Journal of the European Ceramic Society **9** (1992) 27–33

Effect of Alumina Restraints on the Stability of Tetragonal Zirconia in Alumina–Zirconia Composite Powders

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(Received 28 November 1990; revised version received 22 May 1991; accepted 13 June 1991)

Abstract

Zirconia–alumina composite powders were prepared by a method of spray-drying mixed oxalate complex solutions. The prepared powders are highly homogeneous and the stability of tetragonal zirconia is greatly enhanced by the alumina restraints surrounding the zirconia particles. Higher alumina contents lead to retarded grain growth of tetragonal zirconia and the enhanced critical size for the phase transformation from tetragonal to monoclinic. The effect of alumina surroundings is explained with a simple zirconia particle–alumina shell model.

Aus einer Oxalatlösung wurden mittels Sprühtrocknung ZrO_2–Al_2O_3 Pulver hergestellt. Die erhaltenen Pulver sind sehr homogen und die Stabilität des t-ZrO_2 wird durch Spannungen, die von einer die ZrO_2-Körner umgebenden Al_2O_3-Schale verursacht werden, stark erhöht. Höhere Al_2O_3-Gehalte führen zu einer Verzögerung des Kornwachstums des t-ZrO_2 und zu einer Vergrößerung der kritischen Korngröße der tetragonal-monoklinen Phasenumwandlung. Die Wirkung des Al_2O_3-Anteils wird auf das einfache Modell eines von einer Al_2O_3-Schale umgebenen ZrO_2-Teilchens zurückgeführt.

On prépare des poudres composites zircone–alumine par atomisation de solutions oxalates. Les poudres ainsi obtenues sont très homogènes et la stabilité de la zircone tétragonale est nettement améliorée du fait de la gêne stérique provoquée par l'alumine entourant les particules de zircone. Des teneurs plus élevées en alumine conduisent à retarder la croissance des grains de la zircone tétragonale et à augmenter la taille critique pour la transformation allotropique tétragonale–monoclinique. L'effet sur la zircone d'un environnement alumine est modélisé simplement par une particule de zircone entourée par une couche d'alumine.

1 Introduction

Composite powders of nanosize are greatly favored as the sintered bodies of such powders show improved properties.$^{1-4}$ In alumina–zirconia composite powders the phase transformation of zirconia particles is affected by the presence of alumina to different extents according to reports given by different authors.$^{5-7}$ The ultimate mixing of two components in composite powders plays a decisive role in affecting the stability of tetragonal zirconia.[7] For the alumina–zirconia powders prepared in this study an initial scale of mixing homogeneity of less than 20 Å in respect to the component separation range is obtained, and the stability of tetragonal zirconia in the composite powders is studied in relation to alumina contents in the composite powders.

2 Experiment

Alumina–zirconia composite powders were prepared by the spray-drying of oxalate complex solutions followed by calcination. The aluminum oxalate and the zirconium oxalate solutions were obtained from their hydroxides in excess oxalic acid solution, respectively. Spray-drying was conducted with a mini-spray-dryer (Brinkmann/Buchi Model 190, Westbury, New York), and the calcination of the powders has a hold of 25 min at all temperatures except 1550°C (for 3 h). The prepared powders were analysed with XRD (Rigaku RAX-10), AEM (Analytical Electron Microscopy), including TEM—

Journal of the European Ceramic Society 0955-2219/92/$5.00

transmission electron microscopy, ED—electron diffraction, EDS—energy dispersive spectroscopy (Jeol JEM-200CX) and XRD–LB—X-ray diffraction-line broadening (Rigaku RAX-10) techniques for the phase structure, particle morphology and grain size measurements, respectively.

3 Results

3.1 Phase structure analysis by XRD

A typical example of phase structure of the composite powder containing 50 mol.% alumina calcined at different temperatures is shown in Fig. 1. The figure illustrates that tetragonal zirconia crystallizes out at not higher than 800°C and the tetragonal phase is stable below 1200°C. Monoclinic zirconia formed from the phase transformation of the tetragonal when calcined at more than 1200°C. Powder containing only 20 mol.% alumina crystallizes at 400°C or so and the phase transformation from tetragonal to monoclinic takes place below 800°C, as shown in Fig. 2. Higher alumina content in composite powders leads to the enhanced stability of tetragonal zirconia. The XRD spectra of the

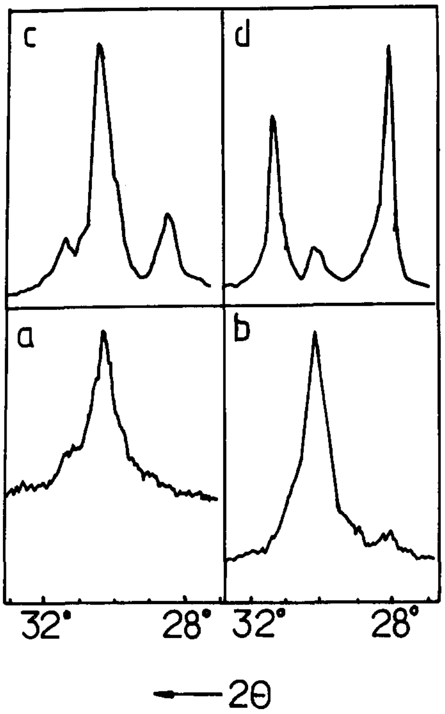


Fig. 2. XRD spectra of 20 mol.% alumina–zirconia composite powder: (a) 420°C; (b) 650°C; (c) 800°C; (d) 1000°C.

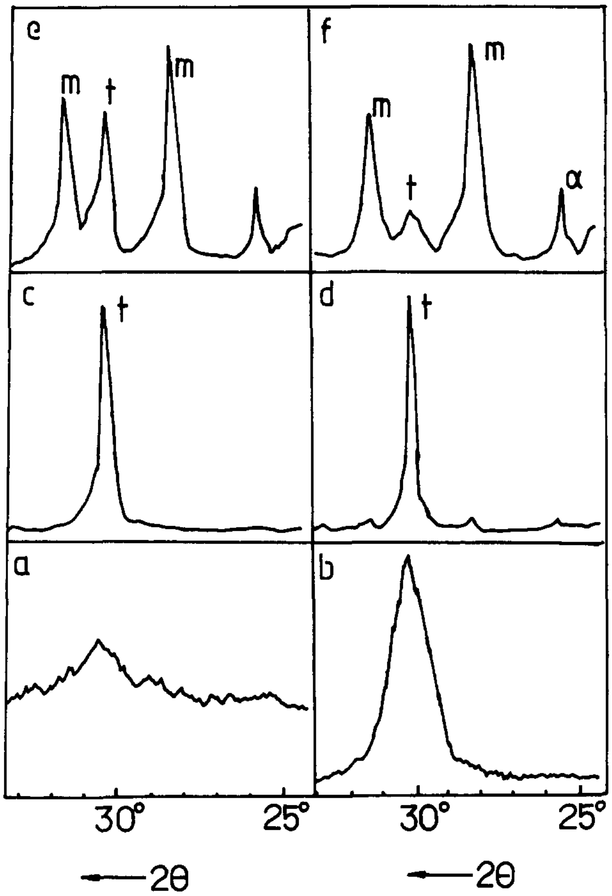


Fig. 1. XRD spectra of 50 mol.% alumina–zirconia composite powder: (a) 700°C; (b) 800°C; (c) 1000°C; (d) 1200°C; (e) 1420°C; (f) 1550°C.

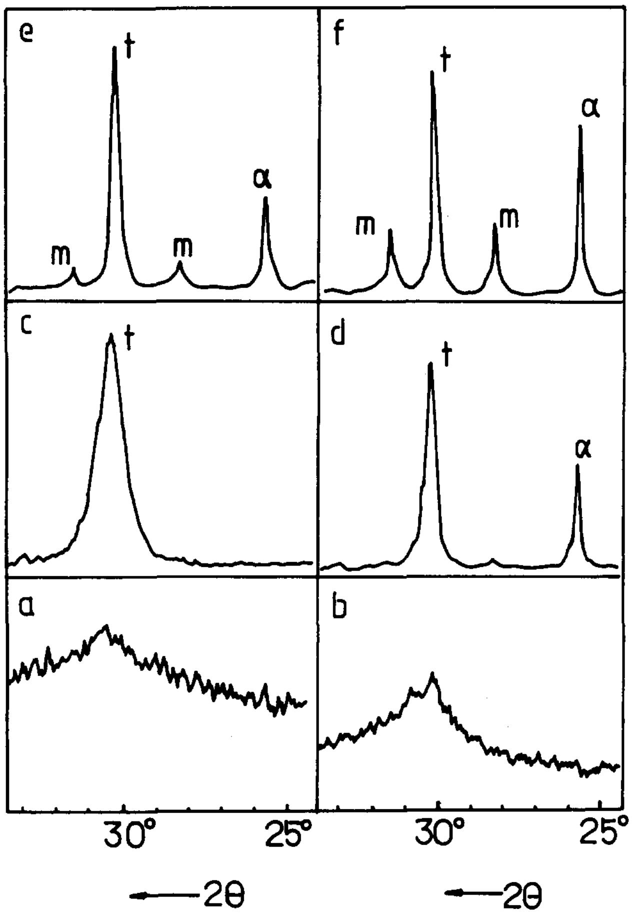


Fig. 3. XRD spectra of 80 mol.% alumina–zirconia composite powder: (a) 700°C; (b) 800°C; (c) 1000°C; (d) 1200°C; (e) 1420°C; (f) 1550°C.

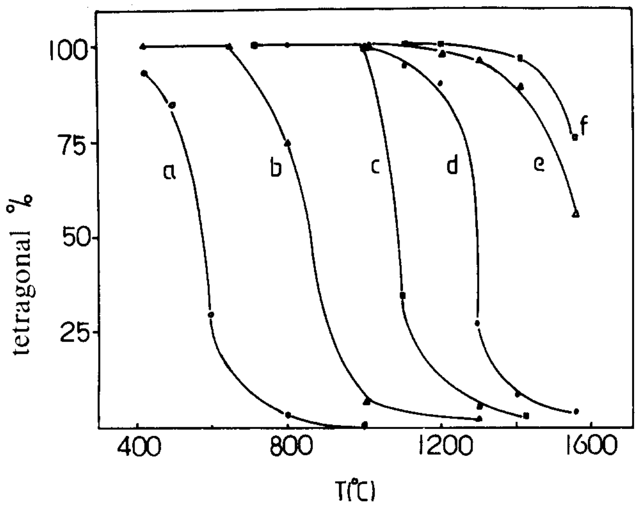


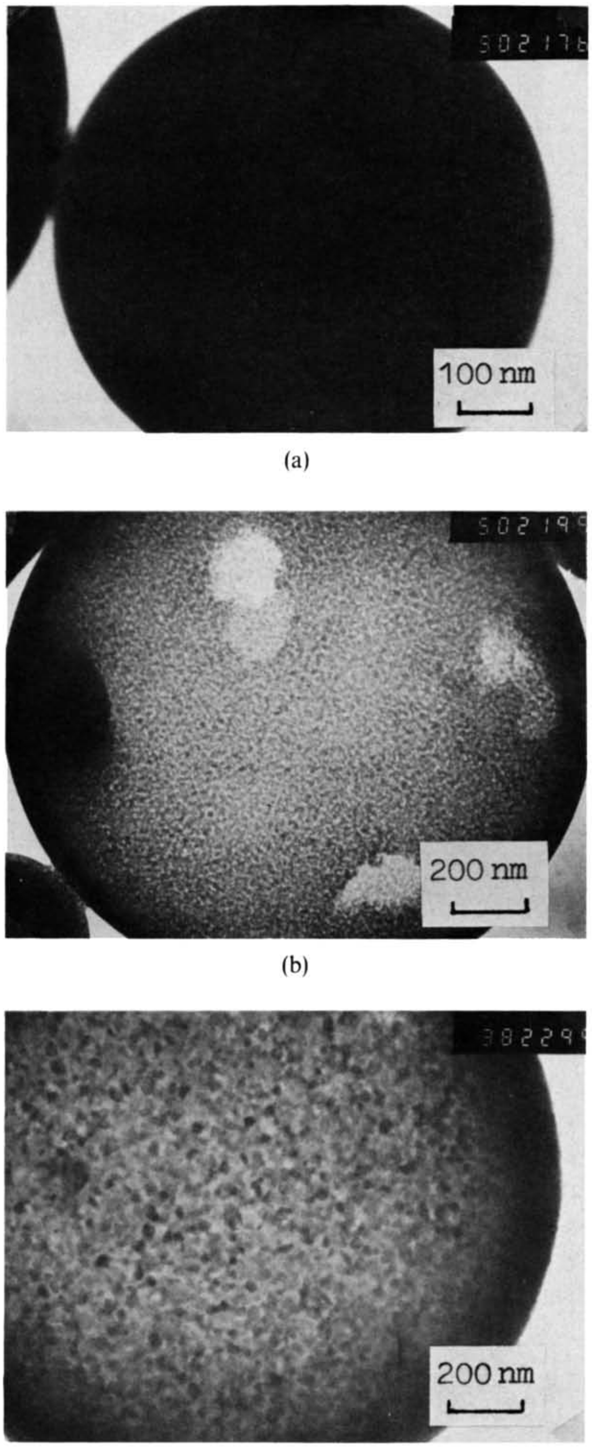
Fig. 4. Tetragonal content versus calcining temperature as a function of alumina content: (a) 0 mol.%; (b) 20 mol.%; (c) 35 mol.%; (d) 50 mol.%; (e) 80 mol.%; (f) 90 mol.%.

composite powder containing 80 mol.% alumina in Fig. 3 show that most tetragonal phase remained after calcining at 1550°C for 3 h. More apparent relationships between alumina content, calcining temperature and tetragonal stability are shown in Fig. 4.

3.2 AEM study of the composite powder

Figure 5 shows the particle morphologies of a 50 mol.% alumina–zirconia powder calcined at different temperatures. It can be seen that at 500°C the spherical particles of micrometer or submicrometer size, which have formed in the spray-drying, are homogeneous to an electron beam and no details of the particles can be seen (Fig. 5(a)). While at 800°C contrasts occur (Fig. 5(b)), illustrating component separation and the crystallization of tetragonal zirconia, as is confirmed in Figs 1 and 4. The components separate from each other more at 1200°C (Fig. 5(c)), and it can also be shown that the darker areas in the spherical particles are an isolated particle-like phase surrounded continuously by the lighter one. Up to 1350°C (Fig. 6) a great morphological change takes place, the previous spherical particles are broken, accompanied by phase transformation at this temperature, as confirmed by the XRD analysis shown in Fig. 4. ED patterns taken on different parts of the particle in Fig. 6(b) show the component separation of alumina and zirconia: zirconia is a particle-like phase with darker contrast (region 'B' in Fig. 6(b)) surrounded by a continuous less dark alumina phase (region 'A'), as illustrated in Fig. 6(d).

Different alumina contents correspond to different phase structures and particle morphologies of composite powders. Figure 7 shows the particle morphology of a 20 mol.% alumina–zirconia powder at 800°C. Spherical particles previously formed in spray-drying are fragmented at this temperature, similar to the phase transformation of tetragonal to monoclinic shown in Fig. 2. As very fine zirconia crystallites are formed from its amorphous state and the phase transformation takes place at a relatively low temperature for pure zirconia[9,10] as well as in

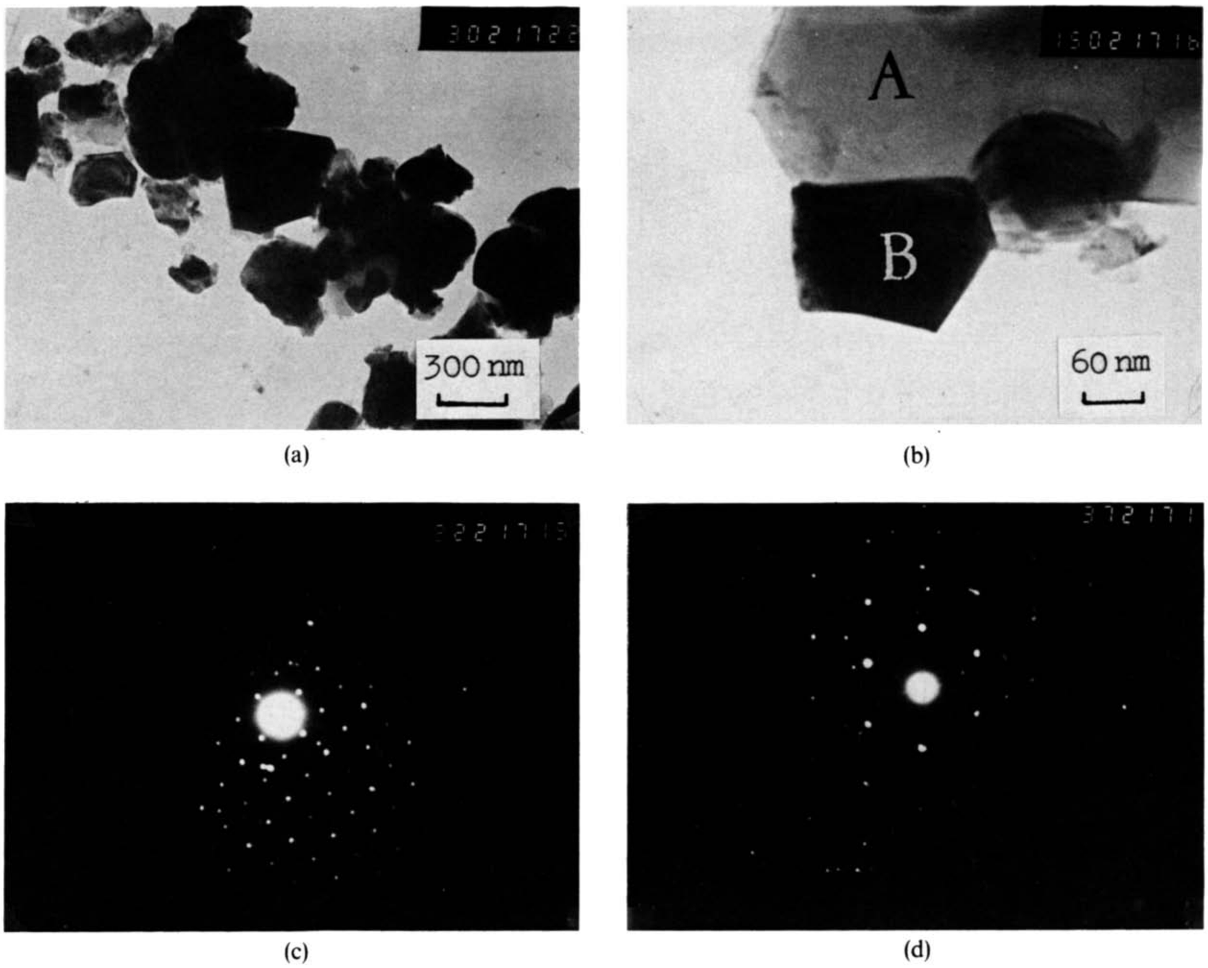


(a)

(b)

(c)

Fig. 5. Particle morphologies of 50 mol.% alumina–zirconia composite powders: (a) 500°C; (b) 800°C; (c) 1000°C.



(a) (b)

(c) (d)

Fig. 6. Particle morphology (a, b) and ED patterns (c, d) of 50 mol.% alumina–zirconia composite powder at 1350°C.

the zirconia-rich composite powders, so the micromorphologies of zirconia continuous phase–alumina isolated particles are not obtained and observed. Higher alumina content can result in a zirconia isolated particle–alumina continuous phase structure and can inhibit the phase transformation, as indicated in Fig. 4, and also prevent the spherical particles from being fragmented, as shown in Fig. 8 for a 80 mol.% alumina–zirconia powder; the spherical particles are maintained up to 1350°C without being fragmented, corresponding to the stability of tetragonal phase shown in Fig. 4. At this same temperature for the 50 mol.% alumina–zirconia powder the spherical particles have been broken and the tetragonal phase starts to transform to the monoclinic phase. The higher magnification of Fig. 8(a) illustrates the homogeneous distribution of darker zirconia particles in the less dark continuous alumina matrix (Fig. 8(b)). Tetragonal zirconia particles are basically spherically shaped, restrained by the alumina surroundings, in the 80 mol.% alumina–zirconia powder.

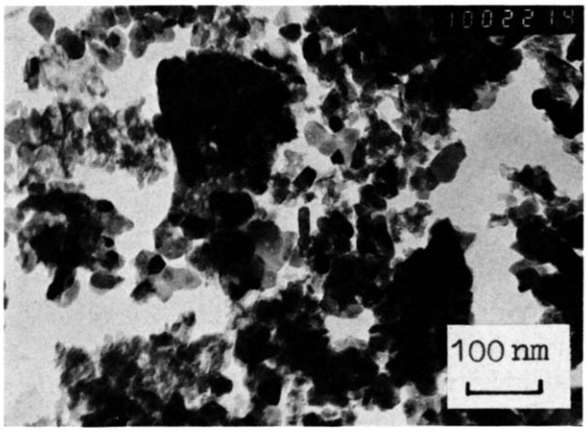
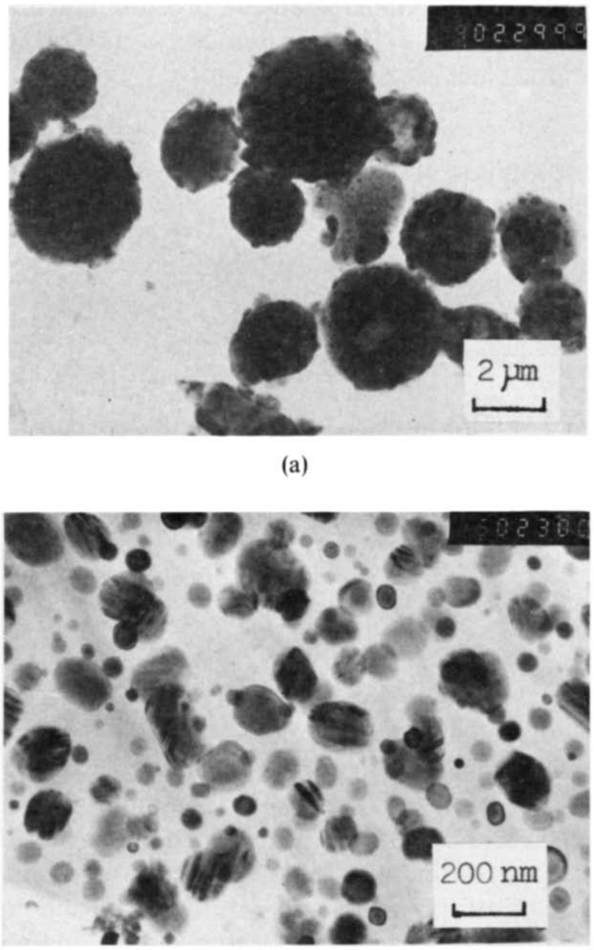


Fig. 7. Particle morphology of 20 mol.% alumina–zirconia composite powder calcined at 800°C.

4 Discussion

For pure superfine zirconia powders particle size plays an important role in the stabilization of the tetragonal phase because of the absence of restraints. Tetragonal zirconia particles larger than a



(a)

(b)

Fig. 8. Particle morphology of 80 mol.% alumina–zirconia composite powder calcined at 1350°C: (a) 5000×; (b) 50 000×.

critical size of about 25 nm[8] are unstable and will transform to monoclinic ones when calcined at about 800°C or less. For the powder prepared in the present study tetragonal zirconia can be stable up to 1350°C for the 80 mol.% alumina–zirconia powder. This phenomenon can result from two factors due to the presence of alumina: the difference in the interface energy between the alumina matrix and the zirconia particles, and the surface energy of the tetragonal zirconia; and the restraints of the alumina surroundings on the tetragonal zirconia particles. As the stability of tetragonal zirconia is ultimately related to alumina content, as shown in Fig. 9, and the surface energy difference is rather limited,[11] so the alumina restraints are thought to be the main factor affecting the stability of tetragonal zirconia.

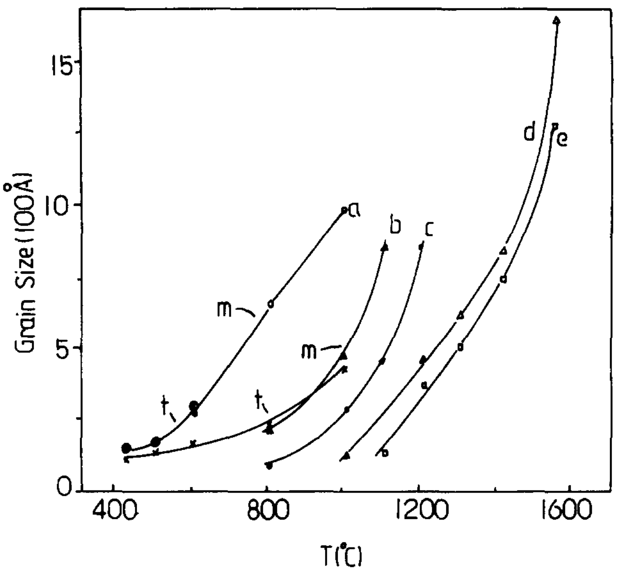


Fig. 9. Grain size of zirconia particles as a function of temperature and alumina content: (a) 10 mol.%; (b) 20 mol.%; (c) 50 mol.%; (d) 80 mol.%; (e) 90 mol.%. All for tetragonal particles except where indicated.

The results have shown the particle morphology characteristics and the relationship between phase transformation and change in particle morphology of alumina–zirconia composite powders. Tetragonal zirconia usually crystallizes out as an isolated phase surrounded by an alumina matrix and the phase transformation is accompanied by the fragmentation of the previously existing spherical particles. Assuming that the crystallized tetragonal zirconia particles in the alumina matrix are spherical and homogeneously distributed in the alumina matrix, and that alumina forms a layer with a certain thickness (t) surrounding the zirconia particles—an alumina shell, which may be amorphous below 1200°C or crystalline (α-phase) at and above 1200°C—and more after the phase transformation, all tetragonal transforms to monoclinic phase with the complete release of the alumina restraints. The assumed particle-shell model and the morphological change during the phase transformation are shown in Fig. 10. Of course, the model only applies when an alumina shell is formed—when the alumina content is not lower than about 50 mol.%, as is true in this study.

XRD spectra are obtained at room temperature after calcination at various temperatures. Above

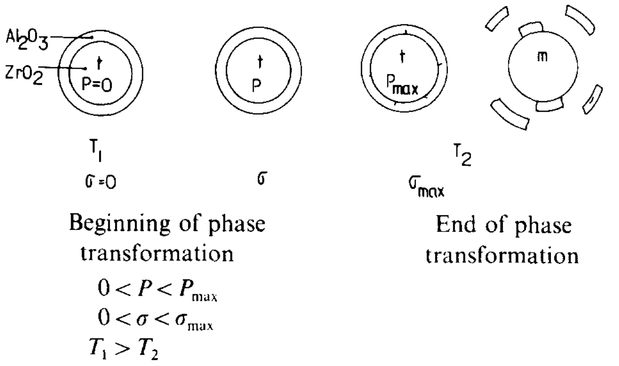


Fig. 10. Schematic of zirconia particle–alumina crust model and the structure change during phase transformation.

1200°C tetragonal zirconia is naturally stable from the thermodynamic point of view. But as the powders are cooled down to room temperature the tetragonal phase tends to transform to the monoclinic phase when particle size exceeds the critical size of 25 nm.[8] The size of most tetragonal particles in the composite powders prepared is above 25 nm, as illustrated in Fig. 9, so during cooling from the calcination temperature the free tetragonal zirconia is expected to transform to monoclinic. Transformation of tetragonal zirconia particles larger than the critical size is, however, restrained by the alumina surroundings for the composite powders, as indicated by the model (Fig. 10). The phase transformation process can be described as

$$\Delta G_{t\rightarrow m} = G_m - G_t + A(\gamma_m - \gamma_{ti}) + V\Delta P$$

where ΔG is the free energy difference for the phase transformation, m and t stand for monoclinic and tetragonal phase, ti means the interface between the tetragonal particles and the alumina matrix, A is the surface (or interface) area, and ΔP is the pressure difference before and after the phase transformation.

If the difference in the expansion coefficients between alumina and zirconia is not considered, the alumina crust will be subjected to a tensile stress (σ) during the phase transformation from tetragonal to monoclinic because of the 3–5% linear expansion accompanying the transformation. When the shell is thin enough the relationship between the pressure on a zirconia particle P and the stress (σ) on an alumina shell is

$$\sigma = Pd/4t$$

here d is the diameter of the particle and t is the thickness of the alumina shell. If the shell thickness is not thin enough to satisfy the equation, the relationship between hoop stress and inner pressure will be complex, but the stress in the shell is certainly a decreasing function of shell thickness and an increasing function of particle size. For simplicity, the model of a thin shell alumina crust is adopted, but the qualitative conclusion may also be appropriate for thick shells.

At the beginning of phase transformation the pressure on the zirconia is zero, and when the transformation reaches the end prior to fragmentation of the alumina shell the pressure reaches a maximum, P_{max}. The tension stress (σ) on the alumina shell is also a maximum, σ_{max}:

$$P_{max} = \sigma_{max} \cdot 4t/d$$

so the phase transformation process can be described as the following:

$$\Delta G_{t\rightarrow m} = G_m - G_t + \frac{6M(\gamma_m - \gamma_{ti})}{\rho d} + \frac{M(4t.\sigma_{max}/d - 0)}{\rho}$$

where M is the molecular weight and t/d is a constant for the given alumina content from the model

$$\frac{[Al_2O_3]}{[ZrO_2]} = \frac{4\pi(d/2)^2.t}{4/3\pi(d/2)^3} = 3/2.t/d = (1-C)/C$$

where C is the zirconia content (volume), so

$$d_k = \frac{6(\gamma_m - \gamma_{ti})}{(\rho/M)(G_t - G_m) - \sigma_{max}.8/3.(1-C)/C}$$

So the alumina restraints can increase the critical size (d_k) phase transformation of tetragonal to monoclinic. With an increase in the alumina content, C decreases and the critical size increases for the phase transformation. Table 1 gives the approximate phase transformation temperature (T, °C) and critical size (d_k) for each composite powder containing different alumina contents. When the alumina content reaches 90 mol.% (91·1 vol.%) the phase transformation basically does not take place for the tetragonal zirconia particles in the alumina surroundings, while the particle sizes of the tetragonal zirconia have reached 140 nm (0·14 μm) after calcination at 1550°C for 3 h. Small amounts of monoclinic phase formed at this temperature are believed to be the result of the phase transformation of those lying at the edges of the previous micrometer or submicrometer ordered spherical particles formed in spray-drying and not fully restrained by the alumina matrix.

The restraining effect is considerably less obvious when alumina contents are less than 50 mol.%. The reason is apparent: at the lower alumina contents the alumina shell is not formed around the zirconia particles and so the resistance for the phase transformation of zirconia particles is limited.

Table 1. Relationship between phase transformation temperature (T_t), critical grain size and zirconia content in Al_2O_3–ZrO_2 composite powders

ZrO_2 (mol.%)	10	20	50	65	80	90	100
T_t (°C)	>1550	≥1550	~1300	~1100	~900	~800	~600
Critical size (nm)[a]	>136	≥200	~90	~40	~35	~30	~30

[a] Estimated from the XRD–LB technique.

5 Summary

The phase transformation of zirconia particles from tetragonal to monoclinic is considerably restrained by alumina presented in highly homogeneous alumina–zirconia composite powders in the alumina-rich region. The increased stability is evidenced by an increase in the critical size for phase transformation by the alumina component surrounding the zirconia particles. With a simple zirconia particle–alumina shell model the restraining phenomenon can be explained. Much less phase transformation restraint by alumina in the zirconia-rich region is because a continuous alumina shell cannot form around the zirconia particles when the alumina contents are low.

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