

Ultra rapid quenching, a method to synthesize homogeneous, reactive oxide ceramic powders.

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The synthesis of mixed oxide ceramic powders was realized by an ultra rapid quenching (URQ) technique. The properties of three different URQ systems were assessed : mullite (URQ-M), mullite-zirconia (URQ-MZ) and forsterite-zirconia (URQ-FZ).

After optimization of the melting and quenching parameters, all URQ powders consist mainly of amorphous phase, and show some secondary metastable crystallographic phases.

Generally, URQ powders show improved homogeneity compared with classically prepared powder mixtures, and can also be sintered to densities close to the theoretical one, without the use of sintering aids.

Mechanical properties of densified products are mainly dependent on the chemical purity of the starting raw materials used for the synthesis of URQ powders, on the microstructure of the sintered materials, and on reinforcement mechanisms due to the presence of tetragonal zirconia.

Contrary to URQ-MZ, URQ-M shows R-curve behaviour, due to its original microstructure consisting of both equiaxed and elongated mullite grains with high aspect ratio.

Evidence for reinforcement by transformation toughening was found in the case of URQ-MZ, explaining the decrease of mechanical properties up to 600 °C. Softening of the intergranular glassy phase at higher temperatures results, first, in an increase of the mechanical properties up to 1000 °C, but, at higher temperature, in a decrease of the mechanical strength due to grain boundary decohesion.

Softening and decohesion phenomena are shifted towards higher temperatures for URQ-M, which can be related to the higher purity of the starting powders used for this system, and therefore the higher glass transition temperature of the intergranular glassy phase present in the sintered material.

URQ-FZ does not show evidence for a contribution of transformation toughening to its mechanical properties, and its room temperature mechanical properties are maintained up to 1300 °C, above which the material only shows plastic deformation during three point bending test.

1. INTRODUCTION.

Ultra rapid quenching consists in a very fast cooling (10^5 to 10^8 K s⁻¹) of a molten material.

The first technique, making it possible to attain such extremely high cooling rates, was the splat cooling technique, developed by Duwez (1960) [1], where the liquid to be quenched is spread over a metallic substrate in the thinnest layer possible, resulting in very high cooling rates due to heat removal from the liquid to a metal with high thermal conductivity.

At first, the splat cooling technique was largely used for quenching of metals and alloys, the principal reasons being their low melting point

(generally below 1000 °C) and high thermal conductivity.

Unlike metals, most ceramics are characterized by high melting points (generally above 1800 °C) and low conductivities (a few W/Km).

Melting of such kind of materials can only be realized using extremely high temperature heat sources such as image furnace, laser, plasma,..., and for particles with small sizes.

Quenching by splat cooling can be realized by shock-wave techniques and squeezing methods (hammer and anvil technique, rollers).

Such kind of techniques are interesting for the study of high temperature metastable phases, but are less suitable for the production of large amounts of powders.

A convenient method to perform ultrarapid quenching, uses a plasma torch, which allows to work in a continuous way. The combined effect of both thermal and kinetic energy exchanges in the plasma makes ultrarapid quenching, on a cold target, possible.

Applied to ceramic systems, this technique enables retention of high temperature phases as well as amorphous phases and generally contributes to an improvement of homogeneity and sinterability [2,3].

The properties of quenched powders and their thermal behaviour depend on the chemical and physical characteristics of the liquid phase formed at high temperature.

In this paper we will discuss the characteristics of three kinds of ultrarapidly quenched powders (mullite, mullite-zirconia and forsterite-zirconia), and the mechanical properties of materials sintered from such kind of powders.

2. EXPERIMENTAL.

2.1. Powder preparation.

Aqueous slips, corresponding to following three oxide type systems, were prepared :

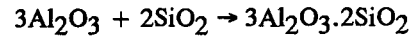
Table I : Oxide content in wt% of raw materials used.

	ZrO ₂	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	Fe ₂ O ₃	TiO ₂	CaO
ZrSiO ₄	61-63	38-36	1.0	-	-	0.15	0.25	-
Al ₂ O ₃	-	0.08	99.85	-	0.06	0.054	0.005	-
SiO ₂	-	>99.9	0.04	-	0.005	0.01	0.02	0.04
MgO	-	0.01	.015	99.4	0.001	0.012	-	0.15
ZrO ₂	99.8	0.05	.05	.005	0.03	0.02	0.005	0.05

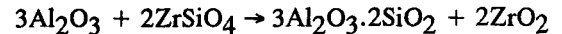
Al₂O₃ : A16SG (ALCOA) - USA, SiO₂ : Sipur A1 (Bremthaler Quarzitwerk) - Germany, ZrSiO₄ : Zircosil One (Cookson) - UK, MgO : Dead Sea Periclase - Israel, ZrO₂ : Dynazirkon F (Hüls) - Germany.

After spray drying of these slurries, mixed, granulated powders, with a grain size distribution typically ranging from 30 to 100 μm are obtained.

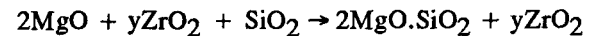
1) Al₂O₃-SiO₂, following the stoichiometry of the chemical reaction leading to mullite formation :



2) Al₂O₃-ZrSiO₄, following the stoichiometry of the chemical reaction leading to mullite-zirconia formation :



3) MgO-ZrSiO₄ (or ZrO₂-SiO₂), following the stoichiometry of the chemical reaction leading to forsterite-zirconia formation :



with $y = 1, 0.5$ and 0.22 , giving 33, 20 and 10 vol % of zirconia, respectively.

The chemical purity of each oxide used is given in table I.

After each milling step in the processing, a chemical analysis is performed in order to correct the starting raw material ratios with the aim of respecting the above mentioned stoichiometric proportions

2.2. Plasma melting and quenching.

After sieving at 50 μm, the coarse fraction of the sieved agglomerates was sprayed into a 24 kW plasma torch, using nitrogen both as plasma and powder carrier gas. (figure 1).

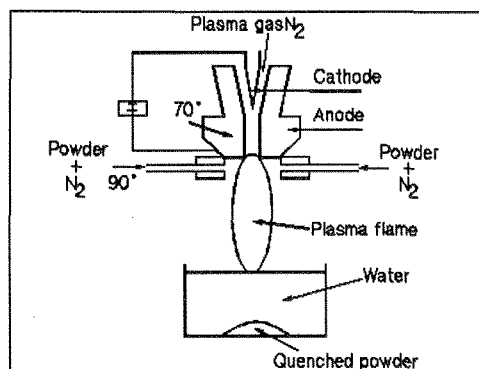


Figure 1 : typical configuration of an arc plasma torch and quenching device.

Two different appliances were used : one outside the nozzle, by perpendicular injection at 5 mm from the nozzle exit, and a second one, inside the nozzle, under a 70 ° angle.

When leaving the plasma, particles were sprayed into water, which surface was as close as possible to the flame extremity.

In order to optimize the heat treatment in the plasma, the influence of powder injection mode and speed were studied.

Therefore, powder injection was studied and optimized by numerical simulation of the trajectories, and calculation of the heat transfer in the plasma. The simulations were realized on the basis of plasma temperature and heat maps published by Fauchais et al. [4].

The results were experimentally verified by measuring the crystallographic phase amounts obtained after quenching, in order to estimate the reaction yield and the degree of amorphisation, which should increase both with improvement of the heat treatment and with the quenching efficiency.

2.3. Milling, shaping and sintering of quenched powders.

After quenching, the powders were milled by vibration milling.

Milling was carried out in water using alumina balls for mullite compositions, whereas zirconia balls and methanol were preferred for forsterite-zirconia.

For each system, micron sized powders could be obtained.

The ground powders were shaped in cylinders by cold isostatic pressing.

The densification of quenched and compacted powders was optimized by dilatometry and by determination of the sintering kinetics at different temperatures.

2.4. Characterization.

Quenched powders and sintered ceramics were characterized by porosity and density measurement, by microstructural SEM observation, eventually using EDXA or WLDXA, and by XRD.

Strength was measured in 3 point bending with a span of 15 mm and a crosshead speed of 0.1 mm/min.

Critical stress intensity factor (K_{IC}) was measured using the single edge notched beam technique, with a notch width of 190 μm .

R-curve behaviour was determined by the chevron notch technique, using a 3 point bending device with a span of 30 mm and a crosshead speed of 5 $\mu\text{m}/\text{min}$. Measurement of the central deflection as function of applied load enabled to calculate crack propagation as function of load following Munz [5].

3. PROPERTIES OF THE QUENCHED POWDERS.

Quenched powders are spherical, have an internal porosity of about 15 vol% and show a high degree of homogeneity (figure 2).

After optimisation of the injection parameters, such as injection speed (5 m/s), angle (70 °) and mode (injection in the nozzle), and of the quenching parameters (distance nozzle-water surface), quenched particles present a transparent aspect, which can be correlated to the presence of mainly amorphous phase, as confirmed by X-ray pattern analysis (figures 3 and 4).

In the case of ultra rapidly quenched mullite (URQ-M), some residual α -alumina and the formation of traces of mullite were revealed by XRD, whereas for ultra rapidly quenched mullite-zirconia (URQ-MZ), α -alumina and zircon were found as starting products, and some tetragonal zirconia was formed.

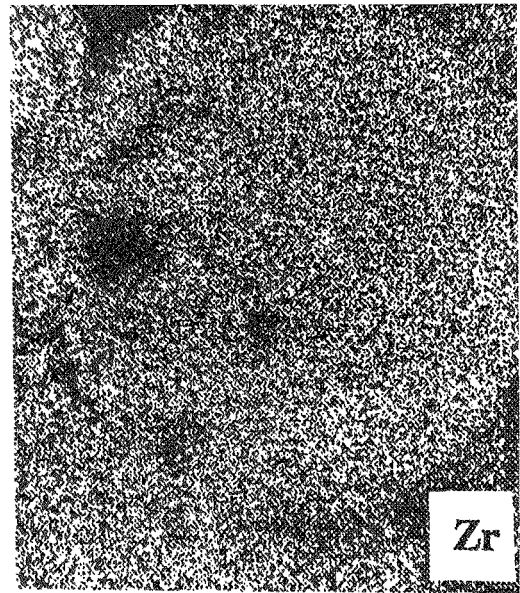
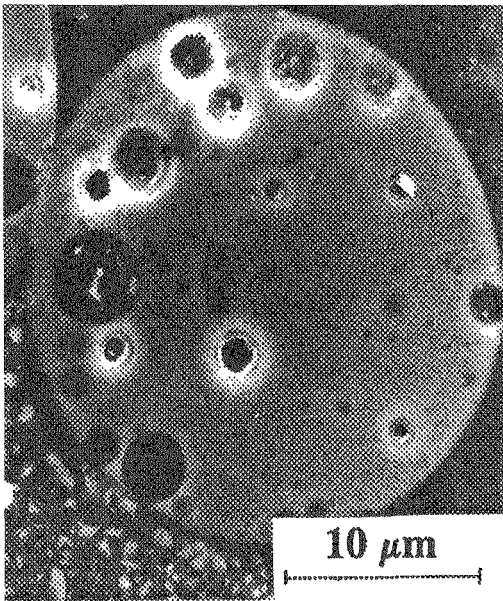


Figure 2 : SEI micrograph of an URQ-MZ particle cross-section and EDX analysis of Al and Zr distribution inside the same particle.

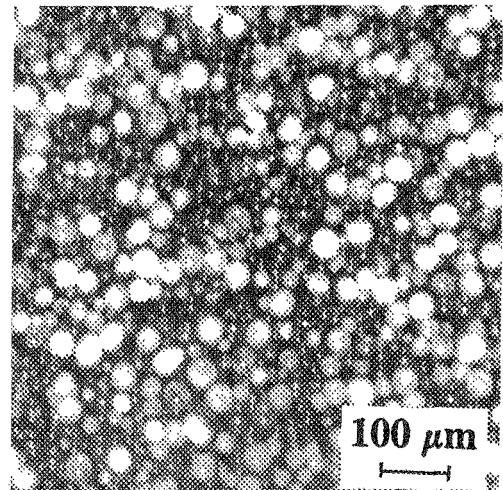
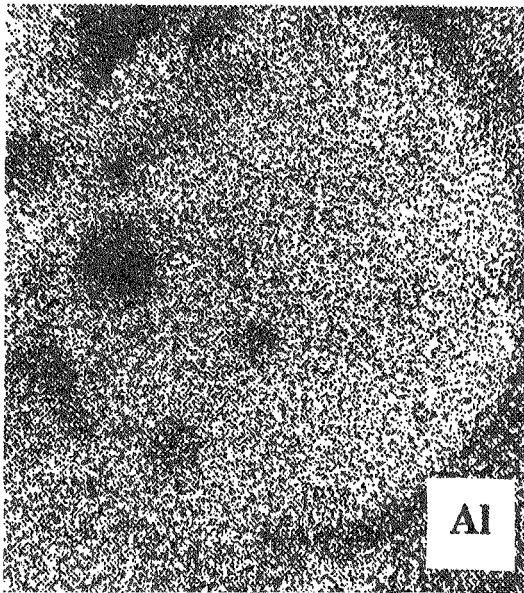


Figure 3 : optical micrograph of URQ-M powder.

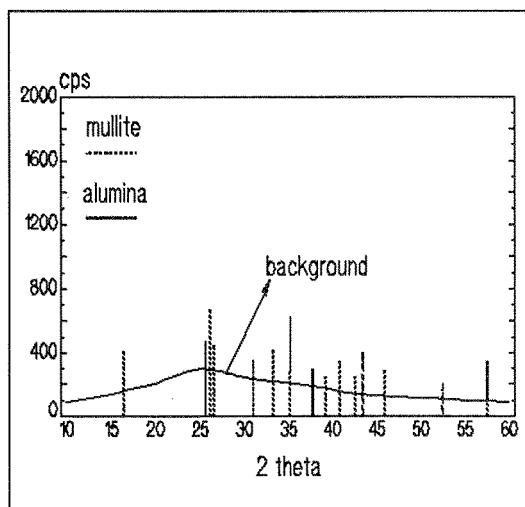


Figure 4 : X-ray diffraction pattern of URQ-M powder.

The crystallographic phases found in ultra rapidly quenched forsterite zirconia systems (URQ-FZ) were some magnesia and zircon as starting products, and forsterite, cubic and tetragonal zirconia as reaction products.

The amount of recrystallized zirconia depends on the zirconia content in the starting compositions. SEM observation also enabled to identify recrystallization of zirconia in the case of the coarser particles. Indeed, figure 5 is a SEM picture of a section of an URQ-FZ particle (33 vol % zirconia) showing dendritic structures appearing near the external particle surface. This phenomenon can be explained when taking into account the particle trajectories in the plasma. Indeed, a particle trajectory is a function of its size.

Whereas the finest particles follow a trajectory close to the plasma central axis, where temperature and plasma velocity are the highest, coarser ones follow trajectories crossing the plasma in the colder and slower plasma regions.

It feels therefore reasonable to assume that quenching will be slower in the latter case, which leads to larger recrystallization.

4. SINTERING AND CHARACTERIZATION.

The best sintering conditions for each material are 1650 °C - 2h (URQ-M), 1600 °C - 1h (URQ-MZ) and 1620 °C - 2h (URQ-FZ).

The main physical and room temperature mechanical properties of each material are given in table II.

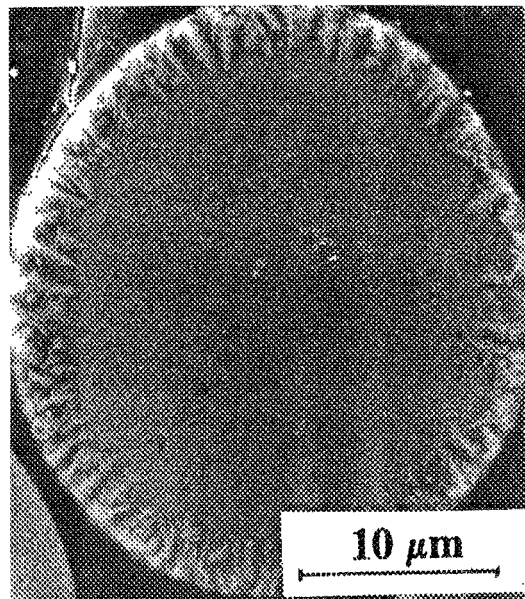


Figure 5 : SEM picture of MgO-SiO₂-ZrO₂ quenched powder containing 33 vol% zirconia.

It can be seen that densities close to 98 % of theoretical density can be achieved by pressureless sintering

The high tetragonal content of forsterite-zirconia can probably be explained by a stabilization of tetragonal zirconia by magnesia.

In figure 6 we show the microstructure of URQ-M, which is composed of a mixture of equiaxed (1-2 μm) and elongated grains having high aspect ratio (up to 10).

The microstructure of URQ-MZ is more equiaxed, with very few elongated grains (aspect ratio of about 2), whereas most zirconia grains have sizes less than 1 μm (figure 7).

Table II : Main room temperature characteristics of materials sintered from URQ powders.

Ceramic	Density g.cm ⁻³	Tet. Content %	E GPa	σ_f MPa	K_{IC} MPa \sqrt{m}
URQ-M	3.02	-	213	230 \pm 19	2.4 \pm 0.2
URQ-MZ	3.65	35	216	340 \pm 53	4.4 \pm 0.1
URQ-FZ (20 vol% zirconia)	3.73	100	214	231 \pm 20	2.7 \pm 0.2

which cannot be measured by the chevron notch technique.

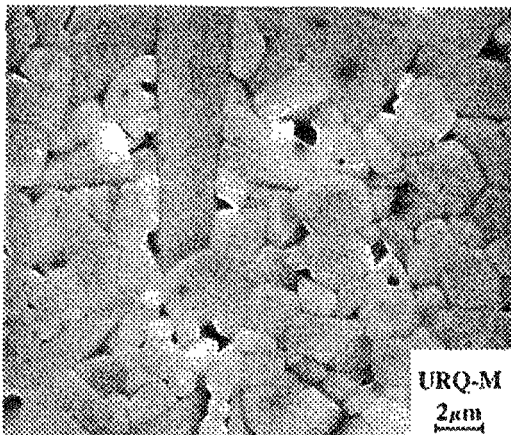


Figure 6 : SEM observation of the microstructure of URQ-M.

The mullite grain shape distribution is particular, and characterized by a composite structure, therefore, the possible rising R-curve behaviour of both the mullite monophase and mullite-zirconia composites was investigated.

Whereas URQ-MZ did not show any increase of K_{IR} during steady state crack propagation, URQ-M clearly displayed R-curve effect (figure 8).

The reinforcement of URQ-MZ can therefore be related to transformation toughening, characterized by a small process zone ahead of the crack tip [6],

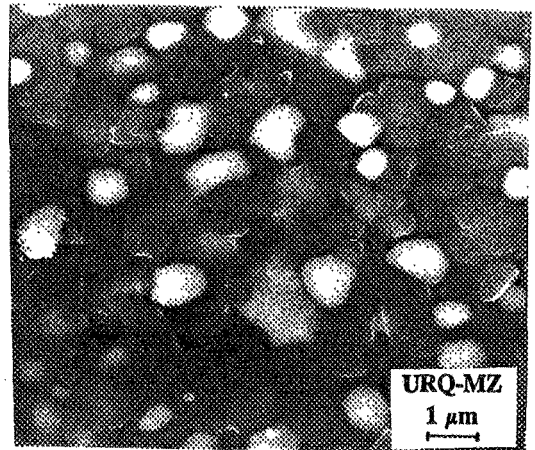


Figure 7 : SEM observation of the microstructure of URQ-MZ.

In the case of URQ-M, its particular microstructure leads to R-curve behaviour.

Indeed, the presence of large grains, as in the case of alumina [7], induces a microcracked process zone. This frontal process zone shields the crack tip from the applied stress, resulting in a fracture toughness increase, with increasing process zone size.

Taking into account the needlelike morphology of mullite grains, crack bridging in the wake zone probably occurs [8]. In this case, load-carrying elongated grains in the crack wake can also contribute to rising R-curve effect.

URQ-FZ has a microstructure consisting of equiaxed forsterite grains (1-2 μm) and micron-sized zirconia grains (figure 9).

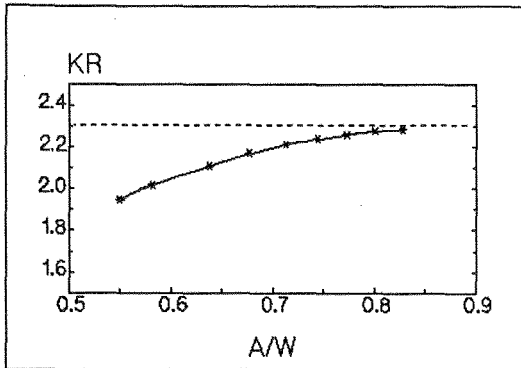


Figure 8 : R- curve behaviour of URQ-M.

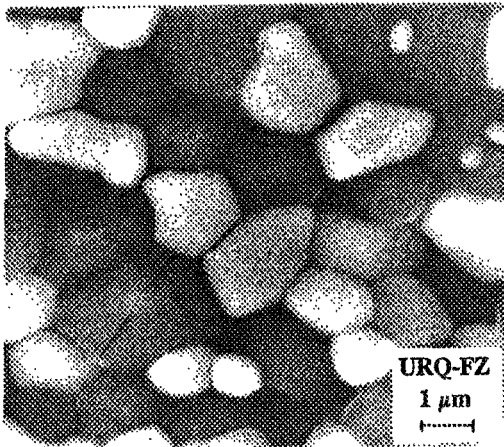


Figure 9 : SEM observation of the microstructure of URQ-FZ with 33 vol% zirconia.

The mechanical properties (σ_f and K_{IC}) of URQ-MZ as a function of temperature are shown in figure 10.

Between room temperature and 600 $^{\circ}\text{C}$, we observe a decrease of the mechanical properties, which can be mainly attributed to chemical bond expansion and to the progressive thermodynamic stabilization of tetragonal zirconia phase with temperature, leading to less efficient transformation toughening.

Between 600 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$, the mechanical properties increase again, and, at the same time, the fracture face, which is purely transgranular at room temperature, becomes mixed (trans and inter) starting from and above 800 $^{\circ}\text{C}$.

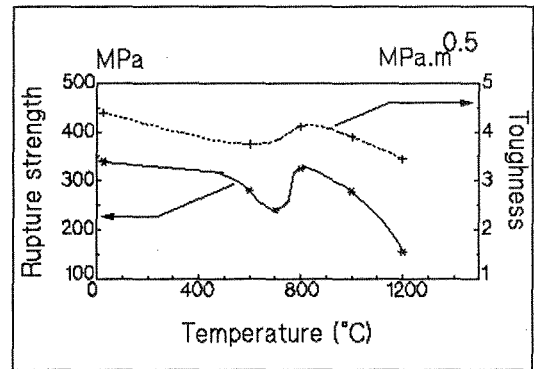


Figure 10 : Mechanical properties as a function of temperature for URQ-MZ.

The increase of the mechanical properties is therefore mainly related to the formation of a plastic zone ahead of the crack tip, occurring above the glass transition temperature of the grain boundary glassy phase.

Above 800 $^{\circ}\text{C}$, the mechanical properties decrease again, which might be due to further softening of the intergranular glassy phase leading to grain boundary sliding and decohesion.

At 1300 $^{\circ}\text{C}$, fracture becomes purely intergranular. The material is no longer elastic and behaves as it would during creep tests, that is, the interlinkage of cavities probably induces failure.

The evolution of mechanical properties for URQ-M is different than in the case of URQ-MZ (figure 11), because of the absence of zirconia and also of higher purity mullite raw materials.

Indeed, a similar increase of mechanical properties happens at higher temperatures, and the maximum strength is attained at 1000 $^{\circ}\text{C}$ (instead of 800 $^{\circ}\text{C}$ in the case of URQ-MZ).

At 1300 °C, the rupture behaviour of the mullite remains brittle (as shown by the rupture faces), and the strength is still half that of the room temperature strength.

The remarkable increase of K_{IC} at 1200 °C, whereas the strength is decreasing at that temperature, can be explained in terms of cavity and/or microcrack formation in a process zone, limited in size, surrounding the fracture origin [9]. The development of such kind of flaws absorbs energy initially devoted to crack propagation, explaining the toughness increase, but leads at the same time to an increase of the defect size, resulting in a decrease of flexural strength.

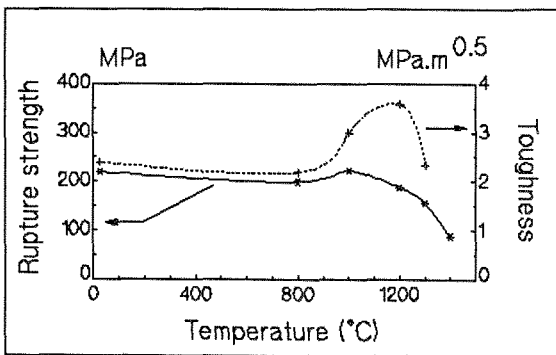


Figure 11 : Mechanical properties as a function of temperature of URQ-M.

The high temperature mechanical properties of URQ-FZ are plotted in figure 12.

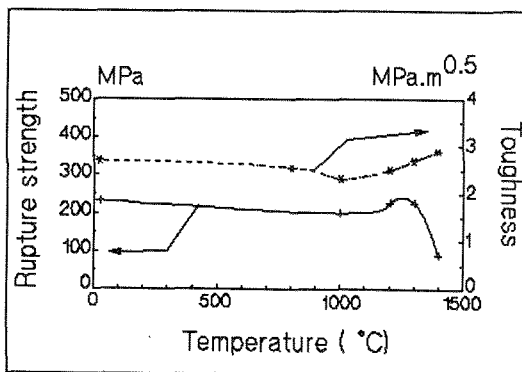


Figure 12 : Mechanical properties as a function of temperature of URQ-FZ.

The room temperature properties are maintained up to 1300 °C. This suggests a less important contribution of transformation toughening at room temperature, explaining the lower toughness value at that temperature, but also the presence of low quantity of glassy phase, owing to the high purity of the raw materials.

Rupture is transgranular from room temperature up to 1200 °C, and completely intergranular at 1300 °C.

At 1400 °C, the material deforms continuously during flexural strength test under a fixed load of about 90 MPa.

This observation, and also the equiaxed forsterite microstructure, are strongly suggesting the possibility of superplastic deformation of this material.

More detailed evidence of this kind of deformation behaviour at high temperature has been recently confirmed, the results being presented elsewhere.

5. CONCLUSIONS.

Ultra rapidly quenching (URQ) of mixed oxide ceramics was carried out by DC plasma melting, followed by projection into water.

Ultra rapidly quenched powders are characterized by the presence of mainly amorphous phase, some residual secondary metastable phase (such as tetragonal zirconia), and also show improved homogeneity and sinterability.

Materials sintered starting from URQ powders are homogeneous and their microstructure depend on the chemical composition.

The room temperature mechanical properties of the studied systems depend on the microstructure and the crystallographic characteristics of the material. URQ mullite shows a mixed microstructure consisting of a micron sized mullite grain matrix with embedded elongated mullite grains with high aspect ratio, explaining the observed R-curve behaviour. URQ mullite-zirconia is characterized by transformable submicronical zirconia grains, resulting in an improvement of its room temperature toughness by transformation toughening, whereas the mullite matrix shows a mixed microstructure consisting of mainly equiaxed and a few elongated, but with low aspect ratio,

micron sized mullite grains. No evidence of transformation toughening was found in the case of URQ forsterite-zirconia, which has an equiaxed forsterite microstructure.

The evolution of mechanical properties from room temperature up to 600 °C is explained by less efficient transformation toughening with temperature in the case of URQ-MZ up to 600 °C.

At higher temperatures plastic relaxation occurs in all cases, but the onset of plasticity depends on the glass transition temperature of the intergranular glassy phase, and therefore, on the purity of the starting raw materials used for the synthesis of URQ powders.

URQ forsterite-zirconia with 20 vol% zirconia, which maintains its room temperature mechanical properties up to 1300 °C, is characterized by important plastic deformation during three point bending tests at 1400 °C. This observation, and also the equiaxed forsterite and zirconia microstructure, strongly suggest the possibility of superplastic behaviour at that temperature.

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Brief biography of F. Cambier

Francis CAMBIER is research director of the Belgian Ceramic Research Centre (BCRC) in Mons (Belgium) since November 1983. Recently, he has also been appointed professor, associated to the University of Valenciennes (France), where he is in charge of two courses for M.Sc. students : *Fabrication of Ceramics* and *Synthesis of Inorganic Raw Materials*.

He received a M.Sc. in 1971 and a D.Sc. in 1978, both in chemistry from the Materials Science Dept. of the University of Mons (B). Francis CAMBIER is with the BCRC since 1979. He is member of the boards of the European Ceramic Society, of the Belgian Ceramic Society, of the scientific journal *Silicates Industriels* and is (or was) member of various International Advisory Boards of scientific journals and international conferences.

He is author or co-author of more than 120 papers, of about 100 presentations and owner of 4 patents. His main topic of interest is structural ceramics, especially the relations between processing, microstructure and thermo-mechanical behaviour.

