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Coating of Oxide Powders with Alkoxide Derived Zirconia

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Abstract. Coating of alumina powders with tetragonal zirconia grains in the nanometric size range was obtained from a modified zirconium *n*-propoxide sol.

Powder sedimentation observations and washing experiments were performed to show modifications of particles surface. Amorphous precursor film formation and crystalline zirconia coating were characterized by transmission electron microscopy. Crystallographic relationships between zirconia and alumina particles were also observed.

Keywords: coated alumina, coating, ZrO_2 film, TEM

1. Introduction

Zirconia dispersed ceramics have attracted an important interest because of their enhanced mechanical properties [1–2]. The addition of ZrO_2 has more than one influence. It may act during processing as grain boundary pinning phase and, according to the matrix nature, it may either induce a liquid phase sintering mechanism [3–4] or control the amount of grain boundary glassy phase. Moreover, the mechanisms by which ZrO_2 second phase improves the mechanical behavior are diverse and variable. They may include transformation toughening [3], microcracking and crack deflection mechanisms [5]. In all cases, the particle size, shape and crystallographic form, and the zirconia dispersion within the matrix are the most important factors [2].

In order to control those parameters, and particularly to avoid agglomeration and hence oversized zirconia particles, various methods have been proposed including mixing of hetero-particulate system powders [6], reaction sintering [7], colloidal or sol-gel processing [8]. H.K. Bowen and coworkers [9–10] have proposed to coat alumina powders with alkoxide derived zirconia particles. Zirconia-cordierite [11–12] and zirconia-mullite [4] composite powders, processed by such a route, exhibited an enhanced sinterability. Materials sintered from coated powders also displayed an improved microstructure.

Obviously, properties of sintered materials depend on coating quality and on attachment of nanosized zirconia particles to the ceramic powder surface. The present paper reports preliminary results obtained as part of a work focused on the characterization of zirconia-alumina interface.

2. Experimental Procedure

2.1. Coating process

Zirconium *n*-propoxide (Alfa Products, Danvers, MA 01923, USA) was used as precursor, acetylacetone (acac) as additive and *n*-propanol as solvent to prepare homogeneous sols. A solution of *n*-propanol and water was added to perform hydrolysis. The main parameters were C: zirconium *n*-propoxide concentration; the molar ratio R = [acac]/[$Zr(OR)_4$] and W = [H_2O]/[$Zr(OR)_4$].

Alumina powder (Baikowski, Annecy 74000 France), with a specific surface area of 6 m^2g^{-1} and a mean particle size of about 0.5 μm, was calcined for 10 hours at 1000°C, hydrated for 24 hours at 110°C in proper atmosphere and then dried.

Alumina powders were slowly added and ultrasonically dispersed in the zirconium sol ($C = 0.5$ mol/l, $R = 0.65$, $W = 0$). Powder suspension was mechanically stirred for 8 hours before water introduction ($W = 5$) and the mixture was stirred for 1 hour more. After that, the new suspension was diluted in *n*-

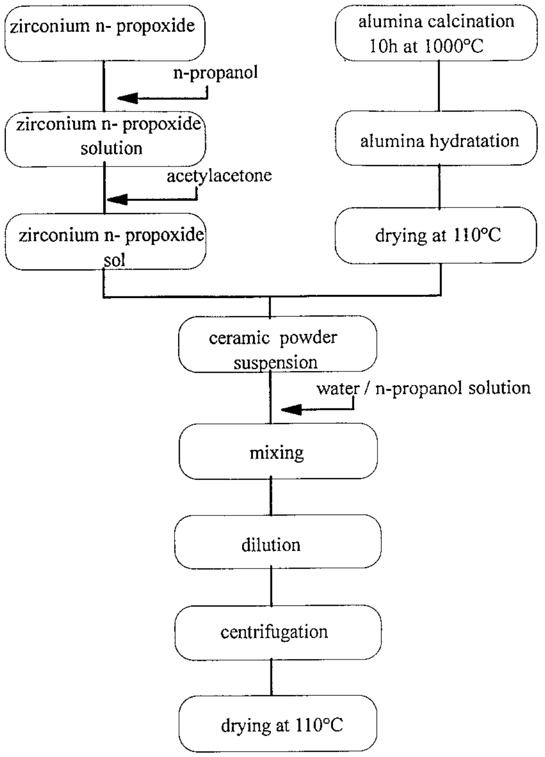

Fig. 1. Flow diagram for coating process.

propanol and then the powder produced was recovered by centrifugation before being dried at 110°C for one day (Fig. 1).

2.2. *Characterization*

The X-rays diffraction experiments were carried out with a Debye-Scherrer camera equipped with a curved position sensitive detector (INEL-CPS120) and a forward quartz monochromator selecting the $\mathrm{CuK}_{\alpha 1}$ radiation.

Transmission Electron Microscopy observations were performed on a Jeol 2010 apparatus fitted with an energy dispersive X-ray spectrometer.

3. Macroscopic Evidences of Surface Modification

3.1. *Sedimentation*

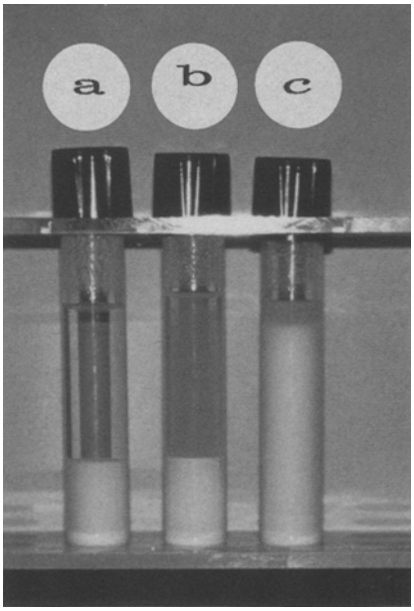

Fig. 2. Alumina particles sedimentation; (a) after dispersion in non hydrolyzed sol ($C = 0.5, R = 0.65, W = 0$). (b) after dispersion into hydrolyzed sol ($C = 0.5, R = 0.65, W = 5$). (c) after dispersion in the same sol. Hydrolysis water was added after alumina powder introduction.

Generally when such alumina powders are dispersed in water sedimentation always occurs, more or less rapidly, according to particle surface interactions. Close to the isoelectric point of alumina, pH9, agglomeration takes place immediately and complete sedimentation of aggregates is observed in a few minutes, leaving a clear supernatant. On the other hand, in acid conditions for example, electrostatic interactions between particles prevent aggregation. Then sedimentation of isolated particles resulting in a rather dense solid sediment is slower and requires at least half an hour. The supernatant has a cloudy appearance. The very small particles that are always present in such powders remain in suspension because of the aggregation free sedimentation mechanism [13].

More specifically for the present case, when alumina particles were mechanically dispersed in the non hydrolyzed sol ($C = 0.5$, $R = 0.65, W = 0$), sedimentation was obtained in a few minutes with a limpid supernatant (Fig. 2a) indicating that agglomeration occurs rapidly.

In the hydrolyzed sol ($C = 0.5, R = 0.65, W = 5$), in which water was introduced before alumina powder dispersion, sedimentation occurred in several hours (Fig. 2b) leaving a cloudy supernatant. This behavior looks like that occurring in water with surface charged particles.

Finally, when the same sol was hydrolyzed after alumina powder introduction, particle sedimentation was

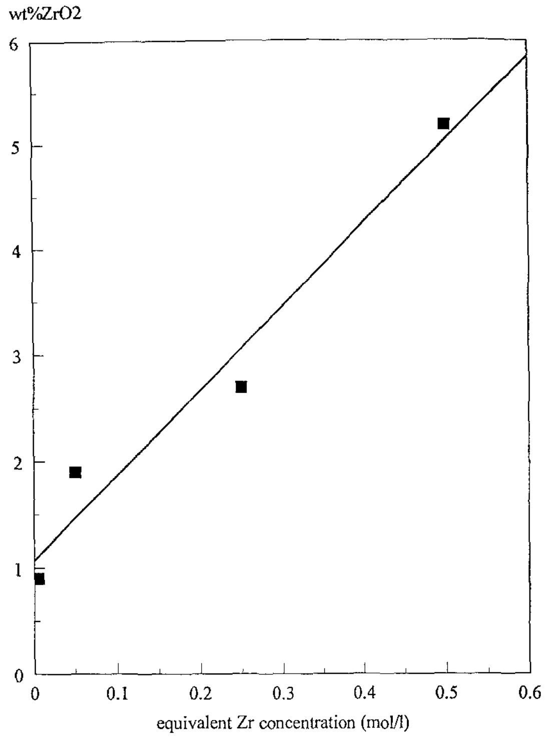

Fig. 3. Final zirconia content (wt%) versus equivalent Zr concentration of diluted slurry (mol/l).

remarkably slowed down (Fig. 2c). It remained incomplete several days later as shown on the photograph of Figure 2 taken four days after introduction of water.

Such striking differences between powder behaviors, and particularly between cases "2b" and "2c", show that the surface of alumina particles is directly and strongly modified by the coating process.

3.2. *Washing*

At the end of the coating process, particles were recovered by centrifugation and the supernatant was poured off. The composite particles were fixed at 1400°C in order to achieve complete crystallization and zirconia content was evaluated from X-ray diffraction pattern. The final ZrO_2 content was much lower than the value anticipated from starting alkoxide concentration.

Some "dilution" experiments were carried out before centrifuging by adding a volume of n-propanol chosen to expand one, ten or hundred times the suspension volume. However, the results plotted in Figure 3 show that some amount of zirconia precursor remained non sensitive to the dilution. This amount of precursor that leads in that case of 1 wt% of final crystalline phase after heat treatment, probably corresponds to a zirconia precursor film covering the alumina particles.

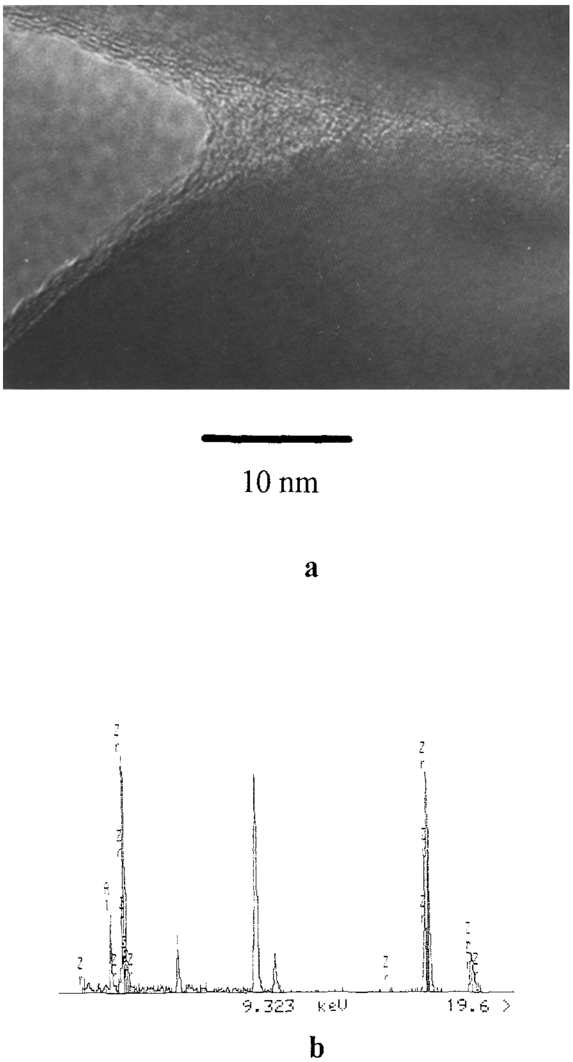

Fig. 4. Coated alumina particle calcined at 600°C for 1 hour. (a) Transmission Electron Micrograph of zirconia amorphous precursor film. (b) Energy Dispersive X-Ray Analysis of precursor film.

4. TEM Observations of Coated Powders

Alumina coated particles, sedimented by centrifugation after "dilution" in n-propanol, were calcined for 1 hour at 600°C. A continuous film of zirconia precursor (Fig. 4), of about 2 nm in thickness, was covering all alumina particles.

Firing for 1 hour at 800°C initiated crystallization and small ZrO_2 tetragonal crystals appeared in the precursor film (Fig. 5).

After complete crystallization at 1400°C, ZrO_2 crystals have grown (Fig. 6a). In several cases the same crystallographic relationships between a zirconia tetragonal crystal and its alumina grain substrate were observed (Fig. 6b); Zirconia [110] direction was parallel to alumina $[11\bar{2}0]$ direction.

5. Conclusion

Coating of Al_2O_3 particles with a continuous film of amorphous ZrO_2 precursor was obtained in a modified Zr n-propoxide sol. The film was directly formed onto the particles surface and did not result from hetero coagulation of condensed entities. The temperature range for crystallization in the film was modified and slightly higher than that of pure xerogels. A high amount of metastable tetragonal ZrO_2 was obtained after heat treating at 1400°C. Crystallographic relationships between zirconia and alumina grains were observed and need to be precisely stated.

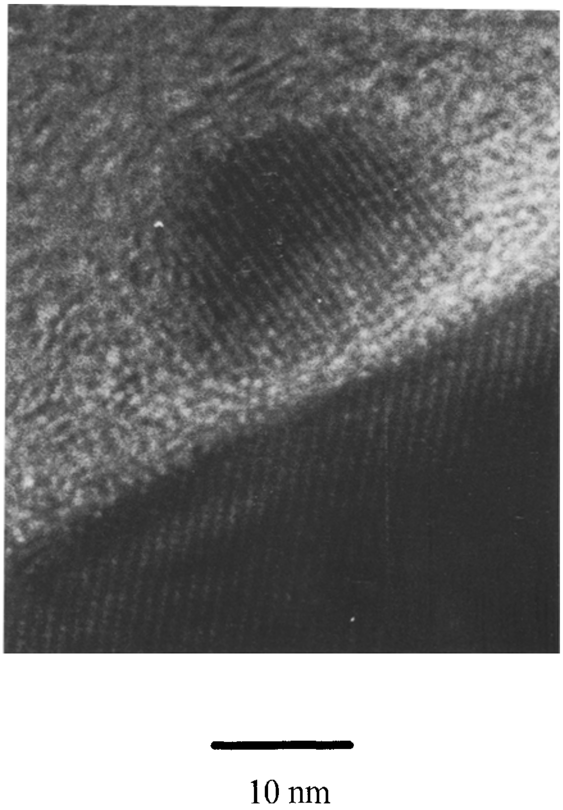

Fig. 5 Transmission Electron Micrograph of coated alumina particle fired at 800°C for one hour, showing an isolated tetragonal zirconia grain.

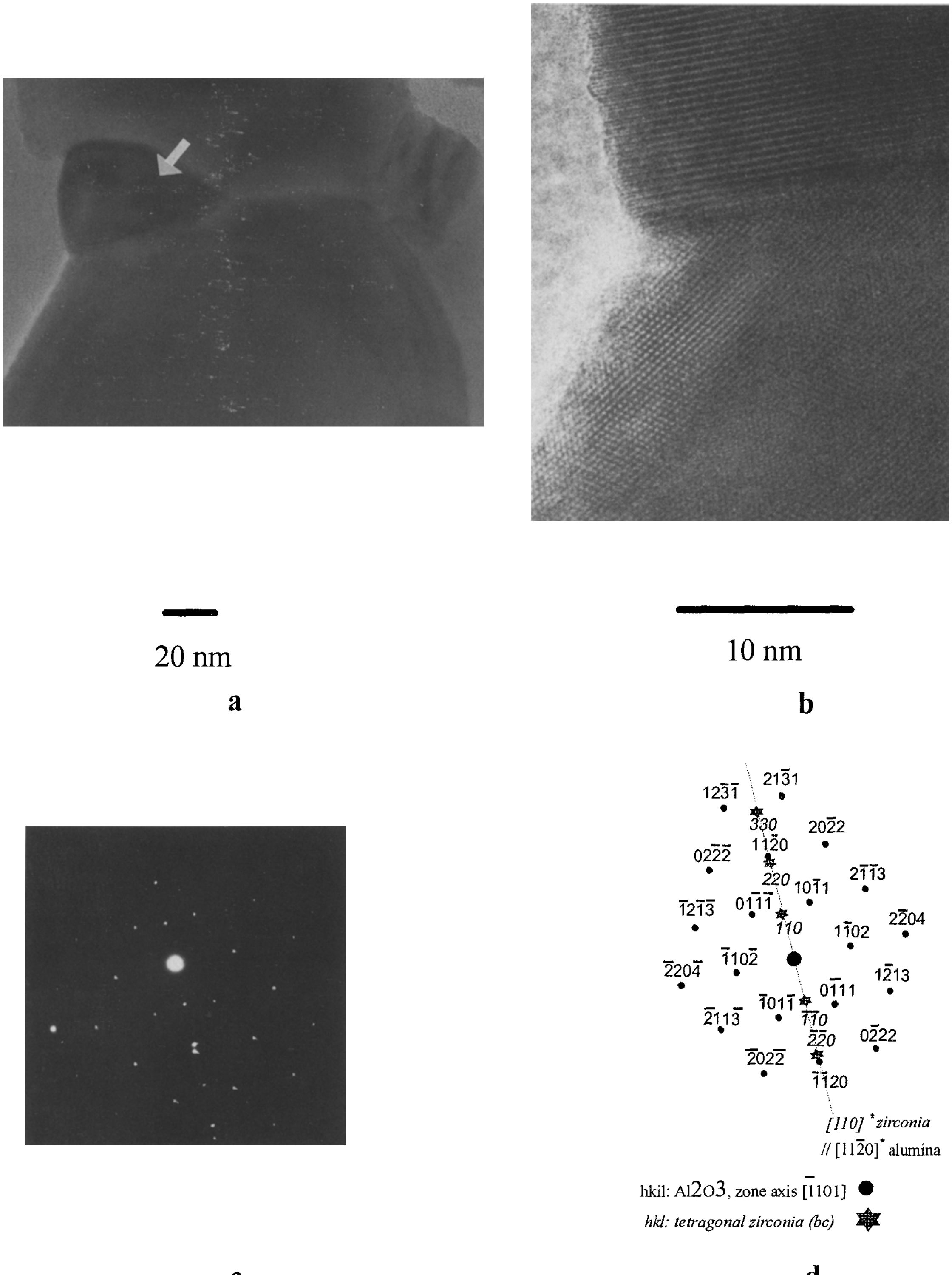

Fig. 6. Coated alumina particle fired at 1400°C for 10 minutes. (a) T.E.M. image showing intercrystalline tetragonal zirconia grain (arrowed). (b) T.E.M. image of tetragonal zirconia alumina interface. (c) Corresponding diffraction patterns. (d) Indexation of diffraction patterns.

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