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Monoclinic to cubic phase transformation of ZrO_2 induced by ball milling

XIANGFA LIU, ZHENQING WANG*, XIUFANG BIAN
Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University (Southern Campus), No. 73, Jingshi Road, Jinan 250061, People's Republic of China
E-mail: wzhtsing@yahoo.com.cn

Besides synthesizing a variety of equilibrium and non-equilibrium alloy phases, e.g., supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys, ball milling is a method of inducing phase transformation in solids. Polymorphic transformations induced by ball milling in some oxides such as Fe_2O_3 [1], Al_2O_3 [2], TiO_2 [3], have previously been observed and the corresponding mechanisms analyzed. Pure ZrO_2 exists in nature in three polymorphs: monoclinic, tetragonal and cubic. The transformation of ZrO_2 from tetragonal to monoclinic phase during ball milling has been found constantly in previous studies [4, 5]. In this paper, we will report the monoclinic $\rightarrow$ cubic polymorphic transformation of ZrO_2 induced by ball milling.

Ball milling of commercial monoclinic ZrO_2 (purity, better than 99.5 wt%) was performed in a QM-1SP2 planetary-type ball mill under air, using steel vials (volume, 250 ml) and balls (diameter, 10 mm). The powder-to-ball mass ratio was 1:20 with a powder mass of 20 g. The rotation speed of the vial was 580 rev min^{-1}. After ball milling for given times, a few powder samples were taken out from the vials for analysis by a Rigaku D/max-rB X-ray diffractometer (XRD) with Cu K_α radiation and a H-800 transmission electron microscopy (TEM).

The XRD patterns of ZrO_2 milled for 0, 6, 11, 16, and 26 h are shown in Fig. 1. After 6 h of milling, great decrease and broadening of the intensities of diffraction peaks of m-ZrO_2 can be observed, a new peak at $2\theta = 30.60$ deg or so begins to appear. After 11 h, the intensities of m-ZrO_2 peaks continue to decrease, while the new peak became the strongest, indicating that phase transformation has occurred in a large proportion of the starting m-ZrO_2 powders. On further milling, the main peaks of m-ZrO_2 became very weak at 16 h and disappeared completely after 26 h, while the new peaks gradually intensified. The four broad reflection peaks revealed in the end product correspond to the four main peaks, i.e., (111), (200), (220), and (311), of either tetragonal or cubic ZrO_2, suggesting m $\rightarrow$ t, m $\rightarrow$ c, or m $\rightarrow$ t $\rightarrow$ c transformations.

Fig. 2 shows the TEM micrographs of ZrO_2 powders milled for 0, 11, and 26 h. In the powder milled for 11 h, electron diffraction patterns corresponding to the following three kinds of particles can usually be found: single-crystalline of m-ZrO_2, single-crystalline of c-ZrO_2 (Fig. 2f), and polycrystalline of c-ZrO_2 (Fig. 2d), whereas only the latter two kinds were found in the powder with milled for 26 h. No trace of tetragonal ZrO_2 was evident in either of the powders, hence confirming the occurrence of m $\rightarrow$ c polymorphic transformation of ZrO_2 during ball milling.

It can be seen from Fig. 2a that the starting m-ZrO_2 particles have regular shapes with smooth surfaces. After ball milling for 11 and 26 h, surfaces of most of the separate particles become rougher with many small crystallites which range between 5 and 20 nanometers in size (Fig. 2b). Sometimes isolated small crystallites below 20 nm in size can also be found (Fig. 2c) and the SAED pattern displays the polycrystalline rings of c-ZrO_2 (Fig. 2d). Fig. 2e shows a large isolated particle about 200 nm in size and with small crystallites on the face, its SAED pattern (Fig. 2f) reveals that it is

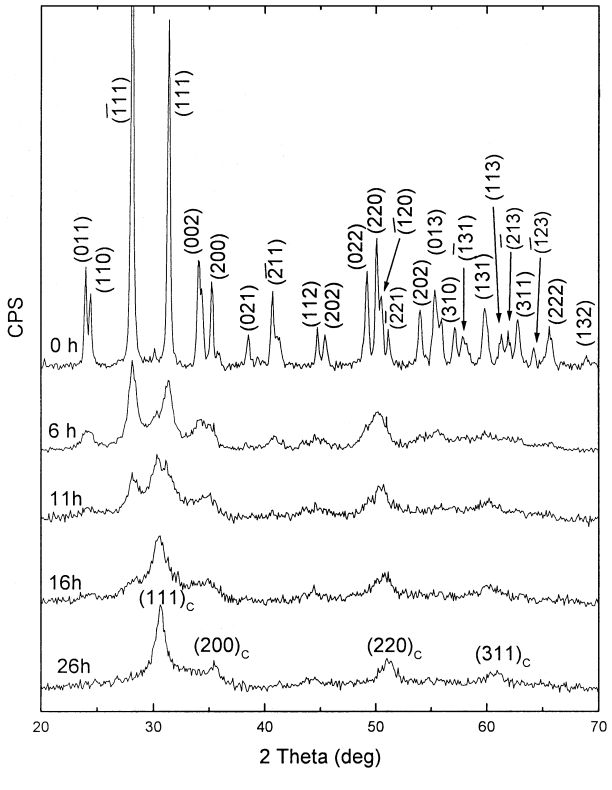

Figure 1 X-ray diffraction patterns of monoclinic ZrO_2 ball milled for different hours, revealing m $\rightarrow$ c polymorphic transformation.

*Author to whom all correspondence should be addressed.

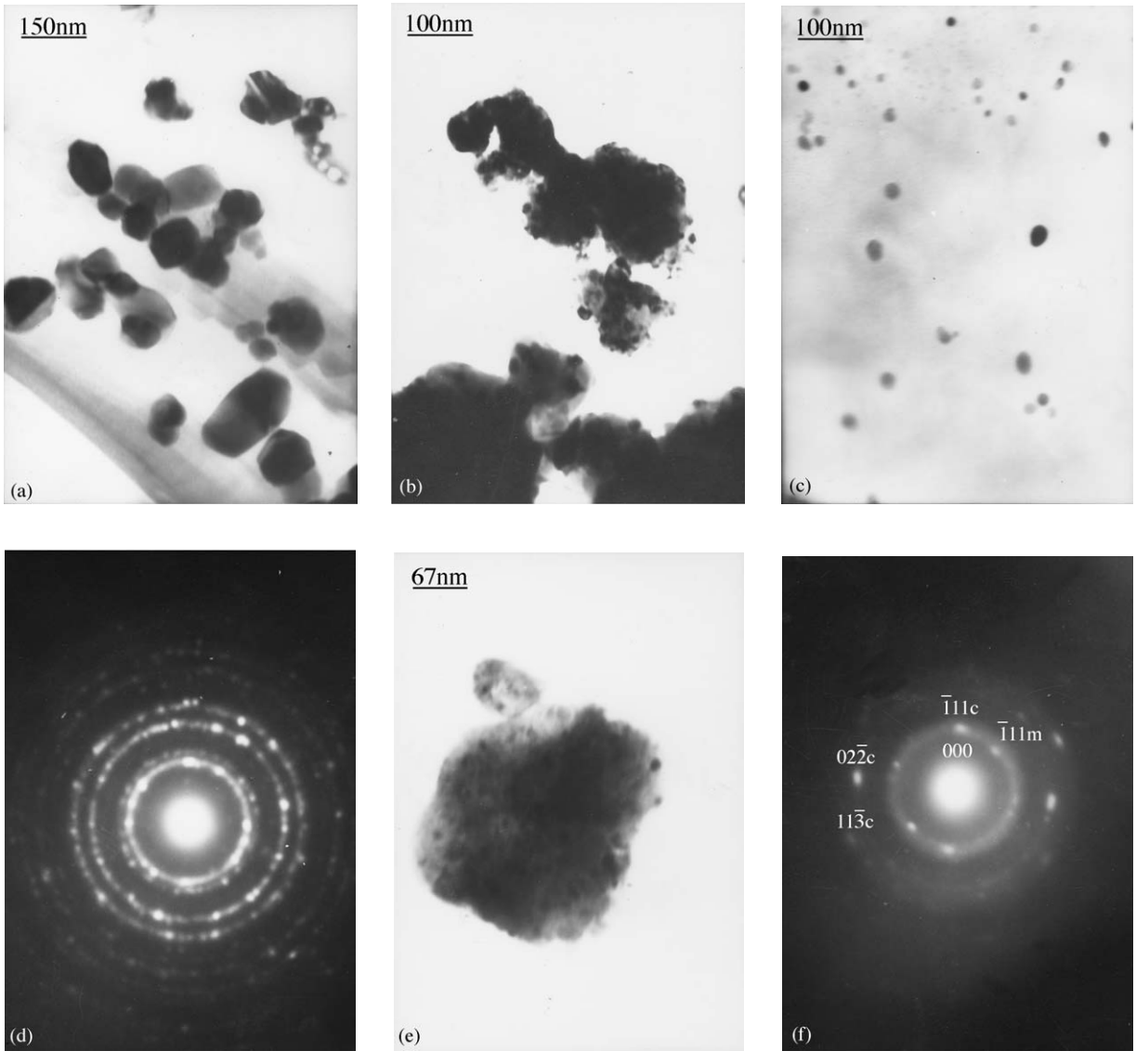

Figure 2 TEM micrographs of ZrO_2 ball milled for different hours: (a) starting monoclinic ZrO_2 particles, showing unaffected surfaces, (b) ZrO_2 particles milled for 11 h, showing rough particle surfaces and small crystallites on surfaces, (c) cubic small ZrO_2 crystallite particles, (d) selected area electron diffraction pattern of polycrystalline cubic ZrO_2, (e) a large cubic ZrO_2 particle, and (f) selected-area electron diffraction pattern of the c-ZrO_2 particle in (e), oriented at [211] direction.

a single crystal of c-ZrO_2, while the diffraction spots corresponding to the (111) reflection of m-ZrO_2 is still present, indicating the occurrence of a direct transformation of this ZrO_2 particle from monoclinic to cubic structure.

It has been found that the reduction in particle size could cause phase transformation in Fe_2O_3: α (above 30 nm) $\rightarrow$ γ (below 30 nm) $\rightarrow$ amorphous (below 5 nm) [6]. Though without direct evidence, this transition mechanism should not be ruled out in this work since small cubic ZrO_2 crystallites with size under 20 nm were observed after ball milling (Fig. 2b, c, and e). It is possible that these small particles, resulting from fracture of the relatively large starting monoclinic particles, transformed directly from monoclinic into cubic structure due to the increase of the unit-cell volume arising from the decrease of particle size, as demonstrated in [6], or that these small cubic particles form through nucleation on the starting monoclinic particle surfaces, which is stimulated by the stresses during milling.

TEM observations in Fig. 2e and f, however, suggest another transition mechanism: the relatively large initial particles transformed directly from monoclinic into cubic structure under the contact forces imposed by balls. Besides triggering direct phase transition, contact forces might also result in strain hardening of particles which activates the phase transition during subsequent relaxation. These have been called "stress-induced" and "strain-induced" transitions, respectively, during milling of anatase TiO_2 [7]. The transitions therein are found to occur locally at contact surfaces of particles, in contrast with observations in this study showing the simultaneous transition in a whole particle.

In summary, monoclinic $\rightarrow$ cubic phase transformation has been observed during ball milling of monoclinic ZrO_2 particles. The structural study shows that this transformation occurred in two distinct conditions: (1) directly in a whole starting particle without fracture under the force imposed by balls; (2) during particle size reduction.

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