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Deformation-induced reactions of ZnO and TiO_2

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Reactions of ZnO and TiO_2 (anatase and rutile) in different mole ratios induced by high-energy ball milling were studied by X-ray diffraction. It was found that three main reactions could involve during high-energy ball milling: (1) $(4 - X)$ZnO + $(2 + Y)$ TiO_2 (anatase or rutile) → $Zn_{4-X}Ti_{2+Y}O_8$; (2) ZnO + TiO_2 (rutile) → $ZnTiO_3$, and (3) TiO_2 (anatase) → TiO_2 (II) → TiO_2 (rutile). Cubic $Zn_{4-X}Ti_{2+Y}O_8$ nanocrystals with an average crystal size of about 15 nm can be prepared by high-energy ball milling, which could be an attractive process to fabricate material in industrial scale. No decomposition of $ZnTiO_3$ into Zn_2TiO_4 and rutile was detected during milling. Anatase shows higher reaction activity than rutile and favours the formation of $Zn_{4-X}Ti_{2+Y}O_8$ while rutile favours the formation of $ZnTiO_3$. During the anatase-to-rutile transformation a transient metastable phase, TiO_2 (II) which is a high-pressure phase of TiO_2, is detected. © *2004 Kluwer Academic Publishers*

1. Introduction

Generally, in the ZnO-TiO_2 system three compounds exist: Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal) and $Zn_2Ti_3O_8$ (cubic). $Zn_2Ti_3O_8$ is stable at temperature up to about 800°C [1, 2]. $ZnTiO_3$ decomposes to Zn_2TiO_4 and rutile at about 945°C, while Zn_2TiO_4 is a stable compound up to its liquid temperature of 1418°C [3]. Recently, $ZnTiO_3$ and Zn_2TiO_4 have received much attention because of their promising applications. Besides their traditional applications in pigments [4], catalysts [5] and gas sensor [6, 7], $ZnTiO_3$ is a potential microwave dielectric in modern microwave applications such as mobile telephones and satellite communication systems [8–12] and Zn_2TiO_4 is an attractively regenerable sorbent for removing sulfur from hot coal gases [13–16].

Zn_2TiO_4 is usually prepared by solid-state reaction, in which a mixture of ZnO and TiO_2 with 2:1 mole ratio is calcined at about 1200°C for 20 h [3, 17]. It is difficult to prepare pure $ZnTiO_3$ phase by solid-state reaction because of the decomposition of $ZnTiO_3$ into Zn_2TiO_4 and rutile at about 945°C. Recently, mechanical milling has been applied to induce a wide range of reactions and prepare nanostructured materials. This technique has become an important mechanochemical means [18, 19]. In this paper, we use X-ray diffraction (XRD) to monitor the structural evolution during high-energy ball milling of ZnO and TiO_2 (anatase and rutile).

2. Experimental

The starting oxides were ZnO (>99.5% pure, British Drug Houses LTD) and TiO_2 (anatase, >99% pure, Merck Eurolab A/S, Germany; rutile, >99.95% pure, Acros Organics). All samples were milled in a planetary mill Pulverisette 5 (Fritsch, Germany) with WC vials (75 mm in diameter, volume of 250 ml) and WC balls (9 balls, 20 mm in diameter) at 200 rpm in air. The XRD patterns of samples milled for different times were recorded by a Philips PW 1050 diffractometer employing Cu-K_α radiation for phase identification.

3. Results

3.1. Reaction behavior of ZnO and TiO_2 in 2:1 mole ratio

The XRD patterns for samples of ZnO and anatase or rutile in 2: 1 mole ratio, which correspond to

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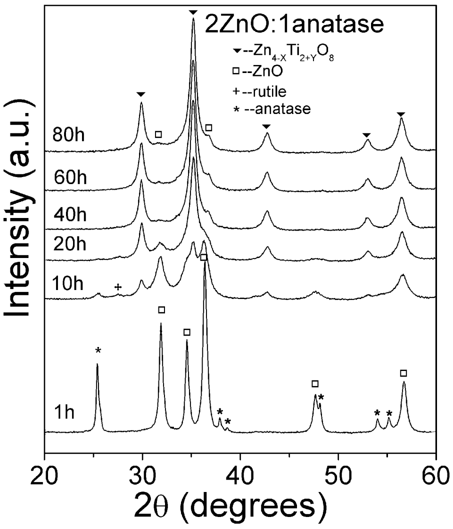

Figure 1 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (anatase) of 2:1 mole ratio after various milling times.

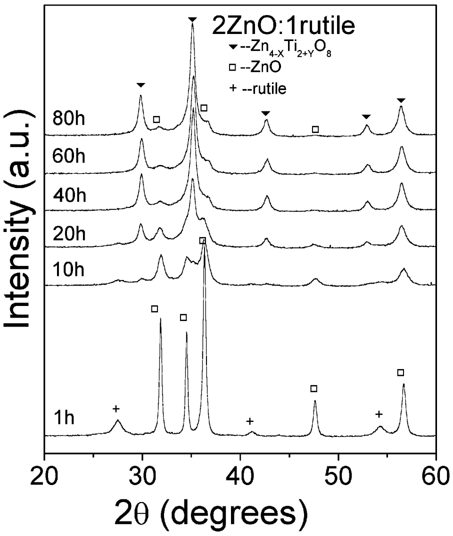

Figure 2 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (rutile) of 2:1 mole ratio after various milling times.

stoichiometric Zn_2TiO_4, are shown in Figs 1 and 2, respectively. After milled for 10 h, new peaks located at about 29.9, 35.2, 42.7, and 53.0 degrees appear, which are indexed to a cubic phase. These peaks increase with milling time at the expense of ZnO and TiO_2. After 80 h, the cubic phase is dominant together with tiny ZnO phase. TiO_2 in both forms of rutile and anatase were not detected, which could be due to tiny amount of the phases, small particles and/or complete reaction with ZnO to form the cubic phase. The cubic phase could be identified to be a $Zn_{4-X}Ti_{2+Y}O_8$ solid solution or mixture produced from coexisting Zn_2TiO_4 and $Zn_2Ti_3O_8$ (see Discussion for detail). It is seen that the conversion of ZnO and rutile to $Zn_{4-X}Ti_{2+Y}O_8$ is apparently slower than that of ZnO and anatase to $Zn_{4-X}Ti_{2+Y}O_8$. After a milling time of 40 h, peak widths saturate and no TiO_2 peaks are observed in Figs 1 and 2.

3.2. Reaction behavior of ZnO and TiO_2 in 1:1 mole ratio

Figs 3 and 4 show the XRD patterns for samples of ZnO and anatase or rutile in 1:1 mole ratio, respectively, which are correspondent to stoichiometric $ZnTiO_3$. In the mixture of ZnO and anatase in Fig. 3, after a milling time of 10 h, peaks from $Zn_{4-X}Ti_{2+Y}O_8$ and rutile are clearly observed while peaks for the $ZnTiO_3$ phase are not detectable. After 20 h, new peaks at approximately $2\theta = 32.8^\circ$ and 48.9° can be observed, which can be assigned to rhombohedral $ZnTiO_3$. After a milling time of 40 h, the sample mainly consists of $Zn_{4-X}Ti_{2+Y}O_8$ together with tiny rhombohedral $ZnTiO_3$ and rutile. Peak widths of the solid solution or mixture saturate. With substituting rutile for anatase in Fig. 4, however, the peak of rhombohedral $ZnTiO_3$ phase at approximately $2\theta = 32.8^\circ$ together with $Zn_{4-X}Ti_{2+Y}O_8$ peaks can be already detected after 10 h milling. With increasing milling time, the peaks for both $ZnTiO_3$ and $Zn_{4-X}Ti_{2+Y}O_8$ increase. After 80 h, the sample is composed of $Zn_{4-X}Ti_{2+Y}O_8$, $ZnTiO_3$, and rutile while the peaks for the $ZnTiO_3$ phase is much stronger than those in Fig. 3 after 80 h.

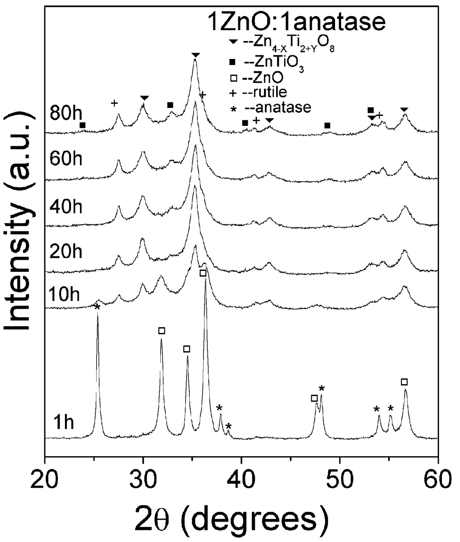

Figure 3 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (anatase) of 1:1 mole ratio after various milling times.

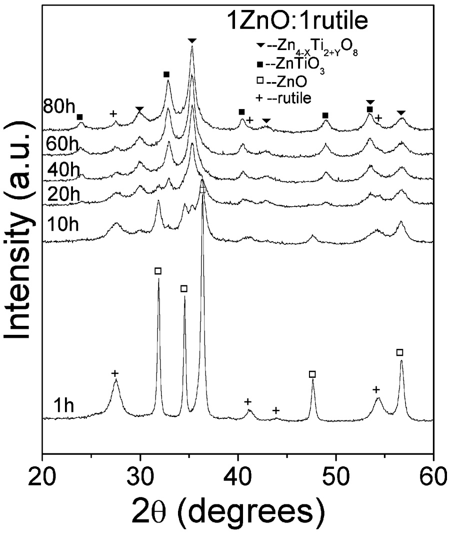

Figure 4 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (rutile) of 1:1 mole ratio after various milling times.

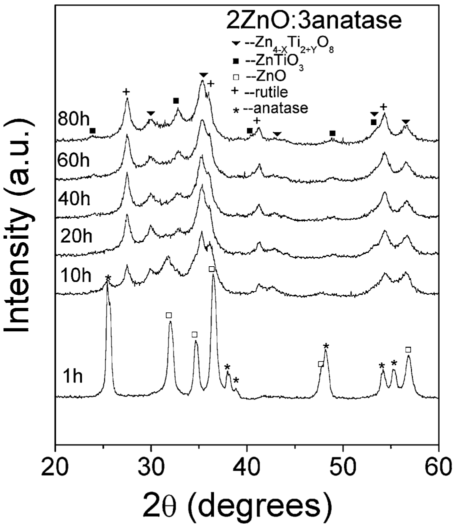

Figure 5 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (anatase) of 2:3 mole ratio after various milling times.

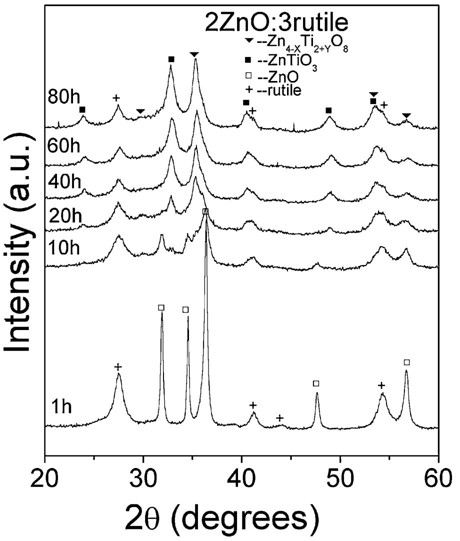

Figure 6 X-ray diffraction patterns recorded for the samples with ZnO:TiO_2 (rutile) of 2:3 mole ratio after various milling times.

3.3. Reaction behavior of ZnO and TiO_2 in 2:3 mole ratio

By high-energy ball milling for 80 h, samples of ZnO and anatase or rutile in 2:3 mole ratio corresponding to stoichiometric $Zn_2Ti_3O_8$ consist of mixtures of $Zn_{4-X}Ti_{2+Y}O_8$, rhombohedral $ZnTiO_3$ and rutile (Figs 5 and 6). Similar to the reaction behavior of ZnO and TiO_2 in 1:1 mole ratio, the presence of anatase favors the formation of $Zn_{4-X}Ti_{2+Y}O_8$ and the presence of rutile favors $ZnTiO_3$. Additionally, rutile is less active before 20 h of milling in terms of ZnO peaks as shown in Figs 5 and 6.

3.4. Transformation of anatase to rutile in pure TiO_2

Fig. 7 shows XRD patterns of anatase TiO_2 milled for various times up to 80 h. After a milling time of 1 h, new broad peaks marked by solid circles as well as the peaks for rutile and anatase appear in the XRD pattern. The broad peaks can be indexed to a polymorphic high-pressure TiO_2 (II) with orthorhombic structure, which was also reported in Ref. [20, 21]. After 10 h, the XRD pattern is dominated by the rutile phase together with the TiO_2 (II) phase and tiny anatase. After 20 h, no obvious anatase and TiO_2 (II) phases can be detected. With prolonging milling time up to 80 h, only rutile is observed.

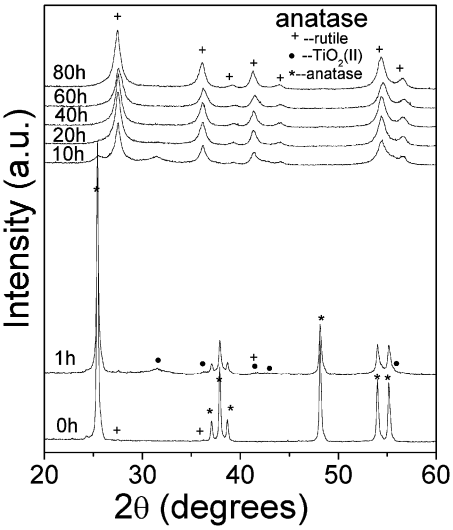

Figure 7 X-ray diffraction patterns recorded for the anatase after various milling times.

4. Discussion

The reactions between ZnO and TiO_2 during solid-state reaction can usually be expressed as follows:

$$2ZnO + TiO_2 \rightarrow Zn_2TiO_4 \qquad (1)$$

$$ZnO + TiO_2 \text{ (rutile)} \rightarrow ZnTiO_3 \qquad (2)$$

$$2ZnTiO_3 \rightarrow Zn_2TiO_4 + TiO_2 \text{ (rutile)} \qquad (3)$$

$$2ZnO + 3TiO_2 \rightarrow Zn_2Ti_3O_8 \qquad (4)$$

$$TiO_2 \text{ (anatase)} \rightarrow TiO_2 \text{ (rutile)} \qquad (5)$$

It is known that Zn_2TiO_4 has a lattice constant of 0.84602 nm (JCPDS 25-1164) and $Zn_2Ti_3O_8$ has a lattice constant of 0.8429 nm (JCPDS 38-0500). Thus, it is difficulty to distinguish them by XRD, especially in the samples produced by high-energy ball milling due to line broadening. However, due to the existence of some residual ZnO and disappearance of TiO_2 in the XRD patterns for the samples with a composition of ZnO:TiO_2 = 2:1 recorded after milling 40 h (see Figs 1 and 2), we suggest the dominant phase observed after 40 h to be $Zn_{4-X}Ti_{2+Y}O_8$. This is most likely a solid solution or mixture of and $Zn_2Ti_3O_8$. Especially, $Zn_{4-X}Ti_{2+Y}O_8$ is Zn_2TiO_4 for $X = 0$ and $Y = 0$, and $Zn_{4-X}Ti_{2+Y}O_8$ is $Zn_2Ti_3O_8$ for $X = 2$ and $Y = 1$. Note that the disappearance of TiO_2 in the XRD patterns may not rule out the existence of tiny TiO_2 in the milled samples. In addition, the results obtained from Figs 5 and 6, in which the starting mixtures are corresponding to ZnO:TiO_2 = 2:3, might also support the formation of the $Zn_{4-X}Ti_{2+Y}O_8$ solid solution or the mixture during high-energy ball milling. If the dominant phase formed in Figs 5 and 6 after 40 h was $Zn_2Ti_3O_8$, $ZnTiO_3$ and rutile would be in the mole ratio of 2:1. But, this is not the case observed. The peak broadening in the XRD patterns recorded for milled samples could be caused by a reduction in crystal size and microstrain induced by milling. The low limit of the average crystal size for $Zn_{4-X}Ti_{2+Y}O_8$ in Figs 1 and 2 is estimated to be around 15 nm after 20 h of milling, which was used the Scherrer formula from (220) reflection.

Many studies [22, 23] reported that Zn_2TiO_4 or $Zn_2Ti_3O_8$ is formed when anatase is used in the starting mixture (Equation 1 or 4) and $ZnTiO_3$ is formed in the presence of rutile (Equation 2) during solid-state reactions because of structural resemblances between Zn_2TiO_4 or $Zn_2Ti_3O_8$ and anatase on the one hand and $ZnTiO_3$ and rutile on the other hand. This could be the reason that the presence of anatase favors the formation of $Zn_{4-X}Ti_{2+Y}O_8$ and the presence of rutile favors $ZnTiO_3$ during high-energy ball milling as shown in Figs 3–6. No matter whether anatase or rutile, however, the reaction between ZnO and TiO_2 in 2:1 mole ratio corresponding to stoichiometric Zn_2TiO_4 gives cubic $Zn_{4-X}Ti_{2+Y}O_8$ nanocrystals together with tiny unreacted ZnO after a milling time of about 40 h. This could provide a novel, simple and low cost method for preparing cubic Ti-Zn-oxides nanocrystals with formula of $Zn_{4-X}Ti_{2+Y}O_8$. Furthermore, cubic Ti-Zn-oxide nanocrystals with formula of $Zn_{4-X}Ti_{2+Y}O_8$ prepared by this method could have high reactivity as a sorbent for removing sulfur from hot coal gases because of mechanical activation, which deserves further investigations. From Figs 3–6, it is seen that the formation of $Zn_{4-X}Ti_{2+Y}O_8$ is prior to $ZnTiO_3$ during high-energy ball milling. There could exist equilibriums among $Zn_{4-X}Ti_{2+Y}O_8$, $ZnTiO_3$ and rutile after a suitable milling time when TiO_2 is excessive with respect to the stoichiometry of Zn_2TiO_4. No obvious evidence for the decomposition of $ZnTiO_3$ to Zn_2TiO_4 and rutile (Equation 3) is observed during high- energy ball milling.

Anatase exhibits higher reaction activity than rutile during high-energy ball milling. One possible reason could be attributed to the fact that the formation of $Zn_{4-X}Ti_{2+Y}O_8$ is prior to $ZnTiO_3$ and the presence of anatase favors the formation of $Zn_{4-X}Ti_{2+Y}O_8$ during high-energy ball milling. It is known [22] that the transformation of anatase to rutile (Equation 5) without a transient phase takes place between 530–830°C during solid-state reaction. However, during high-energy ball milling, a transient phase, high-pressure phase TiO_2 (II), is detected during the anatase-to-rutile phase transformation. More investigations are required to clarify the microstructural relationship during the anatase-to-TiO_2 (II)-to-rutile phase transformations.

5. Conclusions

Three main reactions between ZnO and TiO_2 could take place during high-energy ball milling. They are: (1) $(4-X)$ZnO + $(2+Y)$ TiO_2 (anatase or rutile) $\rightarrow$ $Zn_{4-X}Ti_{2+Y}O_8$; (2) ZnO + TiO_2 (rutile) $\rightarrow$ $ZnTiO_3$, and (3)TiO_2 (anatase) $\rightarrow$ TiO_2 (II) $\rightarrow$ TiO_2 (rutile). Using high-energy ball milling process, cubic Ti-Zn-oxide nanocrystals with formula of $Zn_{4-X}Ti_{2+Y}O_8$ and average crystal size of about 15 nm can be prepared and the formation of $Zn_{4-X}Ti_{2+Y}O_8$ is prior to that of $ZnTiO_3$. This could provide an effective method for the preparation of attractive Ti-Zn-oxide nanocrystals for potential applications. During high-energy ball milling, the presence of anatase, which is more active, favors the formation of $Zn_{4-X}Ti_{2+Y}O_8$ and the presence of rutile favors $ZnTiO_3$. No obvious evidence can be found for the decomposition of $ZnTiO_3$ to Zn_2TiO_4 and rutile during milling. The transformation of anatase to rutile with a transient metastable phase, i.e., TiO_2 (II), is detected.

Acknowledgments

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