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Ultralow expansion ceramics in the HfO_2–TiO_2 system synthesized by an hydrolysis and polycondensation technique

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Ultra-refractory ceramics from the HfO_2–TiO_2 system in the range 30–40 mol % TiO_2, with a near-zero thermal expansion, have been synthesized by hydrolysis and polycondensation of titanium alkoxide and hafnium dichloride alcoholic solutions and sintered at moderate temperature. Thermal stability, crystallization, density and microstructure of these materials have been examined. The as-prepared powder, amorphous at room temperature, crystallized quickly when heated at 500 °C. Entire crystallization occurred after treatment at 1000 °C. Sintering at 1500 °C on cold-pressed samples led to ceramics with weak porosity ($\leqslant$ 7%), low expansion coefficient $<1\times10^{-6}\,°C^{-1}$ with a minimum for 30 mol % TiO_2 content. SEM examination on sintered materials at 1500 °C reveals a grain size from 2–6 μm, increasing with TiO_2 content.

1. Introduction

Ceramics with a near-zero thermal expansivity, in addition to natural materials such as quartz and β-eucryptite have been intensively studied from many years. Thus compounds obtained from the binary HfO_2–TiO_2 system appear to be of great interest. This system, one of the first tested [1–8], is characterized by the existence of a wide solubility range based on the compound $HfTiO_4$, and extending from about 35–53 mol % TiO_2 [9] with a great stability, even under extremely reducing conditions and a high melting temperature ($\simeq$ 1980 °C). Materials from this system with great refractoriness and high thermal shock resistance (CET $< 1\times10^{-6}\,°C^{-1}$) are of interest in many fields. Usually, these products are synthesized by solid state reaction between purchased oxide powders, but this proceeding first requires repeated grindings and high temperature ($>$ 1700 °C). An alternative way is based on double decomposition of organic salts of hafnium and titanium [10], but these are not easy to obtain and are expensive.

The aim of this work was to find a means of synthesis for these HfO_2–TiO_2 ceramics by a liquid route and at moderate temperature. The resulting materials, whose compositions agree with low thermal expansion, have been studied from the view point of crystallization, thermal stability, expansion, density and micro-structure.

2. Experimental procedure

Trials to choose materials with the smallest thermal expansion coefficient led us to retain the following three compositions: 30, 36.75 and 40 mol % TiO_2–HfO_2. The last two contents are at 1500 °C, in the solid solution range based on the compound $HfTiO_4$ existing in the equilibrium phase diagram HfO_2–TiO_2. The third composition with 30 mol % TiO_2, is out at the left-hand side of the solid solution range and is formed of a diphasic mixture: HfO_2 and $HfTiO_4$ according to X-ray diffraction analysis.

Samples were synthesized by hydrolysis and polycondensation of titanium alkoxide (tetrabutylorthotitanate) and hafnium dichloride oxide alcoholic solutions. The two solutions were mixed then hydrolysed at room temperature by pouring on to a glass plate [11].

The powder obtained was cold pressed (3t cm^{-2}) into pellets and then heat treated in air to promote sintering and crystallization.

3. Thermal evolution of the hydrolysis products

The as-prepared powder from hydrolysis and polycondensation of mixed solution was amorphous at room temperature. After only 2.5 h heating at 500 °C, the crystallization of the product detected by X-ray analysis was well advanced. Crystallization improves with time and temperature of treatment and is complete after 15 h at 1000 °C (Fig. 1). The X-ray spectra of the materials heated to 1500 °C show either $HfTiO_4$ solid solution or a mixture of $HfTiO_4$ solid solution with monoclinic HfO_2 as a minor phase depending on the TiO_2 content. The results are listed in Table I.

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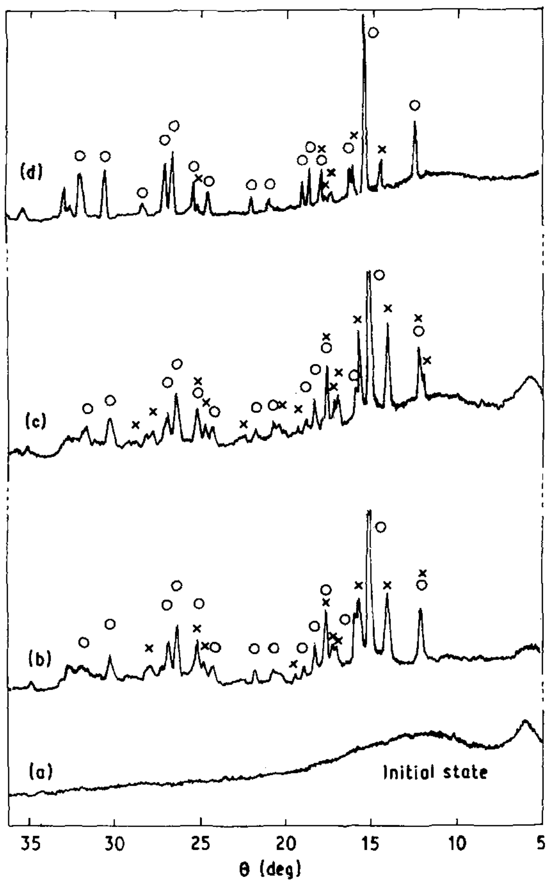

Figure 1 Evolution of X-ray spectra of 36.75 mol % TiO_2–HfO_2 powder with heat treatment. (a) Initial state, (b) 2.5 h at 500 °C, (c) 10 h at 1000 °C, (d) 16 h at 1300 °C. (×) HfO_2 monoclinic, (○) Solid solution $HfTiO_4$.

TABLE I

TiO_2 content (mol %)	Heat-treatment temperature (°C)	Phases
30	Room temperature (RT)	Amorphous
	500	HfO_2 Monocl. + $HfTiO_4$
	1500	HfO_2 Monocl. + $HfTiO_4$
36.75	RT	Amorphous
	500	HfO_2 monocl. + $HfTiO_4$
	1500	$HfTiO_4$
40	RT	Amorphous
	500	HfO_2 monocl. + $HfTiO_4$
	1500	$HfTiO_4$

4. Properties

4.1. Expansion

The dilatometric behaviour of materials sintered at 1500 °C and slowly cooled (2 °C min^{-1}) was measured using a quartz push rod dilatometer in the temperature range 20–1000 °C. Tests were carried out in air on bar samples with a heating or cooling speed of 3 °C min^{-1}. The expansion was recorded during heating and cooling runs. The presence of an hystheresis loop on the dilatometric curve is often found in diphasic materials as well as in ceramics containing microcracks [12–15]. The expansion curve of the prepared materials also showed an hystheresis cycle whose area increased with temperature and time treatments, whereas the expansion coefficient, α, was reduced. In these materials, a microcracking phenomena was observed which rules the dilatometric behaviour. Fig. 2 shows plots of dilatometric curves for 36.75 mol % TiO_2 samples at various temperatures and times. Thus after sintering at 1500 °C for 30 h, and slowly cooling (2 °C min^{-1}), the expansion of the product was stabilized and a mean value could be calculated ($\alpha \simeq 1 \times 10^{-6}\,°C^{-1}$). The material with 30 mol % TiO_2 content was found to have a lower thermal expansivity. It is noticed that α increases when more TiO_2 is added to solid solution (Fig. 3).

Repeated dilatometric runs on the material with a stabilized coefficient, α, induce a weak evolution of the curves. Thus, in the first four cycles, a small increase of expansion and a shrinkage of hystheresis areas are observed. From the fourth run, no evolution is seen (experiment for 9 cycles). This behaviour can be explained using the hypothesis by which, after sintering at 1500 °C, a complex system of stresses within each crystal occurs during cooling due to its high anisotropy. When these stresses exceed the strength of the crystals or the bonds between the crystals, small microcracks are created. This critical step is located at 500 °C and then at lower temperature the material expands due to the opening of microcracks.

During the first dilatometric run up to 1000 °C, no expansion of the material was seen and sometimes a

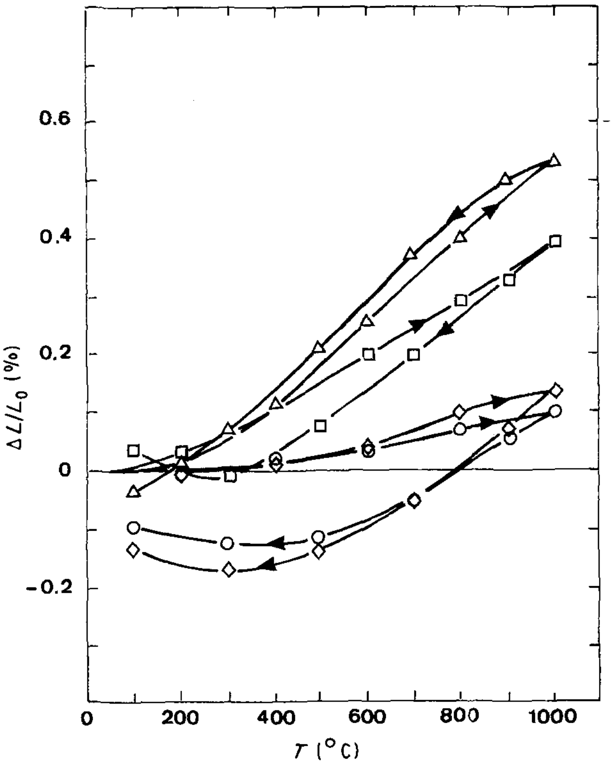

Figure 2 Evolution of dilatometric curves of the 36.75 mol % TiO_2–HfO_2 sample with heat treatment. (△) 2.5 h at 500 °C + 2 h at 1000 °C, (□) 15 h at 1400 °C, (◇) 5.5 h at 1500 °C, (○) 17 h at 1500 °C.

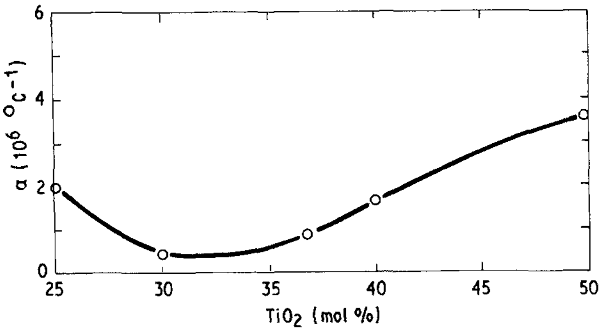

Figure 3 Variation of expansion coefficient, α, with TiO_2 content of TiO_2–HfO_2-based materials.

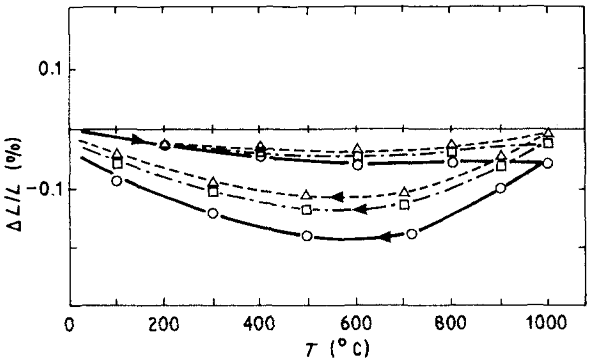

Figure 4 Evolution of dilatometric curves of the composition 30 mol % TiO_2–HfO_2 with repeated runs. (○) First run, (□) second run, (△) third to sixth runs.

shrinkage was observed. The density of microcracks in the sample was so high that even if part of them collapsed, many others remained open and the global expansion of material was zero or negative. During cooling from 1000 °C, the length of the sample decreased and new microcracks were created but at a rate smaller than in the case of a cooling from 1500 °C. After returning to room temperature, a second run yielded, during the heating stage, the collapse of microcracks initiated by cooling from 1000 °C, and also others produced by residual stresses in the material induced by cooling from 1500 °C, resulting in a small expansion of the sample. In the third heating cycle, vanishing residual microcracks cause the product again to expand slightly.

From the fourth run, the expansion curve became stabilized, thus microcracks initiated in the material during cooling from 1000 °C were filled during the further heating run. Thus the thermal coefficient was fixed at a value which is mainly a function of the grains size present in the sample.

Tests made on materials heated at 1500 °C and quenched in air showed an α coefficient which was zero or negative. Repeated runs involved a small increase in α, when the area of the loop decreased. From the fourth cycle, curves were stabilized and α, the expansion coefficient, was near zero (Fig. 4). Thus, quenching in air, has no effect on the area of the hystheresis loop but involves a decrease of the expansion coefficient, α, probably due to the formation at a higher rate of microcracks initiated by this fast cooling compared with a slow fall in temperature.

4.2. Density

Bulk density measurements were made using the toluene displacement technique. The porosity was calculated from density measurements, compared to theoretical densities based on a linear density relation between $HfTiO_4$ and HfO_2. The results, listed in Table II, show that density decreases when the HfO_2 content decreases. Hoagland *et al.* [16] reported that all cold-pressed and sintered samples at 1600 °C in the composition range 30–50 mol % TiO_2 were approximately 75% theoretical density. For hot-pressed specimens with 36.75 mol % TiO_2 content, the porosity falls to 12%. The Octet Franco-Canadian group [7] working on materials in the same range, 30–50 mol % TiO_2, prepared by solar fusion then ball-milled, isopressed and heated again at 1700 °C, found a porosity of about 10%. Under our experimental conditions, results obtained show that porosity is not mainly dependent on the TiO_2 content. The values are weak, near $\leqslant$ 7% according to a strong shrinkage of materials promoted by the mode of synthesis.

TABLE II

TiO_2 content (mol %)	Density (g cm^{-3})	Porosity (%)
30	8.14	5.3
36.75	7.39	7.5
40	7.36	5.7
50	7–7.15 (10)	< 3

4.3. Microstructure

The as-prepared powders with 30, 36.75 and 40 mol % TiO_2 contents are amorphous when analysed by X-ray diffraction. Scanning electron microscopy examination (SEM) of powders showed a typical morphology. Thus for 30 and 40 mol % TiO_2 contents, plates of 20–40 µm in the plane and 5 µm thick were observed with conchoidal fractures (Fig. 5). The composition with 36.75 mol % TiO_2 showed smaller and finer plates (1 µm). Analysis by energy-dispensive spectrometry (EDS) revealed for the three TiO_2 contents, the presence of elements, hafnium, titanium and chlorine, the latter arising from the initial component $HfOCl_2 \cdot 8H_2O$. Powders calcined at 500 °C for 2.5 h showed a microstructure disturbed by the blowing up of the plates induced by the volatilization of chlorine and organic groups, as well as crystallization (Fig. 6). The heating of powders at 1000 °C for 5, 10, 15 h involved a reorganization of the microstructure with a homogeneous area, formed of very small grains (0.1–0.3 µm), whose size increased with heating time (Fig. 7). On fresh fractures of bulk cold-pressed samples after heating at 1500 °C, a microstructure with a grain size of 2 to 5–6 µm was observed. The composition of the material and thermal treatment have a direct effect upon the grain size. So, the sample with 30 mol % TiO_2 content showed a fine microstructure with 2–3 µm grains after heating for 17 h at 1500 °C.

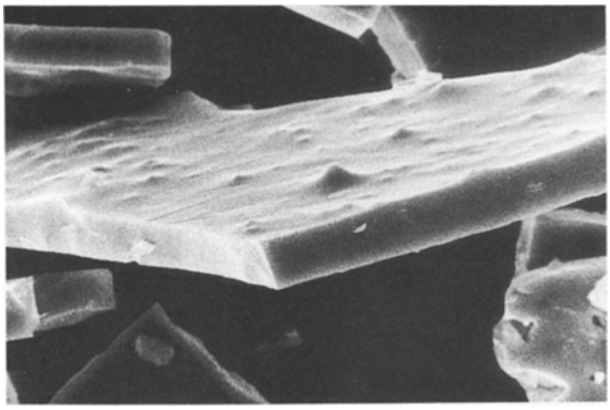

Figure 5 Scanning electron micrograph of 40 mol % TiO_2–HfO_2 as-prepared powder (× 2000).

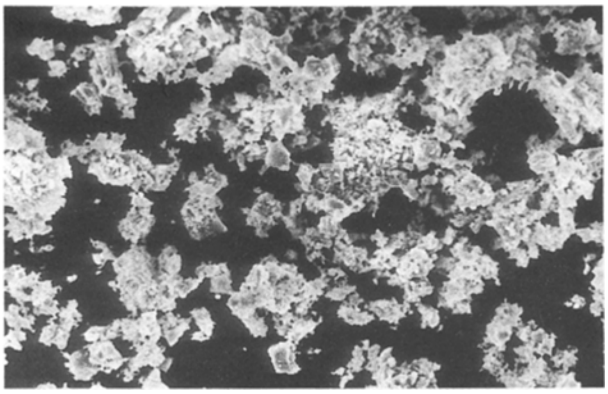

Figure 6 Scanning electron micrograph of 36.75 mol % TiO_2–HfO_2 powder calcined at 500 °C for 2.5 h (× 1000).

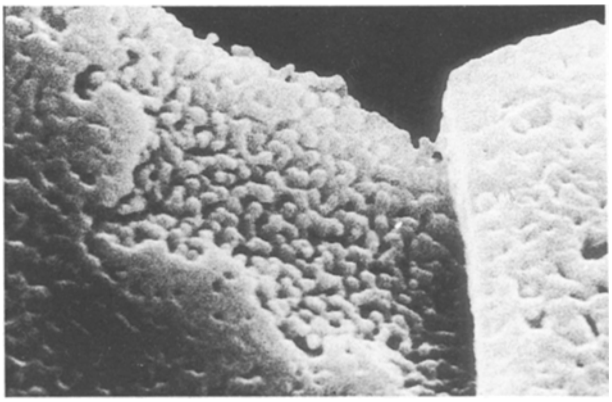

Figure 7 Scanning electron micrograph showing the grain size of 36.75 mol % TiO_2–HfO_2 after 5 h at 1000 °C (× 20 000).

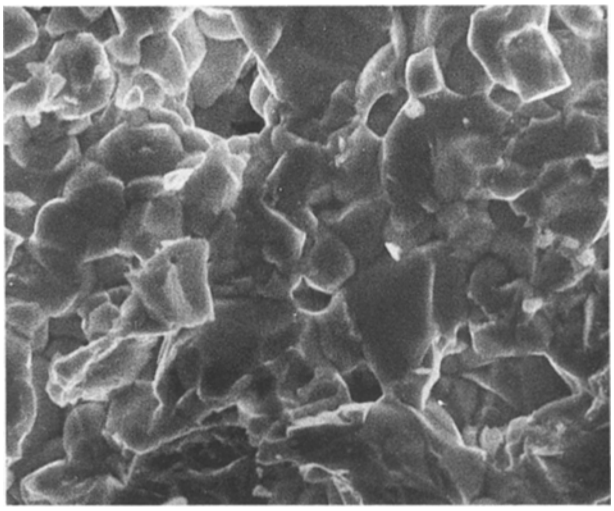

Figure 8 Grain size of the 30 mol % TiO_2–HfO_2 sample heated at 1500 °C for 10 h (× 2000).

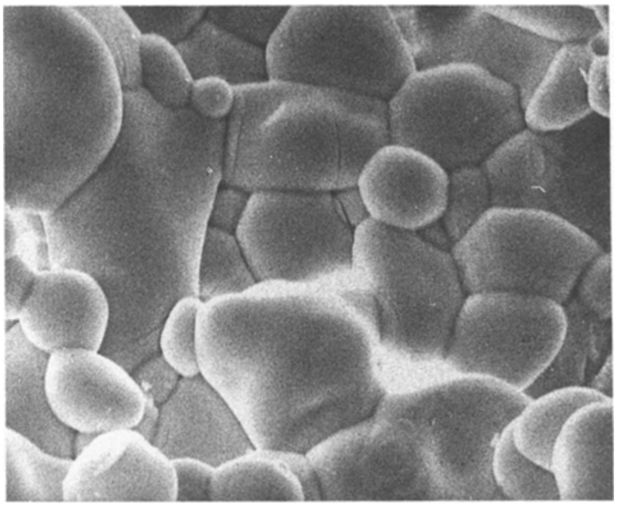

Figure 9 Scanning electron micrograph of 40 mol % TiO_2–HfO_2 material treated at 1500 °C for 15 h (showing the grain size and a few microcracks) (× 2000).

EDS analysis revealed a mixture of grains of HfO_2 and others composed of hafnium and titanium oxides whose composition corresponds to the solid solution $HfTiO_4$ in accordance with the results obtained by X-ray diffraction. Another important point is that both phases of the material were formed by grains of similar size. Fig. 8 shows scanning electron micrographs of microstructure for the sample with 30 mol % TiO_2 heated for 10 h at 1500 °C. The specimens with 36.75 mol % TiO_2 had a microstructure based on $HfTiO_4$ grains with a size from 3–6 µm. Sometimes these grains were assembled forming an extensive microcracked area of about 10–15 µm (Fig. 9). It will be observed that the weak porosity of the materials is in agreement with the density measurements and that for a given heat treatment, the grain size increases with the TiO_2 content.

5. Conclusion

The synthesis of ultra-refractory ceramics with a near-zero thermal expansion coefficient in the HfO_2–TiO_2 system and in the range 30–40 mol % TiO_2 was carried out by an hydrolysis and polycondensation technique using titanium alkoxide and hafnium dichloride oxide alcoholic solutions after heating at moderate temperature. The as-prepared powder, amorphous at room temperature, crystallizes quickly when calcined at 500 °C. Complete crystallization occurs after heating at 1000 °C.

Further thermal treatments at 1500 °C on cold-pressed samples led to ceramics with weak porosity ($\leqslant 7\%$).

The expansion coefficient of products was low ($\leqslant 1 \times 10^{-6}\,°C^{-1}$) with a minimum for 30 mol % TiO_2 content. Dilatometric curves showed an hystheresis loop in relation to a microcracking phenomenon which occurred in the materials. Repeated dilatometric runs involved a small increase of thermal expansion and a decrease of hystheresis loop area. From the fourth run, the curves were stabilized. Quenching in air of the samples after thermal treatment had no effect upon the hystheresis loop area of dilatometric curves but did involve a decrease of the thermal expansion coefficient, probably in relation to the higher rate of microcrack formation during this fast fall of temperature.

SEM examination of as-prepared powders showed a microstructure formed of plates with conchoidal fracture. By EDS analysis, the elements hafnium, titanium and chlorine were detected, the latter arising from the initial component $HfOCl_2 \cdot 8H_2O$.

Heating the powders at 500 °C led to a blowing up of the microstructural plates induced by the volatilization of chlorine, organic groups and crystallization.

After heat treatment at 1000 °C, the powders showed an homogeneous microstructure made of small grains of size 0.1–0.3 μm, increasing with heating time (5–15 h).

SEM examination of fresh fractures on bulk cold-pressed samples fired at 1500 °C, showed a grain size from 2–6 μm. The composition with 30 mol % TiO_2 was a diphasic mixture ($HfO_2 + HfTiO_4$) with the smallest grains (2–3 μm). Higher TiO_2 contents were single phase ($HfTiO_4$) with grains larger in size (3–6 μm). These grains sometimes were assembled forming an extensive fractured area (10–15 μm).

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