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Characterization of Metastable ZrO_2-Y_2O_3-Al_2O_3 Mixed Nanocrystals

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ZrO_2-based materials have a large range of applications such as refractory ceramics, high surface area catalyst/catalyst support, oxygen sensor, solid oxide fuel cells electrolyte and gate dielectrics [1-4]. Doping zirconia with yttria or alumina to stabilize the tetragonal phase provides unusual toughening for a wide variety of mechanical applications. Such kind of ceramic composites are usually prepared by mixing and sintering conventionally available oxide powders. Nevertheless, obtaining dense ceramic composites with inhibition of grain growth during sintering is still a demanding task. Metastable powders were successfully employed to retain small crystallite sizes and good distribution of secondary phase. Several methods, such as atmospheric plasma spraying (APS) [5] and flame spray pyrolysis (FPS) [6] are promising techniques to obtain ceramic materials with a high degree of metastability. Compared to APS, the mixed oxide prepared by FSP has a much higher surface area, smaller size and lower degree of agglomeration what should help, in addition, to increase the sinterability. In this presentation, ZrO_2-5mol%Y_2O_3-5mol%Al_2O_3 prepared by FSP is studied by aberration corrected TEM and EDX spectrum imaging to obtain the crystalline structures and element distribution of the mixed oxides particulates.

Samples with nominal composition ZrO_2-5mol%Y_2O_3-5mol%Al_2O_3 were prepared by flame spray pyrolysis from a solution of Zr(IV)-n-propoxide, Al(III)-sec-butoxide and Yttrium nitrate hexahydrate in toluene. The solution was sprayed with 3 liters/minute of oxygen into a premixed annular methane/oxygen flame where combustion takes place. An additional oxygen sheath gas of 8 liters/minute was added to guarantee complete oxidation of the precursor droplets. The prepared particles were separated from the gas stream using a binder-free glass fiber filter.

The metastable mixed oxide consists of mostly spherical particles with average diameter of about 13 nm. Some particles bigger than 100 nm are also observed. Selected area electron diffraction pattern including a large amount of particles indicates that the crystal is of tetragonal zirconia structure. The aberration corrected HRTEM images show that each particle is perfect single crystal. Figure 1a shows one particle on [111] zone axis. A considerable amount of particles are bound together without specific correlation in orientation, as shown in Figure 1b. Some ill defined surface layers are also observed on spherical shaped particles therefore the particles are not necessarily terminated by low-index planes. EDX spectrum imaging was acquired from a few particles, and the STEM image with Zr, Y and Al maps are shown in Figure 3. It clearly indicates the formation of ZrO_2-Y_2O_3-Al_2O_3 solid solution with fairly homogeneous distribution of the three elements within particles. The quantitative analysis on the integrated EDX spectrum over the mapping area (shown in Figure 2b) suggests a molar ratio of Zr:Y:Al = 70:12:18, i.e., ZrO_2:Y_2O_3:Al_2O_3 = 82:7:11. Statistically, other areas show similar results but with fluctuations to some extent. The deviation of the EDX results from the nominal composition could be due to the standardless analysis used in EDX quantification.

The TEM investigation clearly shows that ZrO_2-5mol%Y_2O_3-5mol%Al_2O_3 nanocrystalline ceramic powders was successfully synthesized by FPS method. The high combustion temperature and the high quenching rate make it possible to obtain metastable mixed oxides between two oxides which

are insoluble to each other. The obtained material can be further sintered to fully dense and fine grained ceramics. The structure evolution during sintering and its effect in obtaining full dense ceramic will be studied in the next step.

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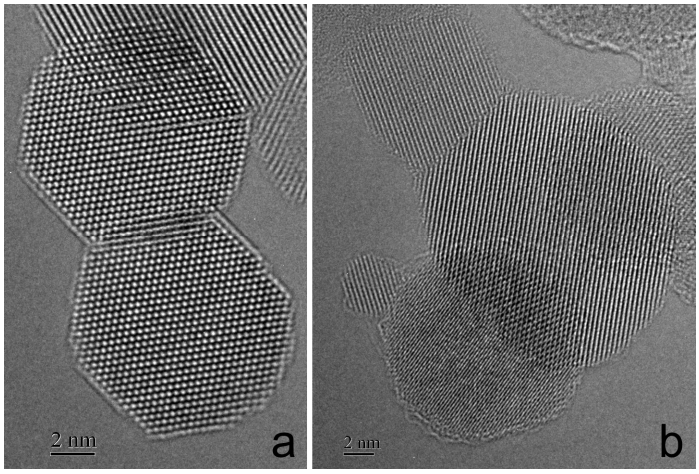

FIG. 1. Aberration corrected HRTEM image of a) two particles with tetragonal zirconia structure on [111] zone axis, and b) particle binding and surface layers for spherical particles.

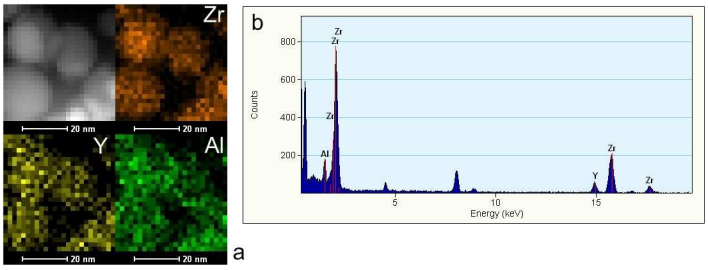

FIG. 2. EDX spectrum imaging. b) STEM image with Zr, Y and Al maps. b) integrated EDX spectrum corresponding to the imaging area.

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