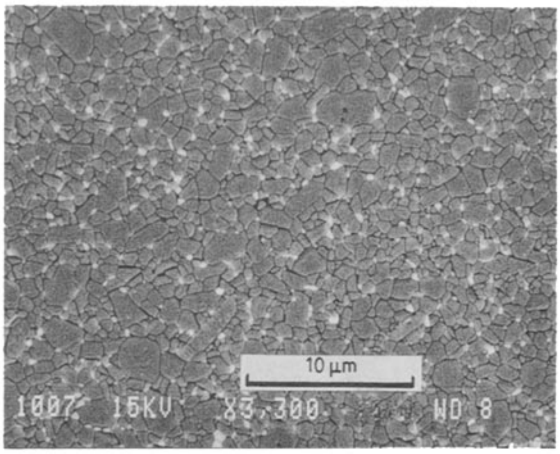


Figure 9 Scanning electron micrograph of a 8.7 vol % zirconia composite prepared from commercial alumina and zirconium acetate. Hot-pressed 1500° C for 15 min.

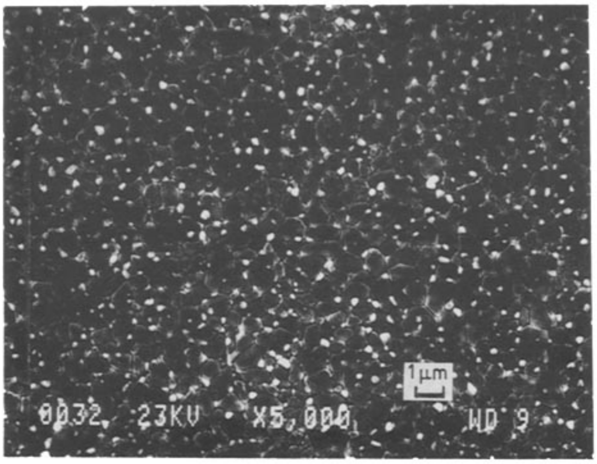


Figure 10 Scanning electron micrograph of a 10 vol % zirconia composite prepared from alkoxides at pH 12. Hot-pressed 1500° C for 15 min.

This strength value then decreases as (i) the grain size of both alumina and zirconia increase and (ii) the zirconia monoclinic content, increases; meanwhile toughness is improved. When the zirconia grain size is larger than a given diameter, zirconia is transformed into the monoclinic form, thus inducing matrix microcracking. When the crystal size defect increases, microcracking induces a slight drop in the rupture strength, but allows the toughness to increase [40].

For the powder prepared at pH 12 and calcined at 1200° C, the finest alumina and zirconia grain size gives rise to a more important increase in the rupture strength (10 vol % ZrO_2), but the toughness values remain close to those of pure alumina. There is little or no matrix microcracking because zirconia grains are too fine to be transformed during cooling. The rupture strength increase is due to the blocking of alumina grains by fine zirconia particles.

5.5. A comparative study of the various composites prepared

5.5.1. Grain size evolution as a function of the composite composition

Fig. 12 shows the evolution of the mean diameter (d_{50}) of alumina and zirconia grains as a function of composition and preparative route. For materials prepared from flame or zirconium acetate, the alumina grain size decreases when the zirconia content increases, i.e. alumina grains are blocked by zirconia, and zirconia grains are well dispersed in the alumina matrix. A tendency for zirconia grains to be placed on triple junctions thus increases their efficiency in hindering alumina grain coarsening. For composites prepared from alkoxides at pH 10, this tendency is not so well marked. In fact, between 10 and 15 vol % ZrO_2, the alumina grain size variation is nil; but for 20 vol % ZrO_2, the alumina grain size increases. In the latter case, the zirconia content increase induces a zirconia agglomeration, that no longer hinders alumina grain coarsening, as observed in previous cases. As the triple junctions are almost completely occupied, this induces either zirconia particle agglomeration or intragranular sites for zirconia.

The zirconia content increase allows zirconia grain coarsening, except for composites prepared from the acetate precursor; in this case attrition milling hinders agglomeration, which generally occurs with other processes.

5.5.2. Evolution of mechanical properties with mean grain size (d_{50})

5.5.2.1. Chlorides (Table IV). Powders were prepared at different pH and had a similar zirconia content. The preparation pH had little influence on the zirconia grain size. The best strength values were obtained for the largest alumina grain size.

TABLE VII Characteristics of ZTA composites obtained by alkoxides hydrolysis (hot-pressed 1500° C, 15 min)

pH	Calcination T (°C)	SS ($m^2 g^{-1}$)	ZrO_2 (vol %)	d	d/d_{th}	t-ZrO_2 (%)	σ_f (MPa)	K_{Ic} (± 0.2 MPa $m^{1/2}$)	d_{50} (µm)	
									Al_2O_3	ZrO_2
10 (ground)	1200	8.5	0	3.98	100		388 ± 41	3.6		
			5	4.05	97.9	100	712 ± 79	–	1.58	0.19
			10	4.12	96.0	100	762 ± 65	4.5	1.42	0.29
			15	4.22	95.4	80	748 ± 68	5.3	1.45	0.45
			20	4.30	95.5	31	406 ± 40	5.4	1.83	0.56
12	1000	71	0	3.97	99.9		645 ± 116	3.8		
			10	4.13	96.3	100	758 ± 108	3.8		
			15	4.24	95.7	85	695 ± 110	4.5		
12	1200	30	0	3.97	99.7		575 ± 83	3.7		
			10	4.15	96.7	100	878 ± 48	4.0	1.01	0.25
			15	4.23	95.4	89	414 ± 36	4.1	0.92	0.23

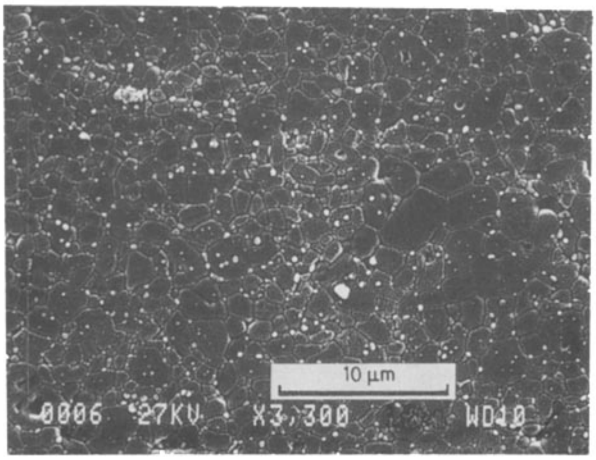


Figure 11 Scanning electron micrograph of a 10 vol % zirconia composite prepared from alkoxides at pH 10. Hot-pressed 1500° C for 15 min.

5.5.2.2. Flame (Table V). A slight variation of alumina grain size occurred, whereas the zirconia grain size increased as the zirconia content increased. The rupture strength was maximum for 6.8 vol % ZrO_2; toughness tended to increase with zirconia content.

5.5.2.3. Acetate (Table VI). The zirconia grains size behaved in almost the same way. Mechanical properties were enhanced when the alumina grains size increased.

5.5.2.4. Alkoxides (Table VII). For pH 12, a strong increase in rupture strength occurred for the 10 vol % ZrO_2 composition, whereas the grains size did not noticeably change. For pH 10, toughness increased with the zirconia particle size. However, rupture strength did not vary or decrease when both oxides grain sizes increased.

5.5.3. *Evolution of mechanical properties with zirconia content and tetragonal zirconia content (acetate method of production)*

In the composites fabricated from zirconium acetate, the tetragonal phase content sharply changed with the zirconia content. Fig. 13 shows the mechanical properties evolution with zirconia content, the monoclinic content being the grey zone.

The rupture strength drops when the tetragonal zirconia content decreases, up to 15 vol %. Then the tetragonal content (~ 10%) is stabilized and the variation of strength is low and near the value for pure alumina. Up to 10 vol % zirconia, the tetragonal content is high (90%), this induces an increase of rupture strength due to stress-induced transformation toughening, cf. Griffith law [40] (nevertheless part of the zirconia is maintained in the tetragonal form because it is stabilized). Above 15 vol %, zirconia is transformed into the monoclinic form during cooling, thus microcracking is important in the matrix and strength drops.

Toughness is slightly influenced by the zirconia phase content variations. The strong matrix microcracking does not induce a significant increase in toughness.

5.5.4. *Evolution of the critical transformation diameters*

The critical transformation sizes of zirconia particles in different composites are given in Fig. 14. These diameters have been determined from volume statistical granulometric repartitions and from X-ray determination of zirconia phases [32]. The critical transformation size varies according to the nature and the parameters of preparation. In the case of composites using a flame-prepared zirconia, the critical transformation size depends on the zirconia powder size before sintering. In the composites fabricated via the alkoxide route, a coarser microstructure involves a higher critical transformation diameter because the matrix strain on zirconia particles is lower: thus the transformation occurs more easily.

For all the preparative routes, for the lower zirconia contents (up to 9 vol %), the zirconia grain size always lies below the critical diameter; these values are not included in Fig. 14, i.e. the composite is not microcracked when its zirconia content is lower than 9 vol %. Above 10 vol % zirconia, the critical transformation diameter decreases, thus part of zirconia

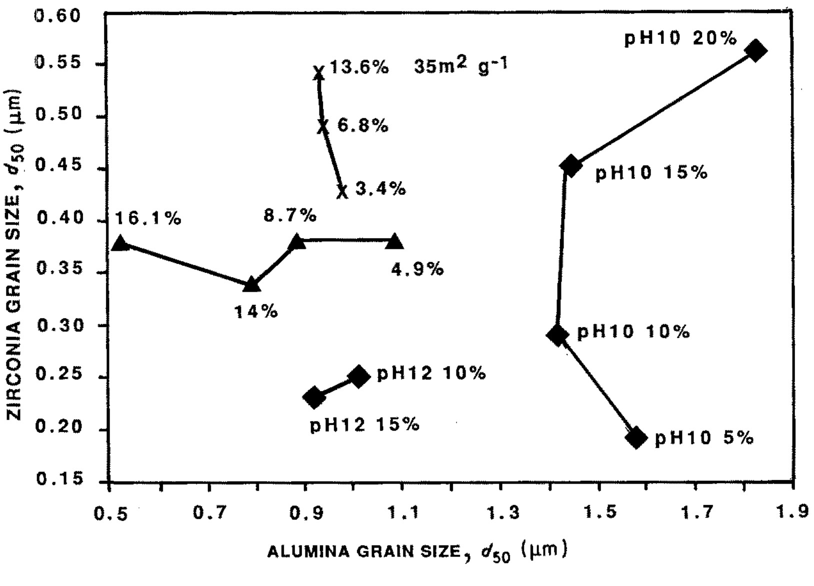


Figure 12 Mean grain size of zirconia plotted against alumina size in composites prepared by (x) flame, (◆) alkoxide and (▲) acetate routes.

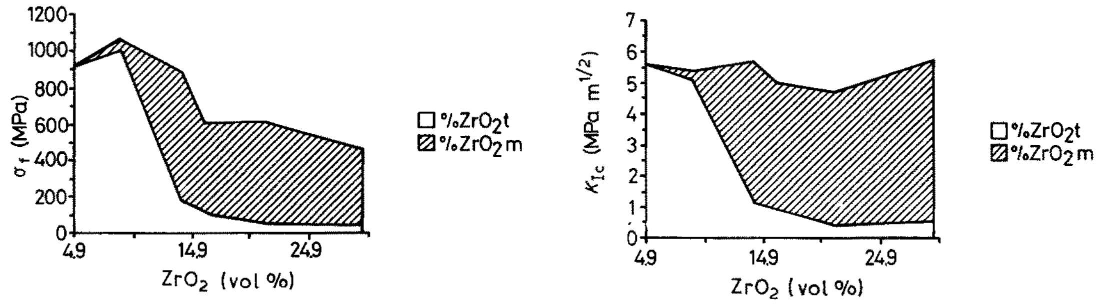


Figure 13 Rupture strength modulus, σ_f, and toughness, K_{Ic}, of composites prepared from zirconium acetate plotted against volume content of zirconia and tetragonal monoclinic phase content.

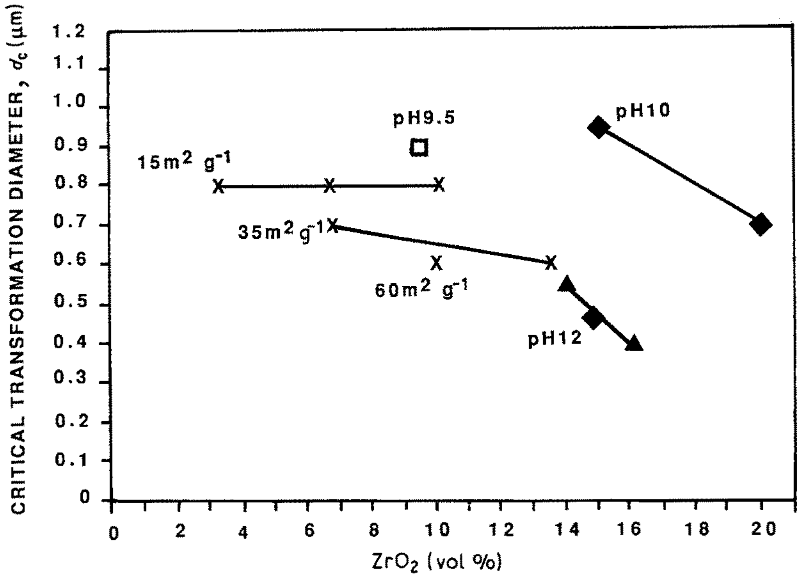


Figure 14 Critical transformation diameter of zirconia plotted against volume content of zirconia prepared by (□) chloride, (x) flame, (◆) alkoxide and (▲) acetate routes.

grains may be transformed during cooling and thus generates microcracks.

In every case, the best rupture strength values are obtained for composites with no more than 9 vol % zirconia, i.e. for non-microcracked materials. This means that toughening may be due to stress-induced phase transformation, but meanwhile toughness is not increased. The main part of zirconia particles is not transformed during cooling, their size is lower than the critical diameter d_c' [41, 42] (Fig. 15), where zirconia particles behave in a metastable state whatever the external stresses.

Microcracks produced in materials with more than 10 vol % zirconia generally induce a decrease in rupture strength, without any toughness increase, i.e. defects generated by microcracks have dimensions which are higher than the critical defect size.

5.5.5. Conclusions

The grain size in composites depends on their composition, but especially on their preparative route (different parameters, dispersion degree, etc.). For the lowest contents, the zirconia particle size is lower than the critical diameter of transformation, i.e. they behave in the metastable tetragonal form during cooling and only a part of them may transform under stress.

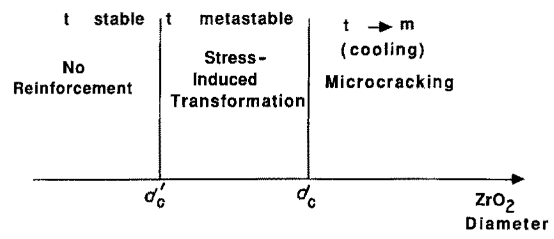


Figure 15 The crystallographic phases of zirconia according to mean grain size in the composite.

When the zirconia content is higher than 10 vol %, the zirconia grain size increases, and a part of the zirconia is transformed into the monoclinic phase during cooling: this induces microcracking in the matrix and, without no increase in toughness, the rupture strength drops. The mechanical properties are little influenced by the composition and grain size.

For zirconia contents lower than 10 vol %, the increase in rupture strength is explained by a fine microstructure ($d_{50\mathrm{Al_2O_3}} < 1.5\,\mu\mathrm{m}$, $d_{50\mathrm{ZrO_2}} < 0.5\,\mu\mathrm{m}$) and a good zirconia dispersion; this increase may be explained either by stress-induced transformation toughening (zirconia grain size between d_c and d_c'; Fig. 15), either by an interaction microcrack-particle which could block, deviate or divide a crack, due to the very fine (size $< d_c'$) and well-dispersed zirconia grains. But as there is no noticeable variation in toughness values, it seems that the second mechanism is predominant.

The critical diameter of transformation of zirconia, d_c, depends on the processing route and on the zirconia content.

Claussen [41] thought that toughness increased while zirconia grain size decreased, whereas Lange [42] predicted the toughness increases with the zirconia grain size. Our study sheds some light on these proposals: ZTA composites are prepared with a zirconia grain size slightly larger than d_c': the quantity of tetragonal transformed zirconia particles is not significant enough to allow the microcracking of the matrix which increases the toughness [32].

References

1. F. F. LANGE, in "Fracture mechanics of ceramics", edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1978).
2. F. CAMBIER, *Silicates Industriels* **11** (1982) 263.
3. G. M. WOLTEN, *J. Amer. Ceram. Soc.* **46** (1963) 418.
4. A. G. EVANS and K. T. FABER, *ibid.* **64** (1981) 394.
5. R. Mc MEEKING and A. G. EVANS, *ibid.* **65** (1982) 242.
6. N. CLAUSSEN and M. RUHLE, in "Advance in Ceramics", Vol. 3, "Science and Technology of Zirconia" edited by A. H. Heuer and L. W. Hobbs (The American Ceramic Society, Columbus, Ohio, 1981) p. 137.
7. P. HOMERIN, F. THEVENOT, G. ORANGE, G. FANTOZZI, V. VANDENEEDE, A. LERICHE and F. CAMBIER, *J. de Phys. Coll. C1* **2** (1986) C1-717.
8. K. S. MAZDIYASNI, C. T. LYNCH and J. S. SMITH, *J. Amer. Ceram. Soc.* **48** (1965) 372.
9. D. GREBILLE, Thèse docteur-ingénieur, Ecole Centrale Paris, F, 21 June 1982, p. 89.
10. E. MATIJEVIK, K. G. MATHAI, R. H. OTTEWILL and M. KERKER, *J. Phys. Chem.* **65** (1961) 826.
11. J. H. PATTERSON and S. Y. TYREE, *J. Coll. Int. Soc.* **43** (1973) 389.
12. T. SATO, *Anorg. Allg. Chem.* **391** (1972) 69.
13. P. H. HSU, *Soil. Sci. Soc. Amer. Proc.* **30** (1966) 173.
14. B. IMELICK, M. V. MATHIEU, M. PRETTRE and S. TEICHNER, *J. Chim. Phys.* **51** (1954) 651.
15. T. SATO, *J. Appl. Chem. Biotechnol.* **24** (1974) 187.
16. G. J. ROSS and P. C. TURNER, *Soil. Sci. Soc. Amer. Proc.* **35** (1971) 389.
17. M. C. GASTUCHE and A. HERBILLON, *Bull. Soc. Chim. (F)* **243** (1962) 1404.
18. B. E. YOLDAS, *J. Appl. Chem. Biotech.* **23** (1973) 803.
19. *Idem, Amer. Ceram. Soc. Bull.* **54** (1975) 289.
20. *Idem, J. Mater. Sci.* **12** (1977) 1203.
21. A. FANELLI and J. U. BURLEY, *J. Amer. Ceram. Soc.* **65** (1986) C174.
22. A. AYRAL and J. PHALIPPOU, IIème Conf. Franco-allemande céramiques techniques, Aachen, Germany, 4-6 March 1987.
23. B. E. YOLDAS, *J. Amer. Ceram. Soc.* **65** (1982) 387.
24. B. MIRHADI and H. HAUSNER, *Cfi-Ber. Dt. Keram. Ges.* **62** (1985) 86.
25. H. ENDL, B. D. KRUSE and H. HAUSNER, *Ber. Dt. Keram. Ges.* (1977) 105.
26. P. F. BECHER, J. M. SOMMERS, B. A. BENDERS and B. A. McFARLANE, *Mater. Sci. Res.* **11** (1978) 79.
27. K. D. FRITSCHE, *Freib. Forsch. H.A.* **657** (1983) 11.
28. J. ULBRICHT, V. POSCHMANN and J. BARTHEL, *Silikat Technik* **34** (1983) 361.
29. P. F. BECHER and V. J. TENNERY, in "Fracture mechanics of ceramics", edited by R. C. Bradt, D. P. H. Hasselman, F. F. Lange and A. C. Evans (Plenum, New York, 1983) p. 383.
30. P. F. BECHER, J. H. SOMMERS, B. A. BENDER and B. A. McFARLANE, *Mater. Sci. Res.* **11** (1978) 79.
31. P. F. BECHER, *J. Amer. Ceram. Soc.* **64** (1981) 37.
32. J. P. BACH, Thèse, Ecole des Mines de Saint-Etienne, 21 January 1988, no. 16 TD, 216, pp.
33. J. P. BACH, P. ORLANS, J. P. LECOMPTE, B. GUILHOT and F. THEVENOT, "Science of Ceramics 14", (Institute of Ceramics, Shelton, Staffs, UK, 1987).
34. J. P. BACH, F. THEVENOT, G. ORANGE, G. FANTOZZI and P. VERGNON, *Silicates industriels*, **53** (1988) 153.
35. G. ORANGE, G. FANTOZZI, P. HOMERIN, J. P. BACH, F. THEVENOT and P. VERGNON, "Optimisation du comportement thermomécanique de composites a dispersoides à base d'alumine: influence des propriétés morphologiques et structurales des poudres et leur frittage" (Compte rendu de l'A.T.P. du CNRS no. 8239, 1986).
36. J. P. BACH, P. HOMERIN, F. THEVENOT, G. ORANGE and G. FANTOZZI, Proceedings of the World Congress on High Technology Ceramics, 6th CIMTEC, edited by P. Vincenzini, Milan, (I), June 1986.
37. J. P. BACH, F. THEVENOT, B. MIRHADI and H. HAUSNER, *Rev. Int. Hautes Temp. Réfract.* **24** (1987) 211.
38. R. C. GARVIE and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **55** (1972) 302.
39. G. ORANGE, G. FANTOZZI, P. HOMERIN, F. THEVENOT, A. LERICHE and F. CAMBIER, "Science and Technology of zirconia III", Tokyo, 9-11 September 1986, in press.
40. A. A. GRIFFITH, *Phil. Trans. Roy. Soc.* **221** A (1920) 163.
41. N. CLAUSSEN, J. STEEB and R. F. PABST, *J. Amer. Ceram. Soc.* **60** (1977) 559.
42. F. F. LANGE, in "Fracture mechanisms of ceramics", vol. 4, edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1978) p. 799.

Received 7 April
and accepted 1 August 1988