

## Phase transformation of nanocrystalline anatase powders during high energy planetary ball milling<sup>①</sup>

PAN Xiao-yan(潘晓燕)<sup>1</sup>, CHEN Yi(陈怡)<sup>1</sup>, MA Xue-ming(马学鸣)<sup>2</sup>, ZHU Li-hui(朱丽慧)<sup>1</sup>  
(1. School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China;  
2. Department of Physics, East China Normal University, Shanghai 200062, China)

**Abstract:** The microstructure evolution of nanocrystalline anatase during high energy planetary milling was studied by X-ray diffraction and transmission electron microscopy. The results show that mechanical activation induces the transformations from anatase to srilankite and rutile at room temperature and under ambient pressure, which should primarily be attributed to the rise of local temperature and pressure at the collision sites of the powders and the balls. In addition, the additional energy caused by defects, lattice distortion and the refinement of the crystallite is responsible for the transformations. As milling time increases, anatase phase content reduces and the amounts of both srilankite and rutile phase increase. And the transformation from srilankite to rutile phase takes place by further milling. In anatase phase, the crystallite size decreases and lattice strain rises with milling time. There is no indication of the formation of amorphous phase during milling.

**Key words:** nanocrystalline anatase; transformation; ball milling

**CLC number:** TF 123.7; TG 111.5

**Document code:** A

### 1 INTRODUCTION

Titanium dioxide is known to exist in three crystalline forms of rutile, anatase and brookite in nature. Rutile is thermodynamically stable while anatase and brookite can transform irreversibly and exothermically to rutile over a range of temperatures<sup>[1]</sup>. In addition, there are two high-pressure phases, srilankite with orthorhombic structure and TiO<sub>2</sub>-III. Under high pressure, anatase and rutile can transform to srilankite<sup>[2-4]</sup>. The srilankite phase can transform back to rutile under appropriate conditions<sup>[5]</sup>.

Over the past few years, mechanical activation has been studied extensively in synthesizing nanocrystalline materials, amorphous alloy, and some novel phases and structures of alloys which can not be obtained by any other method, and hence, has attracted great attention. By this process, many metastable structures existing at high pressure and/or high temperature can even form at room temperature and/or under ambient pressure. Recently, Ren et al<sup>[6]</sup> studied the transformation of TiO<sub>2</sub> and graphite mixtures by high energy vibrational ball milling in argon and found that polymorphic transformations of anatase to srilankite and rutile took place during milling.

In this paper, the microstructure evolution of nanocrystalline anatase TiO<sub>2</sub> during high energy planetary ball-milling was examined by X-ray diffraction

and transmission electron microscopy. The mechanism of the transformation driven by mechanical force is also tentatively discussed.

### 2 EXPERIMENTAL

Nanocrystalline TiO<sub>2</sub> powders were prepared by a precipitation-sol-gel method. H<sub>2</sub>TiO<sub>3</sub>, hydrogen peroxide and ammonia were mixed with the molar ratio of 1:6:2 under continuously stirring in an ice-water bath. After a clear solution was formed, a little surfactant was added into it. After gelation, the samples were filtered, dried at 120 °C and then calcinated for 2 h at 550 °C.

The ball milling was performed in a planetary ball milling in air (QM-1SP). As-prepared nanocrystalline TiO<sub>2</sub> powders were used as the starting materials. Steel balls (8 mm in diameter) were employed as the milling media and mixed with the powders at a ball-to-powder mass ratio of 15:1. The milling speed was fixed at about 220 r/min.

The microstructures of the unmilled and milled powders were examined using X-ray diffractometer (Rigaku D/Max-C, 40 kV / 100 mA) with Cu K<sub>α</sub> radiation. The average crystallite size and lattice strain were determined by corresponding diffraction peak broadening analysis using single line method<sup>[7]</sup>. The

① **Foundation item:** Projects (50071029; 50101004) supported by the National Natural Science Foundation of China.

**Received date:** 2002 - 04 - 08; **Accepted date:** 2002 - 06 - 17

**Correspondence:** Prof. MA Xue-ming, Tel: + 86-21-62232055; E-mail: xmma@phy.ecnu.edu.cn

following relations were used for the estimation of the average crystallite size  $L$  and lattice strain  $\varepsilon$ :

$$L = \lambda / (\beta_C \cos \theta) \quad (1)$$

$$\varepsilon = \beta_G / (4 \tan \theta) \quad (2)$$

where  $\beta_C$  and  $\beta_G$  are Cauchy and Gaussian integral width, respectively,  $\lambda$  is the wavelength of the X-ray radiation, and  $\theta$  is the angle of diffraction. The line width,  $\beta$ , was corrected for instrumental broadening by employing the pattern of standard sample silicon under the same experimental conditions. In the present study, the peak broadening analysis was performed on the (200) diffraction peak at  $2\theta = 48.1^\circ$  of anatase phase and the (111) diffraction peak at  $2\theta = 31.1^\circ$  of srilankite phase, due to the fact that the (101) reflection, the strongest line at  $2\theta = 25.3^\circ$  of anatase phase, almost superimposes with the (110) reflection of srilankite phase.

The different phase amounts in the powders were obtained through the matrix-flushing method<sup>[7]</sup> using crystalline  $\alpha\text{-Al}_2\text{O}_3$  as the additive. To determine the quantity of each phase, the integral intensities (peak area) of the (200), (110) and (113) reflections were used for anatase, rutile and  $\alpha\text{-Al}_2\text{O}_3$ , respectively, to avoid the overlapping peak.

Transmission electron microscopy (Hitachi H-800) was used to observe the morphology of  $\text{TiO}_2$  powders at 175 kV. TEM selected area diffraction pattern (SADP) was taken to analyze the structures of the powders. The samples used for TEM observation were prepared by dispersing some powders in ethanol followed by ultrasonic vibration for 10 min, then allowed a drop of the suspension onto a carbon-coated copper grid.

### 3 RESULTS AND DISCUSSION

#### 3.1 X-ray diffraction

The evolution of XRD patterns of  $\text{TiO}_2$  powders with milling time is displayed in Fig. 1. It can be seen that the as-prepared  $\text{TiO}_2$  powders are anatase phase and the average crystallite size is estimated to be 15 nm or so (Fig. 1). After the milling time of 2 h, the XRD pattern of the powders hardly changes and the powders still remain anatase phase. But after milling 5 h, the diffraction peaks of anatase phase slightly decrease and broaden, and a new peak at  $2\theta = 31.3^\circ$  is detected, which corresponds to the (111) reflection of srilankite phase, a high pressure phase of  $\text{TiO}_2$ . And this new peak gradually strengthens with the increase of milling time. The (110) reflection of rutile phase is clearly found after milling 10 h. Obviously, the transformations from anatase to srilankite and rutile phase are triggered during ball milling. And it is suggested that an incubation period for the transformation

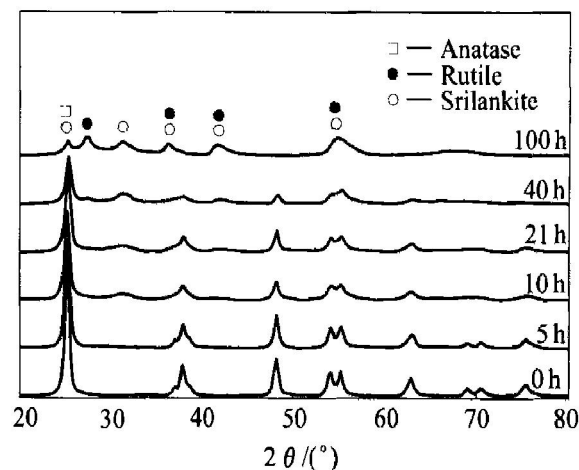
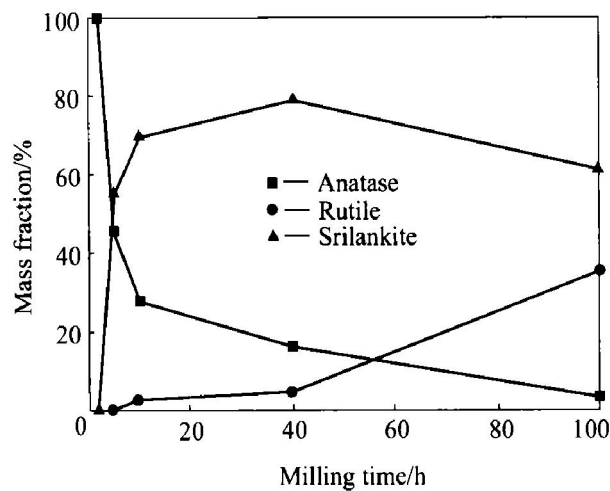


Fig. 1 XRD patterns of nanocrystalline anatase powders milled for different milling times

exists, for no appreciable transformation take place in the early two hours of milling.

With the increase of milling time, the diffraction peaks of anatase phase further weaken and broaden, some of which eventually can not be discernable or merge together to form a broad band, while the diffraction peaks of srilankite and rutile phase gradually strengthen. Until milling 40 h, the second strong diffraction peak for anatase phase at  $2\theta = 48.1^\circ$  is still clear, which is a typical diffraction peak of anatase phase and does not overlap with the peaks for srilankite and rutile phase. However, after milling 100 h, it seems that most of the diffraction peaks for anatase phase disappear apart from the strongest diffraction peak at  $2\theta = 25.3^\circ$ . Considering the fact that the two diffraction peaks almost superimpose, the peak at  $2\theta = 25.3^\circ$  should be caused by the (110) ( $d = 0.350$  nm) of srilankite phase and (101) ( $d = 0.352$  nm) reflection of anatase phase.

The evidence that the diffraction peaks of anatase decrease and those of srilankite and rutile enhance with the milling time indicates that more anatase powders transform to srilankite and rutile. On the basis of the above XRD analysis, it can be inferred that after milling 100 h, most of anatase powders transform and only a small amount of anatase phase exists in the powders, which is proved by the following quantitative estimation of the phases. As shown in Fig. 2, the anatase content decreases from 100% in the starting powders to 27.2% after milling 10 h and then the rate of the transformation slows down. And only 3.2% anatase phase exists in the powders at the milling time of 100 h. The srilankite phase amount sharply increases to 70.2% after milling 10 h, slowly amounts to the maximum at milling time of 40 h, and then gradually reduces as the result of the transformation from srilankite to rutile phase.



**Fig. 2** Different phase amounts in powders as function of milling time

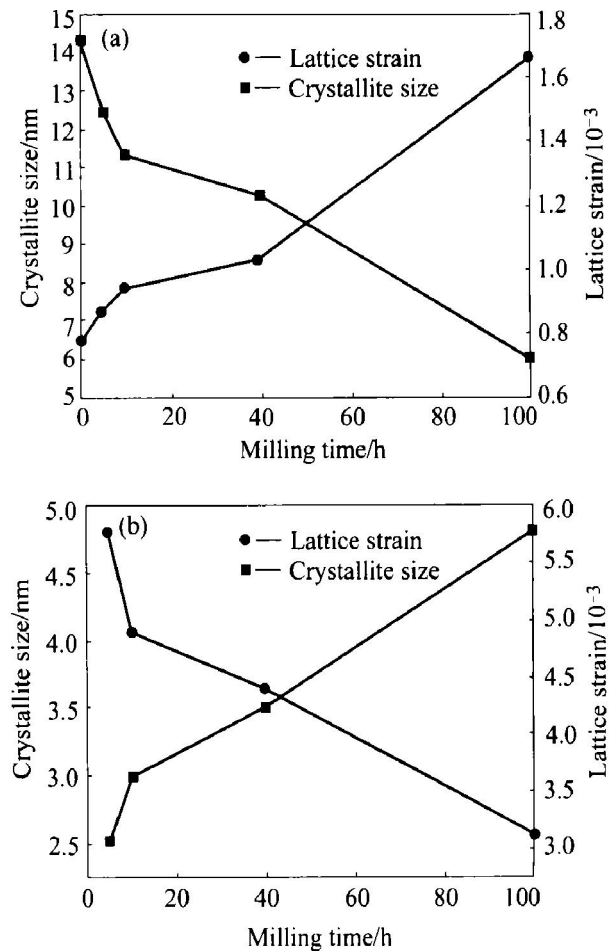
While the rutile phase content slowly rises with milling time increasing and increases at a relatively large rate at the later stage of milling.

As shown in Fig. 1, the diffraction peaks of anatase gradually broaden with the increase of milling time, which is due to the refinement of grains and the lattice distortion caused by milling. As shown in Fig. 3(a), the average crystallite size of the anatase phase gradually reduces with the increase of milling time. At the early stage of milling, the anatase crystallite size drastically reduces, but the rate with which the crystallite refines slows down as the milling time further increases. It may be due to the fact that the resistance to fracture of particles gradually increases with milling time and the further refinement of particles needs much more energy. According to the theory of milling comminution, the energy leading to fracture,  $E$ , is a decreasing function of the particle size  $D$ <sup>[8]</sup>:

$$E = KD^{(3m-5)/m} \quad (3)$$

where  $K$  is a factor relative with conditions of milling and the particles,  $m$  is coefficient of Weibull distribution, that is, the energy for fracture increases with the decrease of the particle size. The resistance to fracture stems from the rise of the relative strength of the particles as they decrease in size, the large particles shielding the smaller particles from impact, and agglomeration of the smaller particles to reducing the specific surface energy of the system<sup>[9]</sup>.

However, for srilankite, its diffraction peaks show broadening at the beginning of its formation, because the high pressure phase prepared from anatase was always intergrown with a short-range ordered phase which produced broad diffraction peaks<sup>[10]</sup>. With the increase of milling time, the diffraction peak for srilankite phase gradually sharpens. Based on diffraction peak broadening analysis, the average crystallite size of the srilankite phase gradually

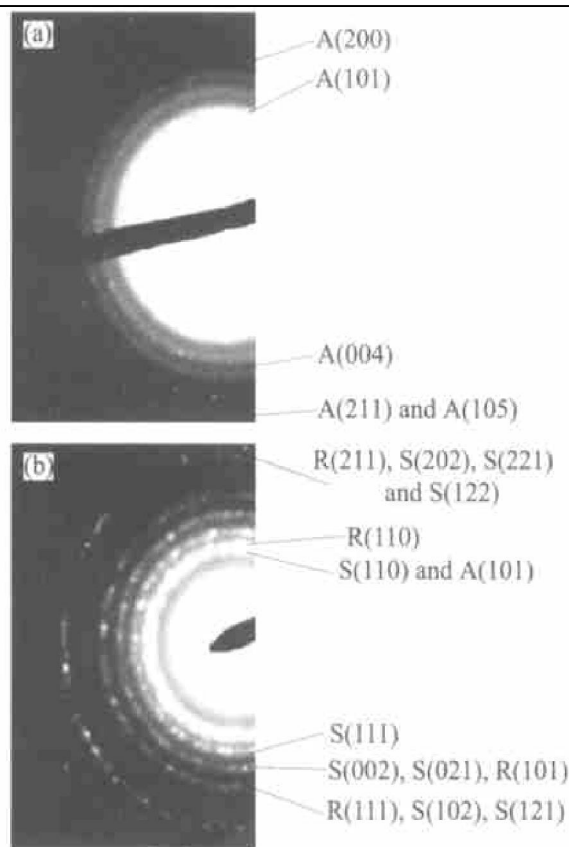


**Fig. 3** Average crystallite size and lattice strain of both anatase (a) and srilankite phase (b) as function of milling time

increases and the lattice strain lowers with milling time. As depicted in Fig. 3(b), the crystallite size is very small and the lattice strain is comparatively high in the initial srilankite phase, which contribute to high free energy in srilankite phase. Therefore, the srilankite phase is liable to grow to decrease the free energy and thus lattice strain also lowers.

### 3.2 Transmission electron microscopy

Figs 4 (a) and (b) show TEM selected area diffraction patterns for unmilled and 100 h milled nanocrystalline TiO<sub>2</sub> powders. The analysis of TEM selected area diffraction pattern (SADP) also indicates that as-prepared nanocrystalline TiO<sub>2</sub> is anatase phase. As shown in Fig. 4 (a), the diffraction rings are identified as (101), (004), (200), (211) and (105) reflections of anatase phase, respectively. The selected area diffraction pattern in Fig. 4 (b) is different from that in Fig. 4 (a). The analysis shows that some new rings form, which are attributed to rutile and srilankite phase (A, R and S stand for anatase, rutile and srilankite phase, respectively). It is confirmed that the structure transformation in nanocrystalline anatase powders is induced during ball milling. The ring corresponding to A(200) reflection of anatase phase disap-



**Fig. 4** SADPs of nanocrystalline  $\text{TiO}_2$   
(a) —Unmilled; (b) —Milled for 100 h

pears. The amorphization is often induced during high energy ball milling. However, in our case, there is no indication of the formation of amorphous phase, due to no highly diffuse ring in the SADP of the powders<sup>[6]</sup>.

### 3.3 Mechanism of transformation

In general, the anatase-rutile transformation takes place at high temperature and the anatase-srilankite under high pressure. Liao et al<sup>[5]</sup> found that during high pressure/low temperature sintering, nanocrystalline anatase transform to either rutile or srilankite, depending on the combination of pressure and temperature. According to the temperature-pressure diagram of nanocrystalline  $\text{TiO}_2$ , anatase could transform to srilankite at pressure and temperature as low as 4.75 GPa and 250 °C, respectively. With the rise of pressure, the temperature of the anatase-rutile transformation gradually decreased from 550 °C at 0.1 MPa to 150 °C at 2.5 GPa. But below 150 °C, the anatase-rutile transformation was not observed even at pressure up to 8 GPa. However, during ball milling, mechanical activation triggers the transformation from anatase to srilankite and rutile at room temperature and under ambient pressure, which should primarily be attributed to local temperature and pressure increasing at the collision sites of the powders and the balls.

According to the theory by Maurice and Court-

ney, the average pressure developed across the contacting surfaces at maximum compression for powderless collision is expressed as<sup>[11]</sup>

$$P_{\max} = g_p v^{0.4} (9.8 \rho_b / E)^{0.2} E \quad (4)$$

where  $g_p$  is a geometrical constant, which is 0.464 6 for collision of ball on ball;  $\rho_b$  and  $E$  are the density and the elastic modulus of the balls, respectively; and  $v$  is the precollision relative velocity of the balls. In a planetary mill,  $v$  can be calculated through the formula<sup>[12]</sup>:

$$v = \frac{MR_1^2 + 4[m_v + m_p(1 + R_{BP})](r^2 + 2R^2)}{8r^2[m_v + m_p(1 + R_{BP})]} \Omega \quad (5)$$

where  $M$ ,  $\Omega$  and  $R_1$  are mass, angular velocity and radius of the rotational disk, respectively;  $m_v$  and  $m_p$  are mass of the vial and the powders;  $R$  is the distance between the center of the disk and that of the vial;  $r$  is radius of the vial; and  $R_{BP}$  is the mass ratio of balls to powders. Therefore, under the milling condition used in this study, it can be estimated that the precollision relative velocity of the balls is about 3.5 m/s and the impact pressure amounts to 8.08 GPa. Although the presence of powders will reduce the pressure reached on collision, the pressure experienced by some powders is still expected to be high enough to trigger the anatase-srilankite transformation.

Mechanical activation can lead to the local temperature rise of the powders at collision sites,  $\Delta T$ , which can be determined by<sup>[13]</sup>

$$\Delta T = \rho_b v_s v^2 (\Delta t / \pi k_0 \rho_p C_p)^{1/2} \quad (6)$$

where  $v_s$  is the velocity of a longitudinal wave in the balls;  $\rho_p$ ,  $K_0$  and  $C_p$  are density, thermal conductivity and specific heat capacity of powders, respectively; and  $\Delta t$  is the impact time given by<sup>[11]</sup>

$$\Delta t = g_{\tau} v^{-0.2} (9.8 \rho_b / E)^{0.4} R \quad (7)$$

where value of  $g_{\tau}$ , a geometrical constant, is 5.574 4 for collision of ball on ball;  $R$  is radius of the ball. The impact time is estimated to be about  $4.67 \times 10^{-5}$  s. And thus the local temperature rise at the surface of powders is about 420 °C.

Therefore, it is reasonable that local temperature and pressure may approximate or even exceed the temperature and the pressure limit of the anatase-rutile and the anatase-srilankite transformation. In addition, ball milling leads to an additional energy produced in the powders, which results from a considerable number of defects, lattice distortion and the reduction of the particle size (i. e. the growth of the special surface area). The additional energy contributes to raise the free energy of the anatase phase and lower the potential barrier of the transformation. After a certain milling time,

$$(G_a + \Delta G^*) > (G_s + G_r) \quad (8)$$

where  $G_a$ ,  $G_s$  and  $G_r$  are the free energy of anatase, rutile and srilankite phase, respectively; and

$\Delta G^*$  is the additional energy.

#### 4 CONCLUSIONS

1) During high energy ball milling, mechanical activation induces the transformations of nanocrystalline  $\text{TiO}_2$  from anatase to srilankite and rutile phase at room temperature and under ambient pressure.

2) The transformation primarily is attributed to the rise of local temperature and pressure at the collision sites of the powders and the balls. In addition, an additional energy as the result of defects, lattice distortion and the refinement of the crystallite is responsible for the transformations.

3) As milling time increases, anatase phase content reduces and the amounts of both srilankite and rutile phase increase. The transformation from srilankite to rutile phase takes place by further milling, and are triggered.

4) In anatase phase, the crystallite size decreases and lattice strain rises with milling time. There is no indication of the formation of amorphous phase during milling.

#### REFERENCES

- [ 1 ] Shannon R D, Pask J A. Topotaxy in anatase-rutile transformation [ J ]. American Mineralogist, 1964, 49 ( 11/12 ): 1707 - 1717.
- [ 2 ] Mammone J F, Nicol M, Sharma S K. Raman spectra of  $\text{TiO}_2$  II,  $\text{TiO}_2$  III,  $\text{SnO}_2$  and  $\text{GeO}_2$  at high pressure [ J ]. Journal of Physics and Chemistry of Solids, 1981, 42 ( 4 ): 379 - 384.
- [ 3 ] Ohsaka T, Yamaoka S, Shimomura O. Effect of hydrostatic pressure on the raman spectrum of anatase (  $\text{TiO}_2$  ) [ J ]. Solid State Communications, 1979, 30( 6 ): 345 - 347.
- [ 4 ] Malcolm Nicol, Fong Mei Y. Raman spectrum and polymorphism of titanium dioxide at high pressures [ J ]. The Journal of Chemical Physics, 1971, 54 ( 7 ): 3167 - 3170.
- [ 5 ] Liao S C, Chen Y J, Mayo W E, et al. Transformation assisted consolidation of bulk nanocrystalline  $\text{TiO}_2$  [ J ]. Nanostructured Materials, 1999, 11( 4 ): 553 - 557.
- [ 6 ] Ren R, Yang Z G, Shaw L L. Polymorphic transformation and powder characteristics of  $\text{TiO}_2$  during high energy milling [ J ]. Journal of Materials Science, 2000, 35 ( 23 ): 6015 - 6026.
- [ 7 ] FAN Xiong. X-ray Diffraction of Metal [ M ]. Beijing: Mechanics Industry Press, 1989. ( in Chinese ).
- [ 8 ] LI Feng-sheng. Ultrafine Powder Technology [ M ]. Beijing: National Defense and Industry Press, 2000. ( in Chinese ).
- [ 9 ] Lin L J. Implications of fine grinding in mineral processing [ J ]. Journal of Thermal Analysis, 1998, 52( 2 ): 451 - 461.
- [ 10 ] Dachille F, Roy R. A new high-pressure form of titanium dioxide [ J ]. American Ceramic Society of Bulletin, 1962, 41( 1 ): 225.
- [ 11 ] Maurice D R, Courtney T H. The physics of mechanical alloying: A first report [ J ]. Metallurgical Transactions, 1990, 21A( 2 ): 289 - 303.
- [ 12 ] YANG Jun-you, ZHANG Tong-jun, CUI Kun, et al. Analysis of impact behavior during ball milling [ J ]. Acta Metallurgical Sinica, 1997, 33( 4 ): 381 - 385. ( in Chinese ).
- [ 13 ] Schwarz Ricardo B, Koah Carl C. Formation of amorphous alloys by the mechanical alloying of crystalline powders of pure metals powders of intermetallics [ J ]. Applied Physics Letters, 1986, 49( 3 ): 146 - 148.

( Edited by LONG Huai-zhong )