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Stability of tetragonal ZrO_2 phase in Al_2O_3 prepared from Zr–Al organometallic compounds

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Zr–Al organometallic compounds have been spray-dried and heated at temperatures 600 to 1400° C to prepare ZrO_2–Al_2O_3 composite powders. The powders consist of balloon-like particles 0.5 to 2 μm in diameter with homogeneously dispersed tetragonal ZrO_2 grains 0.1 to 0.2 μm in diameter. The tetragonal fraction of ZrO_2 in the composite powders is higher than that in the powders prepared from sols of $Zr(OBu^n)_4$* and $Al[OCH(CH_3)_2]_3$*. The fraction is affected by the organofunctional group in the Zr–Al compounds.

1. Introduction

Al_2O_3 ceramics containing dispersed tetragonal ZrO_2 (t-ZrO_2) have high fracture toughness and strength due to microcrack and stress-induced transformation of t-ZrO_2 into monoclinic ZrO_2 (m-ZrO_2) during the fracturing process [1–4]. For dispersed t-ZrO_2 of larger grain size, the transformation to m-ZrO_2 takes place more easily during the sintering process [5], which results in a lesser toughening effect. Therefore, such a toughening may be optimized by reduction of the ZrO_2 grain size. A homogeneous distribution of the grains may favour the toughening effect because it impedes the grains from getting together. ZrO_2-dispersed Al_2O_3 powders have already been fabricated by the sol–gel method [4–6]. The sol–gel process results in a much more intimate mixing of the components than the conventional processes [7]. This suggests that the use of some Zr–Al compounds might yield much better ZrO_2-dispersed Al_2O_3 powders. In these experiments t-ZrO_2-dispersed Al_2O_3 powders have been prepared by spray-drying and heating Zr–Al organometallic compounds (zircoaluminates). The stability of t-ZrO_2 is compared between the powders from the zircoaluminates and those from sols of zirconium and aluminium alkoxides. The effect of the organofunctional groups of the zircoaluminate on the stability of the t-ZrO_2 phase in the calcined powder is also reported.

2. Experimental procedure

A model of the fundamental structure of the zircoaluminate compounds is illustrated in Fig. 1 [8]. The actual structure is not understood exactly, though it is estimated to be more complex than indicated. The compounds are denoted as F, C and A, depending on the organofunctional group R; F = $(CH_2)_{12}CH_3$, C = $(CH_2)_4COOH$ and A = $(CH_2)_2NH_2$. They are supplied by Cavedon Chemical Co., Inc. (Woonsocket, Rhode Island, USA) in the form of about 20% alcohol solutions (commercial names: Cavco Mod F, C and A). Preliminary experiments showed that the ignition loss ranges from 64 to 66 wt % and that the ceramics prepared from F and C consist of 16 vol % ZrO_2 and 84 vol % Al_2O_3 (atomic ratio Zr/Al = 0.12), and that from A consists of 20 vol % ZrO_2 (Zr/Al = 0.16).

The as-received solutions of F, C and A were diluted 5 times with methyl or ethyl alcohol, spray-dried, and dried in an oven at 100° C for 12 h in order to eliminate the solvent. Solutions (0.5 M) of $Zr(OBu^n)_4$ and $Al(OPr^i)_3$ in isopropyl alcohol were mixed together to prepare two solutions, ALK1 and ALK2, of different atomic ratio Zr/Al; ALK1 has the same Zr/Al as F, and ALK2 as A. They were hydrolysed into gels by dropwise additon of water and subsequently 10% solution of NH_4OH. The gels were spray-dried and dried at 110° C for 12 h for evaporation of the solvents. These powders were heated at a rate of 300° C h^{-1} up to temperatures between 600 and 1400° C in air, held at the temperature for 0 to 6 h, and cooled down in the furnace.

The crystalline phases in the heated powders were identified by the X-ray diffraction (XRD) technique using Cu$K\alpha$ radiation. The fraction X_t of t-ZrO_2 in the total amount of ZrO_2 for the powders is a measure of the stability of t-ZrO_2 and can be evaluated by the following equation [9]:

$$X_t = \frac{I(1\,1\,1)_t}{I(1\,1\,1)_t + I(1\,1\,\bar{1})_m + I(1\,1\,1)_m} \times 100 \quad (\%)$$

where I values denote the diffraction intensities corresponding to the (1 1 1) and (1 1 $\bar{1}$) planes of t- and m-ZrO_2. The morphology of the particles was observed under a scanning electron microscope (SEM).

3. Results

3.1. Phases in the heated powders

The amorphous phase, t-ZrO_2, m-ZrO_2 and α-Al_2O_3

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*$Zr(OBu^n)_4$ = $Zr(OC_4Hg^n)_4$; $Al[OCH(CH_3)_2]_3$ = $Al(OPr^i)_3$.

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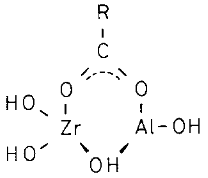

Figure 1 Fundamental structure of a zircoaluminate molecule. (For the organofunctional group, R, see text.)

appeared after the heat treatment, e.g. of C at 800, 1000 and 1400° C as indicated by the XRD patterns in Fig. 2. Table I summarizes the stable phases in each temperature range for all powders. The X-ray amorphous phase was found at lower temperatures in every powder. t-ZrO_2 is the stable phase for C and A at $T \geqslant 900°$C, in F at $T \geqslant 1000°$C, and in ALK1 and ALK2 at $T \geqslant 800°$C. The transformation from amorphous phase to t-ZrO_2 takes place in the powders prepared from the zircoaluminates at temperatures higher than in the powders from alkoxides. The α-Al_2O_3 phase is found after treatment at $T \geqslant 1200°$C in every powder, and the m-ZrO_2 phase appears at $T \geqslant 1200°$C except in F.

3.2. Variation of X_t

X_t is plotted in Figs 3a and b as a function of the heating temperature for powders of different ZrO_2 contents. The effect of the soaking time on X_t for 1400° C treatment is shown in Figs 4a and b. From these figures, one can derive the following:

1. X_t decreases with the heating temperature and time.
2. X_t is larger in the powders prepared from the zircoaluminates than in the alkoxide-derived ones when compared among the powders of the same ZrO_2 content.
3. t-ZrO_2 is stabler in the powders of lower ZrO_2 content.
4. The stability of t-ZrO_2 is dependent on the organofunctional groups in the zircoaluminates.

Fig. 5 illustrates the XRD patterns of powder F (a) as-heated at 1400° C and (b) ground for 5 min in an agate mortar. The intensity of the (1 1 1) diffraction of t-ZrO_2 decreased by grinding, whereas that of (1 1 1) and (1 1 $\bar{1}$) m-ZrO_2 increased. Such changes in the XRD intensity corresponding to the stress-induced transformation from t- to m-ZrO_2 [10, 11] have been observed for all the powders heated at $T \geqslant 1200°$C, but not for those heated at $T \leqslant 1100°$C.

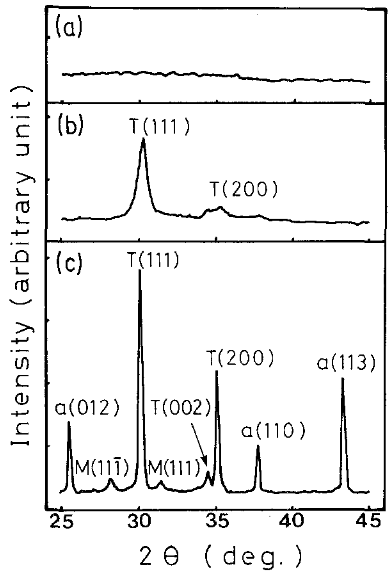

Figure 2 The XRD patterns (Cu*Kα*) of Powder C heated at (a) 800, (b) 1000 and (c) 1400° C. T = tetragonal ZrO_2, M = monoclinic ZrO_2, a = α-Al_2O_3.

3.3. Morphology of the particles

Fig. 6 illustrates SEM photographs of F, C, A and ALK2 heated at 800° C. Fine primary particles have been aggregated to form secondary particles 1 to 4 µm in diameter in ALK2. Hollow balloons 0.5 to 2 µm in diameter are seen in F, C and A where the number of dimples on the balloons seems dependent on the organofunctional group. These balloons, formed in the spray-drying process, hold their shape during the heating. In the SEM photographs (Fig. 7) of F, C, A and ALK2 heated at 1400° C, t-ZrO_2 grains 0.1 to 0.2 µm in diameter are indicated by the brighter spots and distributed homogeneously in the particles of F, C and A, while fine ZrO_2 grains cannot be clearly seen in ALK2.

4. Discussion

It has been observed that the t-ZrO_2 phase transforms to m-ZrO_2 during grinding of the powders after heat

TABLE I Crystalline phases in the heated powders of F, C, A, ALK1 and ALK2*

Temperature (° C)	Crystalline phases			
	F	C	A	ALK1, ALK2
600	Amorphous	Amorphous	Amorphous	Amorphous
700				
800				t-ZrO_2
900		t-ZrO_2	t-ZrO_2	
1000	t-ZrO_2			
1100				t-ZrO_2, δ-Al_2O_3
1200	t-ZrO_2, α-Al_2O_3	t,m-ZrO_2, α-Al_2O_3	t,m-ZrO_2, α-Al_2O_3	t,m-ZrO_2, δ,α-Al_2O_3
1300				t,m-ZrO_2, α-Al_2O_3
1400				

*t-ZrO_2 = tetragonal ZrO_2, m-ZrO_2 = monoclinic ZrO_2.

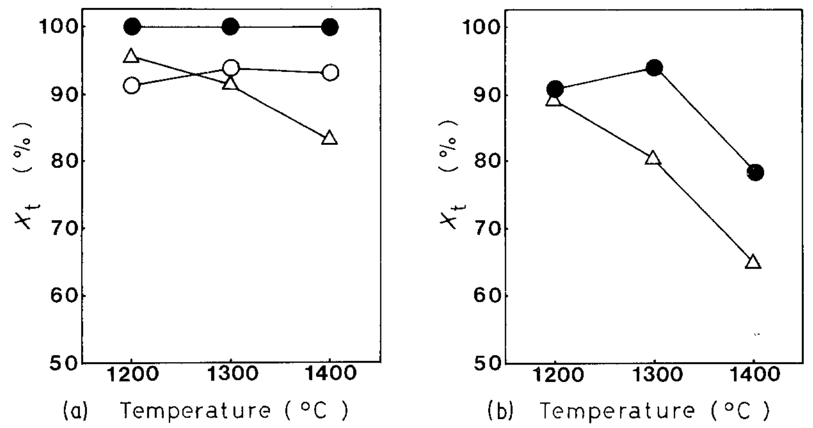

Figure 3 X_t against heating temperature. (a): (●) F, (○) C and (△) ALK1 (16 vol % ZrO_2). (b): (●) A and (△) ALK2 (20 vol % ZrO_2). Heating time 2 h.

treatment at $T \geqslant 1200°C$ but not after treatment at $T \leqslant 1100°C$. Such metastability of t-ZrO_2 in powders heated at $T \leqslant 1100°C$ has been interpreted in terms of the surface energy or the effect of chemically bonded OH groups [12, 13]. In this paper, the stability of t-ZrO_2 will be discussed for the powders treated at $T \geqslant 1200°C$.

Although t-ZrO_2 is stable in every powder during the treatment at $T \geqslant 1200°C$, a part of the tetragonal phase transforms to monoclinic phase during cooling to room temperature. In order to toughen the ZrO_2–Al_2O_3 composites, it is important that a greater amount of t-ZrO_2 should be distributed homogeneously in the Al_2O_3 matrix. A few factors have been proposed to affect the stability of t-ZrO_2. Heuer *et al.* [5] reported that the transformation from the tetragonal phase to the monoclinic one takes place if the temperature M_s for t → m martensite transformation is higher than room temperature, and M_s decreases with decreasing grain size of ZrO_2 in the matrix. It was also shown [5] that t-ZrO_2 grains 0.6 μm or less in diameter were stable. Such dependence of M_s on the grain size is explained on the nucleation crystallization scheme [5]. Moreover, the transformation temperature is dependent on whether the ZrO_2 grains are inter- or intragranular. Intragranular grains are stabler than intergranular ones [5]. Thus, in practice, the stability of the t-ZrO_2 phase in the powders is governed by the grain size of ZrO_2 and whether the grains are inter- or intragranular.

The grain size of ZrO_2 generally increases with the heating temperature, heating time and ZrO_2 content. On this basis, the decrease in X_t can be explained which has been indicated in Figs 3 and 4 and summarized in Section 3.2. The difference in X_t between the powders with the same Zr/Al ratio prepared from different starting materials, e.g. among F, C and ALK1, or between A and ALK2, can be attributed to the homogeneity of distribution of zirconium atoms in the matrix as follows. Metal alkoxide molecules are usually present in alcoholic solutions as polymerized species like $[Al(OPr^i)_3]_n$ or $(Zr(OBu^n)_4]_n$ [14], and thus the co-precipitation of the two oxides from the mixed solution might be difficult due to the difference in the hydrolysis rate of the alkoxides. On the other hand, for the zircoaluminates, the zirconium and aluminium atoms compose molecules together. Therefore, the distribution of zirconium and aluminium atoms can be more homogeneous in the powders prepared from F, C and A than in those from ALK1 and ALK2. The nucleation or growth of ZrO_2 might be retarded by the homogeneous distribution of zirconium atoms in the powders. Thus, such homogeneity in the zirconium distribution results in smaller grains of ZrO_2 in the Al_2O_3 matrix and a higher stability of the tetragonal phase. Moreover, it can be considered that the ZrO_2 grains in F, C and A are of intragranular type, because the ZrO_2 phase appears from a homogeneous amorphous ZrO_2–Al_2O_3 matrix through the nucleation crystallization process. On the other hand, since the individual particles of ZrO_2 and Al_2O_3 are aggregated together in the powders from alkoxides, the ZrO_2 grains are mainly of intergranular type for ALK1 and ALK2. This is another reason for the higher stability of t-ZrO_2 in the powders from the zircoaluminates.

Furthermore, the difference in the stability (X_t) of

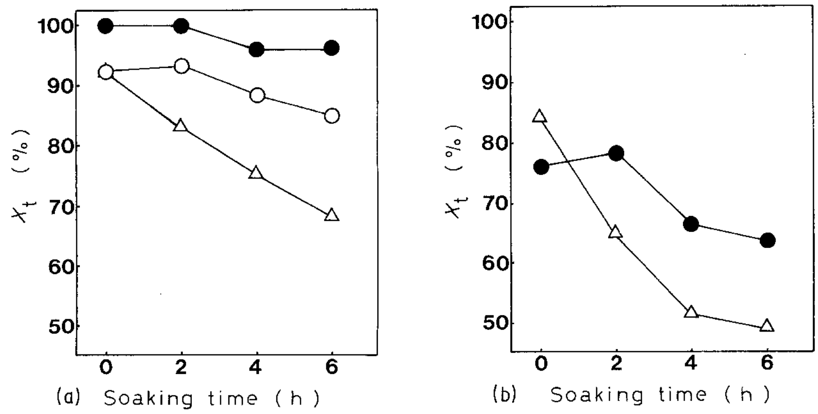

Figure 4 X_t against soaking time. (a): (●) F, (○) C and (△) ALK1 (16 vol % ZrO_2). (b): (●) A and (△) ALK2 (20 vol % ZrO_2). Treatment temperature 1400° C.

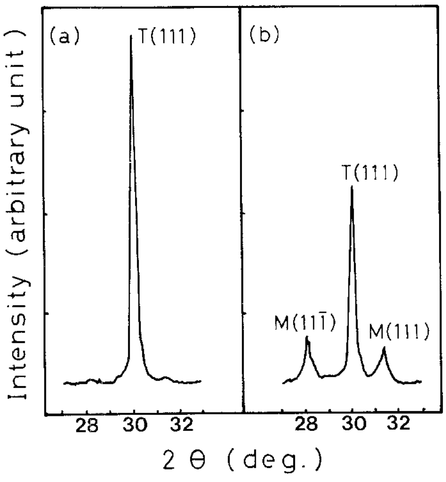

Figure 5 The XRD patterns (Cu$K\alpha$) of Powder F treated at 1400° C (a) as-heated and (b) ground for 5 min. T = tetragonal ZrO_2, M = monoclinic ZrO_2.

t-ZrO_2 between F and C, indicated in Figs 3 and 4, can be attributed to the effect of the organofunctional group on the homogeneity of dispersion of zirconium and aluminium atoms. Although the details of this effect are not thoroughly understood at this stage, this experimental result suggests that the organofunctional groups in organometallic compounds like alkoxides could modify the properties of the gels or ceramics derived from them.

5. Summary

The ZrO_2–Al_2O_3 composite powders prepared by spray-drying and heating zircoaluminates consist of fine balloon-like particles 0.5 to 2 μm in diameter with homogeneously dispersed t-ZrO_2 grains in the Al_2O_3 matrix. The t-ZrO_2 phase is stabler in the powders prepared from zircoaluminates than in the powders from mixtures of $Zr(OBu^n)_4$ and $Al(OPr^i)_3$ because of

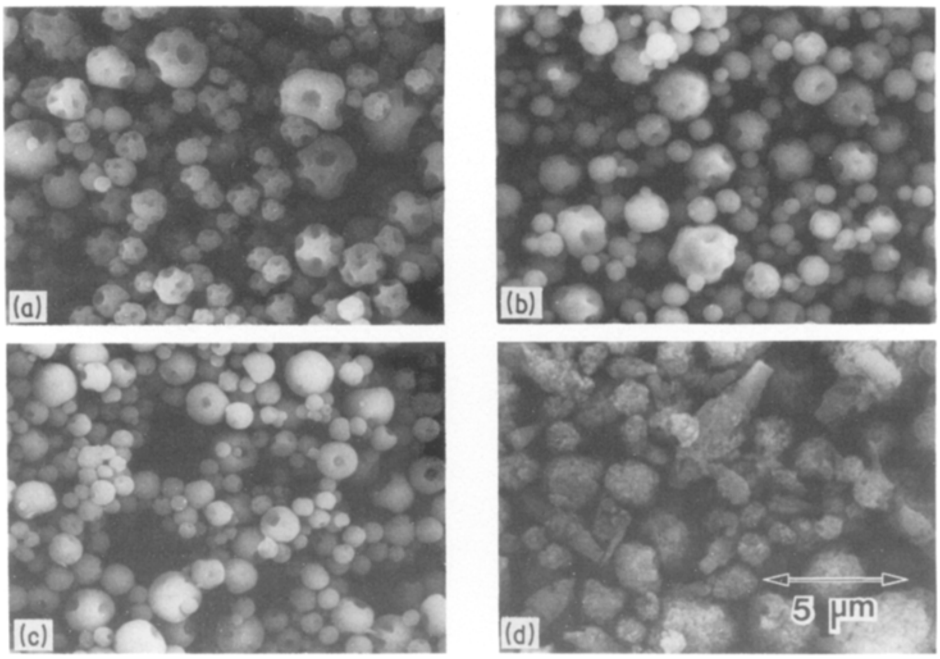

Figure 6 **Scanning electron micrographs of Powders: (a) F, (b) C, (c) A and (d) ALK2 heated for 2 h at 800° C.**

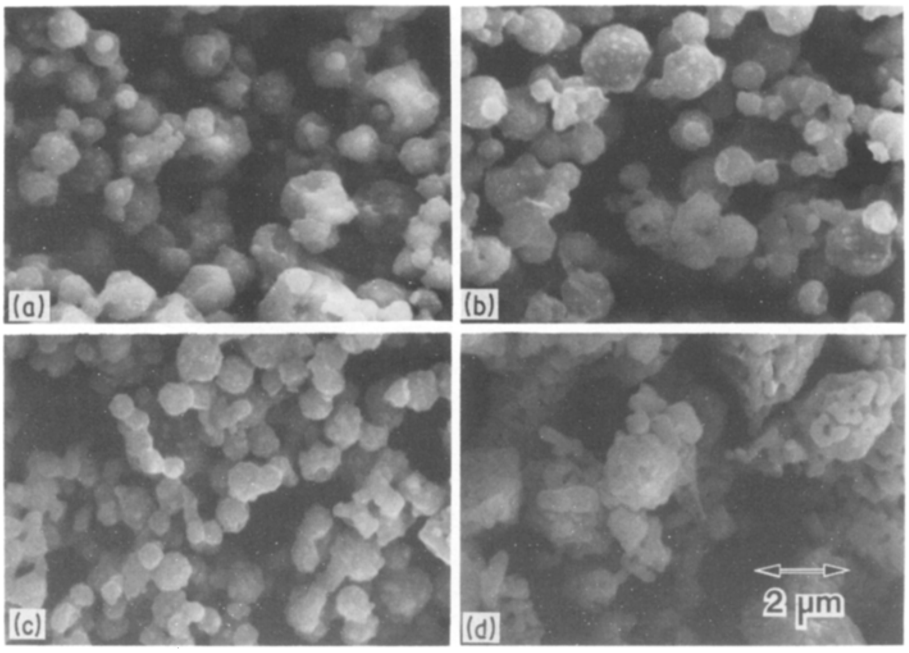

Figure 7 Scanning electron micrographs of Powders: (a) F, (b) C, (c) A and (d) ALK2 heated for 2 h at 1400° C.

the more homogeneous and intragranular distribution of the t-ZrO_2 grains. The stability is also dependent on the organofunctional groups in the zircoaluminates.

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