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Phase amorphization during high-energy milling of mixtures of zirconia with yttria or ceria powders

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Abstract. Phase amorphization studies were carried out on mixtures of commercial zirconia and yttria or ceria powders prepared by to high-energy milling. The structural characterization of powders was performed by X-ray diffraction. The specific surface area was determined by nitrogen adsorption, and morphology of powder particles was observed by scanning electron microscopy. For the mixture of zirconia and yttria, the amorphization of yttria is clearly observed for short times of milling, whereas the structure of zirconia remains almost unchanged. The mixture of zirconia and ceria reveals a different degree of amorphization, which occurs simultaneous and gradually with large milling times.

Introduction

Zirconia-based ceramics are important materials for high-technology applications not only as a structural ceramic but also as a functional material [1]. Interest in nanocrystalline zirconia ceramics has increased in the last decade as their properties are often considerably improved compared with conventional zirconia ceramics.

Over the last few years, a great deal of work has been made on the production of ultrafine ceramic powders. Both technological and scientific interests in ultrafine-grained powders for processing of ceramic components are motivated by the promise of improved sinterability, reduction in flaw sizes and low-temperature superplastic deformation. Other improvements in materials properties are related to enhanced homogeneity, transparence in opaque ceramics, and giant magnetoresistance [2].

Nanocrystalline materials have been synthesized by a number of techniques comprising all three phases, namely, the solid phase, the solution phase, as well as the vapor phase [3].

High-energy milling is a solid phase technique more recently proposed for the preparation of ultrafine ceramic powders, because the brittle components get fragmented during milling and their particle size gets reduced continuously [4]. Besides the reduction of the average particle size, in the case of zirconia-based ceramics, other phenomena have been observed during high-energy milling, such as solid solution formation [5], structural phase transition [6], and amorphization [7]. The mechanism of amorphization by high-energy milling is not clearly understood. However, the amorphous phase formation is known to be critically dependent on the milling conditions [8].

The present paper reports the amorphization behavior during high-energy milling of zirconia and ceria or yttria mixtures. The structural characterization was carried out by X-ray diffraction, the main microstructural characteristics were obtained by scanning electron microscopy, and the evolution of specific surface area was followed by nitrogen adsorption.

Experimental Procedures

ZrO_2 (99.7%) and Y_2O_3 (99.9%) were mixed to provide a composition of ZrO_2-10 mol.% Y_2O_3. For milling experiments, a cylindrical teflon vial and stainless steel balls were used. The ball-to-powder mass ratio was 9:1. For the mixture zirconia-12 mol.% ceria, high purity ZrO_2 (TZ0, Tosoh) and CeO_2 (99.9%, Aldrich) powders were charged in a zirconia vial together with zirconia balls. In this case, the ball-to-powder mass ratio was 3:1. Typical mass of starting materials was 10 g. High-energy milling was carried out in air in a vibratory mill (Spex 8000, Spex Industries) at an oscillation frequency of 20 Hz. Milling was interrupted every 4 h to prevent the temperature of powder mixture from rising too high, for longer milling times.

The morphologies of powder materials were characterized by scanning electron microscopy, SEM, (XL30, Philips) using secondary electrons. The specific surface area of powder mixtures was analyzed using five-point Brunauer, Emmett and Teller (BET) method by nitrogen adsorption (ASAP 2010, Micromeritics). Powder X-ray diffraction patterns were recorded with a diffractometer (D8 Advance, Bruker-AXS) using a Ni-filtered Cu K_α radiation (40 kV and 40 mA), in the 20º to 80º 2θ range. Differential thermal analysis (STA409, Netzsch) was conducted in synthetic air up to 1200 ºC heating at a rate of 5 ºC. min^{-1}. α-Alumina was used as reference material.

Results and Discussion

Fig. 1 shows X-ray diffraction patterns of zirconia-ceria powders with different milling times. It can be seen the main reflections of monoclinic zirconia structure (P21/c space group), and the fluorite-type structure (Fm3m space group) of ceria before milling (0 h). Similar diffraction patterns were obtained for milling times up to 20 h. After milling for 30 h, the sharp crystalline reflections of the starting powders have disappeared, indicating that the crystal structures of the starting materials were modified by high-energy milling. A similar result was obtained for zirconia-30 mol.% ceria milled under different experimental conditions [7].

X-ray diffraction patterns for the mixture of zirconia-yttria before (0 h) and after milling are shown in Fig. 2. It may be observed the monoclinic structure of zirconia and the C-type structure (Fm3 space group) of yttria, before milling (0 h). The main monoclinic reflection at 2θ equal to 28.2º remains unchanged with milling time. In contrast, the (111) main reflection of yttria at 2θ equal to 29.4º decreases gradually with milling. This result indicates that only yttria became amorphous with milling.

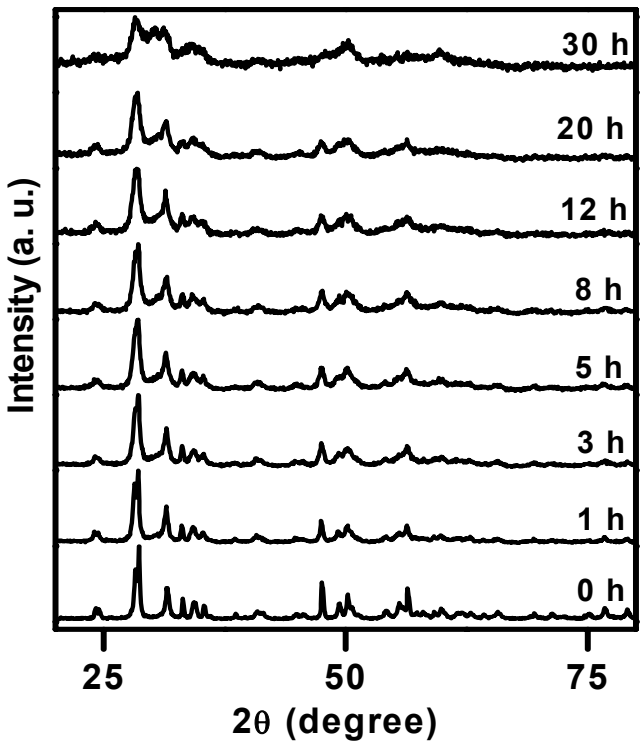

Fig. 1: X-ray diffraction patterns of zirconia-12 mol.% ceria mixture before (0 h) and after high-energy milling.

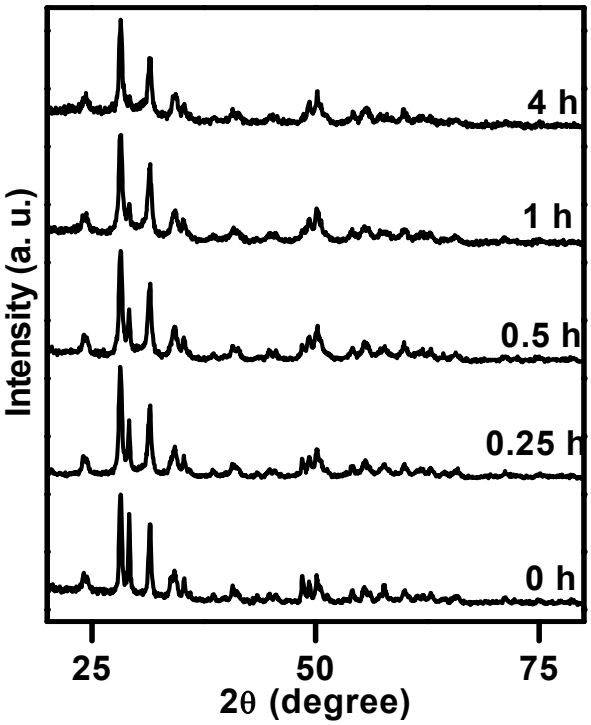

Fig. 2: X-ray diffraction patterns of zirconia-10 mol.% yttria mixture before (0 h) and after high-energy milling.

Fig. 3 shows SEM micrographs obtained for the zirconia-ceria mixture after milling for 1 h (Fig. 3a) and 30 h (Fig. 3b).

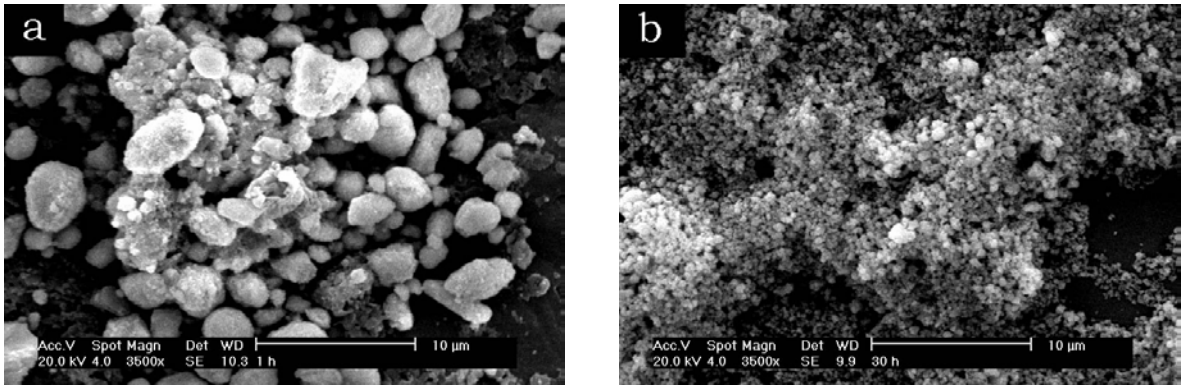

Fig. 3: SEM micrographs of zirconia-12 mol.% ceria mixture after milling for 1 h (a) and 30 h (b).

The morphology of powder mixtures consists of agglomerated particles. The main difference concerning the microstructure of these powders is related to the agglomerate size. An average size of 5 µm may be estimated for the powder milled for 1 h, whereas after 30 h of milling the size of agglomerates was drastically reduced to a submicron range.

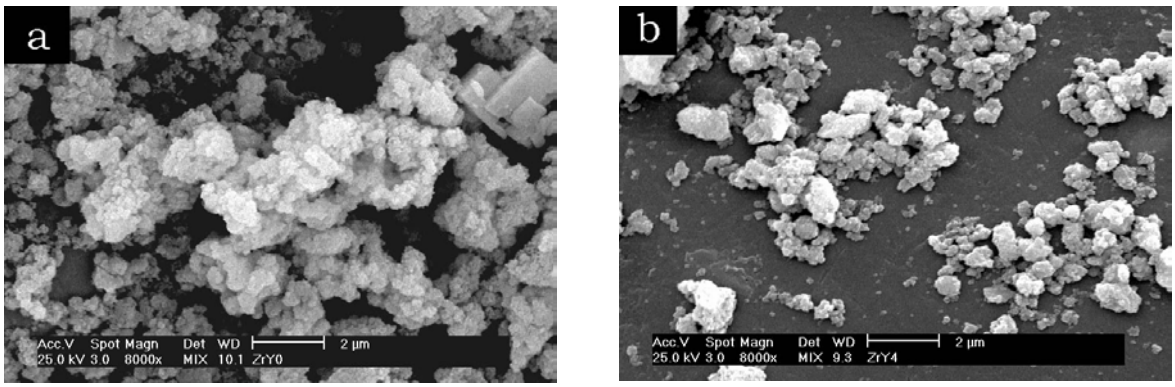

Fig. 4: SEM micrographs of zirconia-10 mol.% yttria mixture before (a) and after (b) 4 h milling.

SEM micrographs of zirconia-10 mol.% yttria mixtures before (a) and after (b) 4 h milling are shown in Fig. 4. The commercial zirconia powder was originally fine with particle size about 40% below 1 µm, whereas ceria particles had an initial average particle size of 4 µm. After milling for 4 h, uniform distributions of particle and agglomerate size were obtained.

The evolution of the specific surface area with milling time is shown in Fig. 5. For zirconia-ceria mixed powders the specific surface area increases up to 3 h of milling, and then it remains almost constant up to 20 h . For longer times of milling the specific surface area value slightly decreases. The initial increase in the specific surface area may be related to the fragmentation of particles. The decrease in S value for longer milling times seems to be associated with the start of the amorphization process of this powder mixture, since it occurred simultaneous with the widening of characteristic diffraction peaks.

The variation of the specific surface area for the mixture of zirconia and yttria powders, in contrast, increases greatly with milling time. This is a typical result of fragmentation of brittle particles.

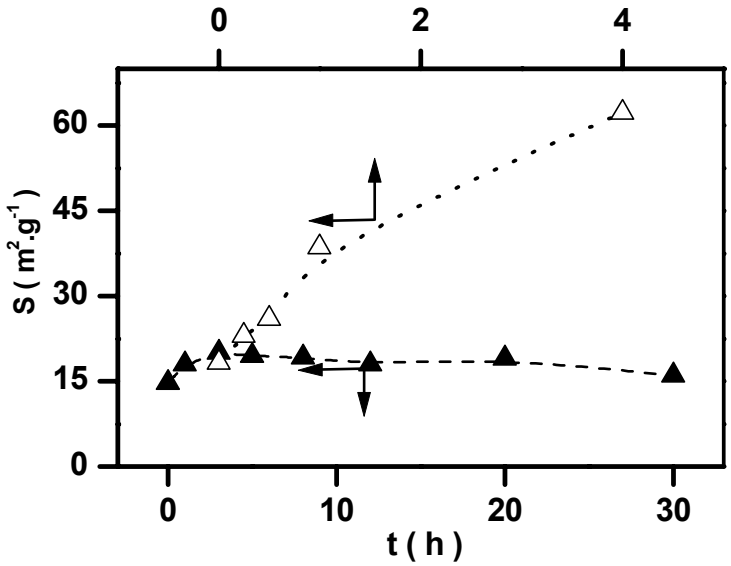

Fig. 5: Variation of the specific surface area with the milling time for zirconia-ceria (full symbol) and zirconia-yttria (open symbol) mixtures.

As discussed in [8], the presence of broad peaks in X-ray diffraction patterns is not sufficient to distinguish amongst materials which are amorphous or extremely fine grained, or a material in which very small crystals are embedded in an amorphous matrix. Results obtained for the zirconia-ceria mixture point to the amorphization process during high-energy milling. For the zirconia-yttria mixture, the reduction in the intensity of the most prominent X-ray peak along with the decrease in the particle size indicates that a very fine structure was obtained with milling.

To determine the exact nature of the observed phenomena, DTA experiments were carried out on these powder materials after milling (Fig. 6).

The presence of an exothermic peak (300-400 ºC) on heating the samples indicates that crystallization of an amorphous phase has occurred. It should be noted the broad exothermic peak in the case of zirconia-ceria showing that not all powder material is amorphous in agreement with the X-ray diffraction pattern.

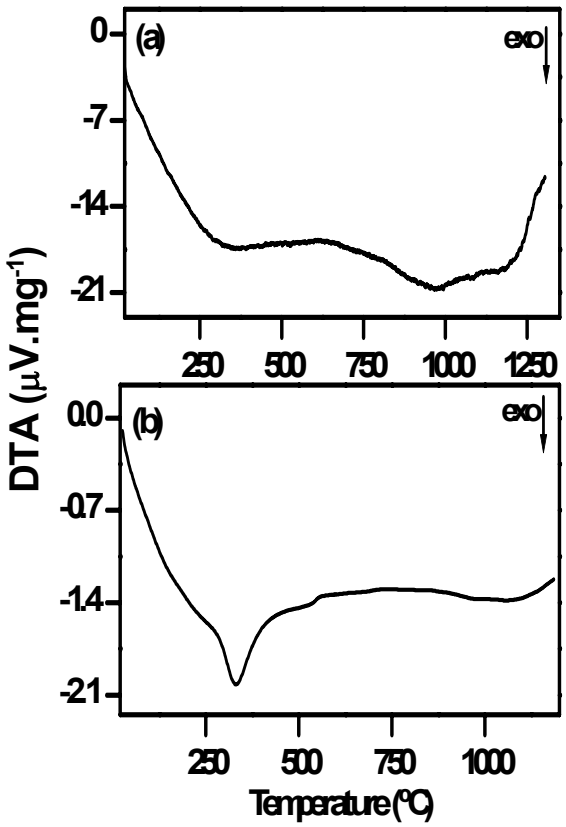

Fig. 6: DTA curves of zirconia-ceria (a) and zirconia-yttria (b) powder mixtures after milling for 30 h and 4 h, respectively.

Conclusions

High-energy milling of zirconia-ceria and zirconia-yttria mixtures resulted in a modification of the structure and agglomeration state of powder materials. The evolution of the specific surface area with milling time is different for these mixtures. The amorphization phenomenon in somewhat different extents was verified by differential thermal analysis.

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