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TEM observation of growth and phase transformation in nanometer-sized titanium oxide powder

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Abstract The growth and phase transformation in the nanocrystalline titania powders were studied using TEM and X-ray diffraction. Titania particles consisting of anatase phase grow through coalescence. After a nucleus of rutile is formed, it grows at the expense of the nearest anatase particles. A nucleus of rutile is formed in two ways. The nucleation of rutile occurs at the amorphous interface between the small anatase particles. In a large anatase particle, the martensitic transformation is dominant. It is estimated that these two kinds of phase transformation mechanisms are controlled by the intrinsic and extrinsic defects. A rutile particle has the low-energy surfaces with a lot of terraces. The growth direction of a rutile particle is related to the orientation of twin. A rutile particle grows along a $\langle 1\bar{2}1 \rangle$ direction on the $\{101\}$-twin plane.

Introduction

The titanium oxide has been studied for years because of its various applications and superior properties. Especially, titania has superior properties in photocatalysis. It has been known that the increased surface area improves an ability of photocatalysis [1–3]. Therefore, there have been many efforts to increase the surface area of titania, in other words, to produce the nanocrystalline titania. It have been reported that the nanocrystalline titania powders produced by various methods have only anatase phase, which is known to have the better photocatalystic ability [4, 5]. However, the mechanism for phase transformation from anatase to rutile during heating process of nanocrystalline titania is not well understood.

Titania is a polymorphic material with three phases: rutile, anatase, and brookite. Rutile is the thermodynamically stable phase while anatase and brookite are metastable. However, it has been known that the fast arrangement of octahedra during production process of nanocrystalline titania powders enables anatase and brookite to be formed. Therefore, anatase and brookite are sometimes called kinetically stable phases [6]. The formation of anatase in the nanocrystalline titania has been explained thermodynamically in terms of its low surface energy. As the surface energies of anatase and rutile are, respectively, 1.32 and 1.91 J m^{-2}, the anatase is more favorable than rutile in the nanoscale. However, it becomes unstable with an increasing particle size and then transforms to rutile. The critical size where the reversal of phase stability occurs is known to be 13–16 nm [7–9].

The fact that dopants with a similar lattice parameter with rutile, such as CuO, La_2O_3, and SnO_2, promote phase transformation from anatase to rutile showed that the presence of nucleation sites is a critical factor for the phase transformation [10–12]. Therefore, there have been a lot of efforts to reveal the nucleation sites of rutile in anatase particles. Penn and Banfield suggested that {112} twin interfaces between anatase particles heated hydrothermally could be the nucleation sites of rutile [13]. Gouma and Mills reported that rutile nuclei form on the surface of coarser anatase particles and the newly transformed rutile particles grow at the expense of neighboring anatase particles [14, 15]. Weinberg proposed a model that the nucleation of rutile occurs on the surface first and bulk

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nucleation follows so that the surface nucleation is dominant in anatase nanoparticles [16]. Other researchers suggested that small amount of metastable brookite phase acts as a nucleation site because it is a intermediate structure from anatase to rutile in nanocrystalline titania prepared from solution of various pH [6, 9, 17].

In this study, the growth and phase transformation of nanocrystalline titania powders during heating process were studied through in situ and ex situ TEM observations. The commercial nanocrystalline titania powders of high purity produced by physical vapor synthesis were used to avoid the effect of defects formed in nanocrystalline titania powders produced by solution-based production methods [18]. The mechanisms for nucleation and growth of rutile from anatase particles will be suggested here on the basis of results of XRD analyses and TEM observation.

Experimental

The nanocrystalline titania powders (99.9% anatase, 32 nm, Aldrich Chemical Co., USA) produced by physical vapor synthesis were used for this study. The growth and phase transformation of nanocrystalline titania powders were observed ex situ and in situ by transmission electron microscopy (TEM; JEOL-2010F, JEOL, Japan, 200 kV). For the ex situ TEM observation, the nanocrystalline titania powders were heated in a tube furnace under air condition first and observed by TEM. The changes in phase were analyzed by X-ray diffractometer (XRD; RU200, Rigaku, Japan, 60 kV, 200 mA). The particle size was calculated from the Scherrer equation with (110) peak of rutile and (101) peak of anatase. The broadening due to instrumental effects was corrected by subtracting peak broadening of the titania powder with micron particle size from the measured one of nanometer-sized titania powder. The percentage of rutile transformed from anatase was measured through the method of Spurr and Myers from XRD peaks [19].

In addition, the changes in particle morphology and phase transformation during heating process were in situ observed by TEM. The powders were scattered in acetone by ultrasound, then dispersed on the holy carbon copper grids. The selected area diffraction was recorded on the image plates to identify phases and structures of the individual titania particles.

Results

X-ray analysis of phase transformation

Nanocrystalline titania powders consist of spherical anatase particles with the average particle size of 32 nm as shown in Fig. 1. The size distribution of starting anatase particles are in the range from 5 to 50 nm. It was confirmed that the anatase particles are defect-free by TEM. The high resolution image and electron diffraction pattern in Fig. 1b certify that an anatase particle is a single crystal. Figure 2a shows the evolution of growth and phase transformation in the nanocrystalline titania powders heated in a tube furnace under air condition at different temperatures for 4 h. Rutile started to appear around 650 °C and increased with the heating temperature. It has been known that anatase-to-rutile phase transformation temperature varies according to powder preparation methods and properties of anatase particles like a particle size [20]. After heated at 800 °C, titania powders were fully transformed into rutile. The growth and phase transformation of titania particles

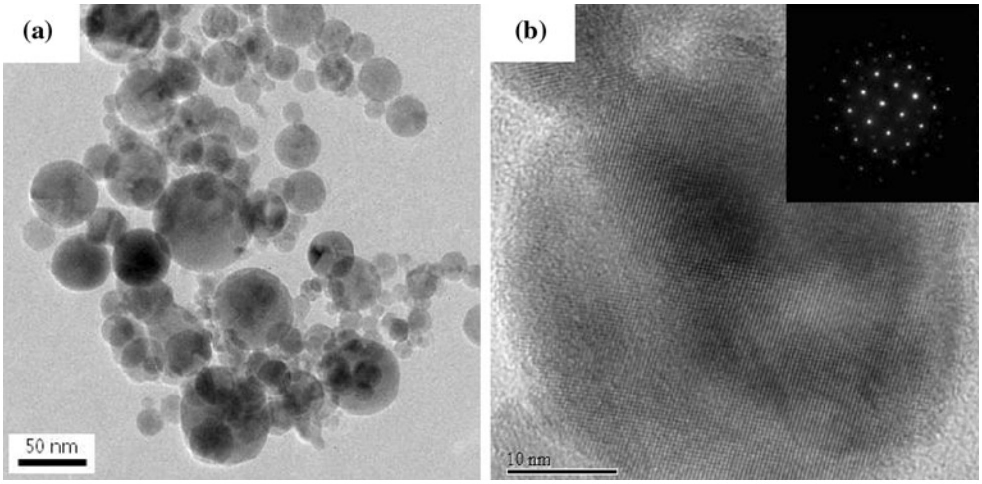

Fig. 1 **a** TEM micrograph of starting titania powder and **b** high resolution image of an anatase particle. The electron diffraction pattern in the *inset* of (**b**) certifies that an anatase particle is a single crystal

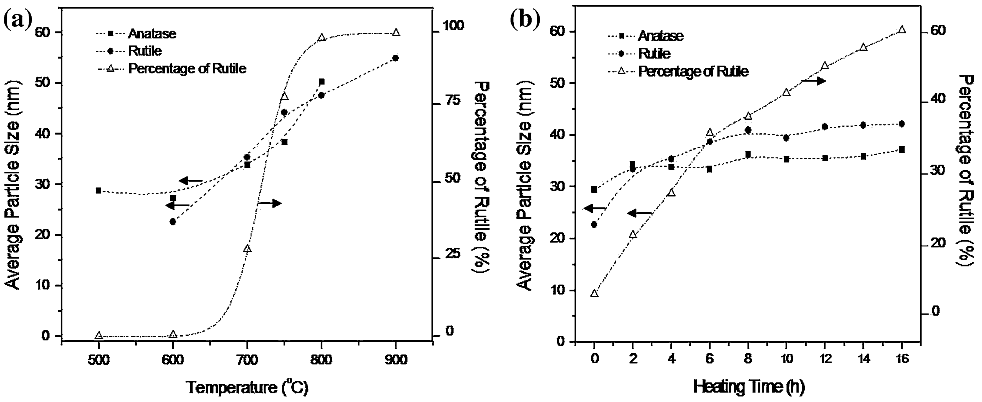

Fig. 2 Results obtained from X-ray diffraction for particle size and percentage of transformed rutile in titania powder heated (**a**) at various temperatures for 4 h and (**b**) at 700 °C for a different time

occurred simultaneously. Anatase and rutile particles grew with the similar change of particle size in the temperature range where the phase transformation proceeded. Even after the complete phase transformation, rutile particles continued to grow. Even though brookite phase has been suggested to be an intermediate phase from anatase to rutile [6, 9, 17], it was not observed in this study.

Figure 2b shows the evolution of growth and phase transformation in nanocrystalline titania powders heated at the fixed temperature, 700 °C, for different time. The percentage of transformed rutile increased linearly with heating time. The size of anatase and rutile particles remained unchanged after heating of 8 h. However, the size of rutile particles was generally larger than that of anatase particles.

TEM observations of growth and phase transformation

The titania powders were heated in TEM in order to in situ observe the evolution of the growth and phase transformation. Figure 3 shows the coalescence of the anatase particles heated at 450 °C. A small anatase particle in the region 1 of Fig. 3 rotated and propagated into a large anatase particle as indicated by an arrow. The rotation of particles was confirmed by the direction change of lattice fringes of anatase (101) plane indicated with short lines. Enlarged high resolution images of the region 1 are shown in Fig. 4. It turned out that the interface between anatase particles is amorphous as shown in the enlarged high resolution images of Fig. 5. The boundaries of anatase particles are drawn by the dashed lines.

It was observed that the rutile particles grow in two ways. One is the absorption of anatase particles into a rutile particle involving the simultaneous phase transformation as reported before [14, 15, 21]. Another is the coalescence among rutile particles as well as anatase particles. The growth of a rutile particle through the absorption of small anatase particles was in situ observed as shown in Fig. 6. A rutile particle with a rod-like shape grew by absorbing the nearest anatase particles and then became spherical. After the anatase particles near the rutile particle were consumed, the rutile particle started to coalesce with other rutile particles. (The pictures are not shown here.) However, the growth rate of rutile particles through the coalescence was slower than that through the absorption of anatase particles.

TEM observations of nucleation and twin formation

The nucleation of rutile was difficult to be in situ observed by TEM during the heating process, because of the reaction of titania particles with the carbon film. The carbon on the holy carbon copper grid formed the layers surrounding the titania particles as shown in Fig. 3. Moreover, the nanocrystalline titania particles were easily damaged by the electron beam. Therefore, the titania powders were heated in a tube furnace previously and then observed by TEM in order to find a nucleus of rutile.

Figure 7a and b shows the nucleation of rutile at the interface and on the surface of anatase particles. It was confirmed that the rutile nucleus is formed at the amorphous interfaces between anatase particles. The regular stripes of Fig. 7b show that the rutile nucleus is formed on the surface of anatase particle. These regular stripes called the Moiré fringes are generated by the combination of anatase (101) and rutile (110) lattice fringes as shown in the inset of Fig. 7b. When the nanocrystalline titania powders were heated until 700 °C and cooled immediately, many twins were observed in a titania particle as shown in Fig. 7c. It turned out that a titania particle contains the shallow regions of anatase and rutile divided by twins.

Figure 8 shows the sequence of twin formation in an anatase particle. The twins indicated with arrows in the picture were formed on the surface of an anatase particle and expanded along the direction normal to twin planes as heating process proceeded. After cooling, it turned out that the titania particle is a faceted rutile particle.

Figure 9 shows the morphology of grown rutile particles. A rutile particle has twins and grain boundaries. In

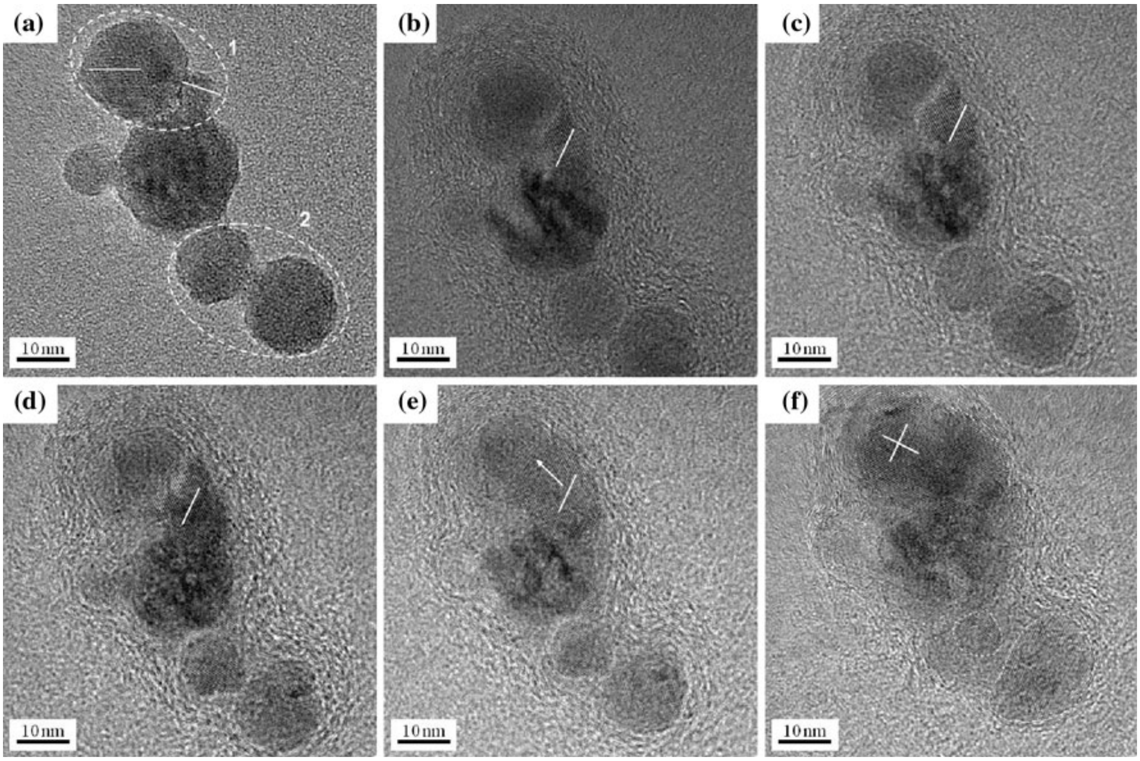

Fig. 3 In situ TEM observation of titania powders heated at 450 °C. The TEM micrographs show the continuous sequence of rotation and coalescence in anatase particles (region 1) and the amorphization at the interface between anatase particles (region 2) during heating process: **a** before heating, **b** 450 °C (11 min), **c** 450 °C (31 min), **d** 450 °C (37 min), **e** 450 °C (41 min), and **f** 450 °C (53 min). The lines of each picture indicate the (101) lattice fringe of anatase to show the rotation of anatase particles

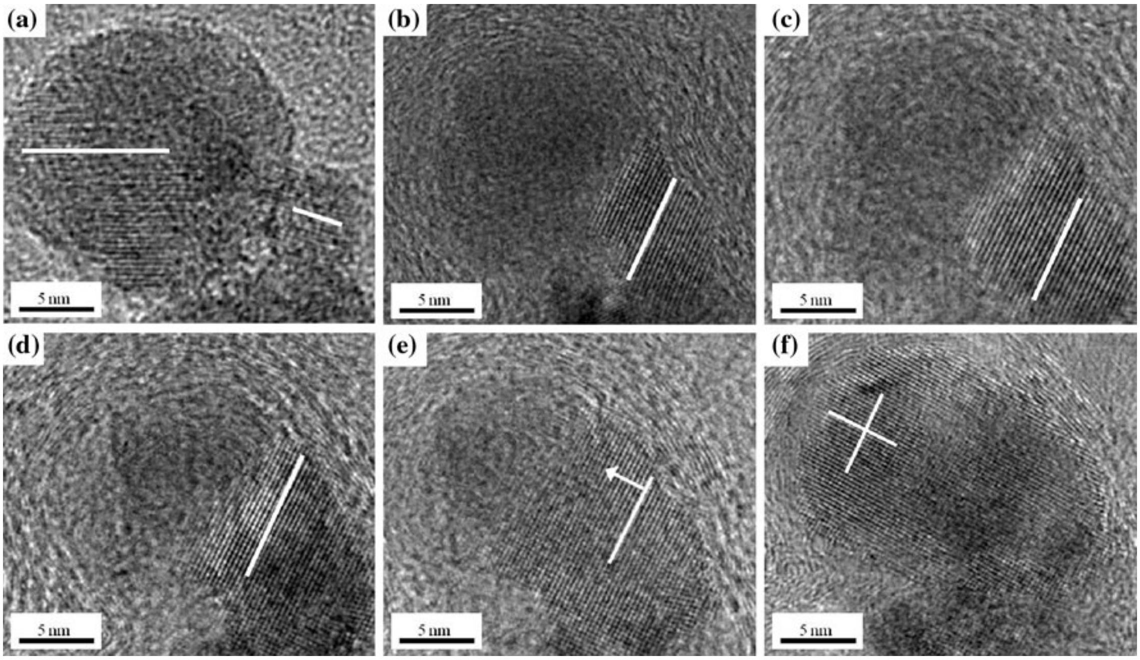

Fig. 4 High resolution TEM images of region 1 in Fig. 3. The TEM micrographs show the continuous sequence of rotation and coalescence in anatase particles during heating process: **a** before heating, **b** 450 °C (11 min), **c** 450 °C (31 min), **d** 450 °C (37 min), **e** 450 °C (41 min), and **f** 450 °C (53 min). The multilayers surrounding the particles are the carbon layers resulted from the reaction of titania particles and carbon film on the holy carbon copper grid. The lines of each picture indicate the (101) lattice fringe of anatase to show the rotation of anatase particles

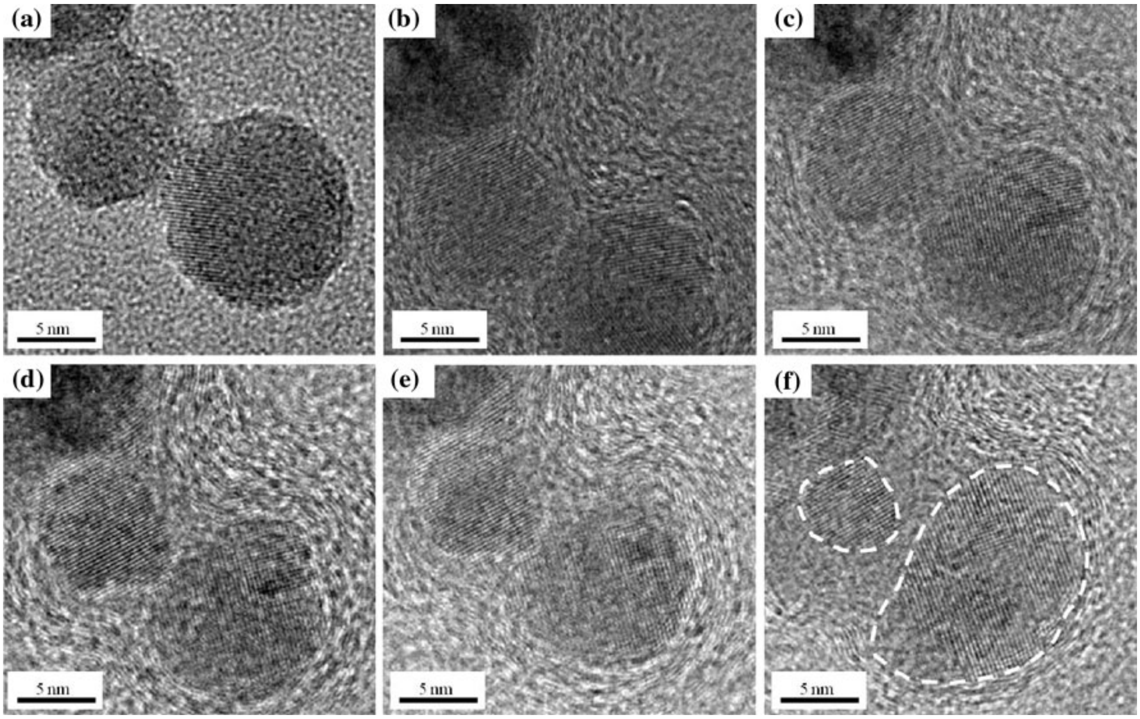

Fig. 5 High resolution TEM images of region 2 in Fig. 3. The TEM micrographs show the amorphization at the interface between anatase particles during heating process: **a** before heating, **b** 450 °C (11 min), **c** 450 °C (31 min), **d** 450 °C (37 min), **e** 450 °C (41 min), and **f** 450 °C (53 min)

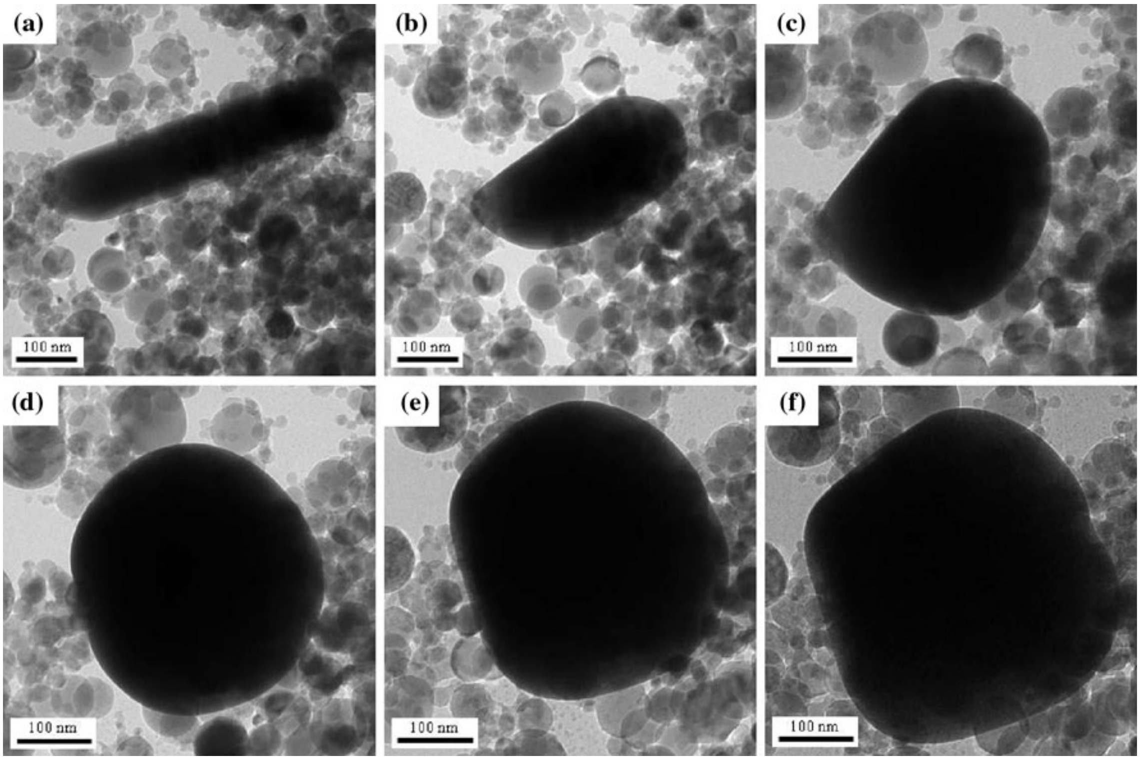

Fig. 6 In situ TEM observation of rutile particle growth. The TEM micrographs show the absorption of the anatase particles into a rutile particle heated at 800 °C: **a** 12 min, **b** 18 min, **c** 28 min, **d** 45 min, **e** 63 min, and **f** 87 min (Note the scale bar varies; they are shown for each picture)

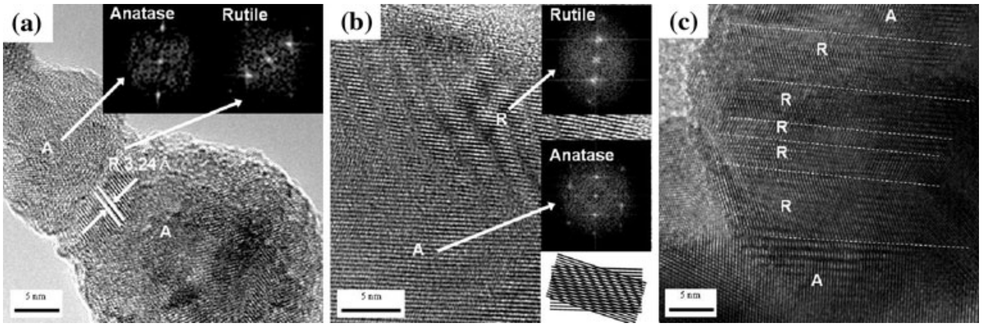

Fig. 7 TEM micrographs showing the rutile phase nucleation in anatase powder heated at different temperature and for different time: **a** 500 °C, 4 h, **b** 600 °C, 4 h, and **c** 700 °C, 0 h. The pictures of (**a**) and (**b**) show the rutile nuclei at the interface between anatase particles and on the surface of an anatase particle. The *inset* of (**b**) shows the Moiré fringe resulted from the combination of lattice fringes of anatase and rutile. The picture (**c**) shows the martensitic transformation by twins

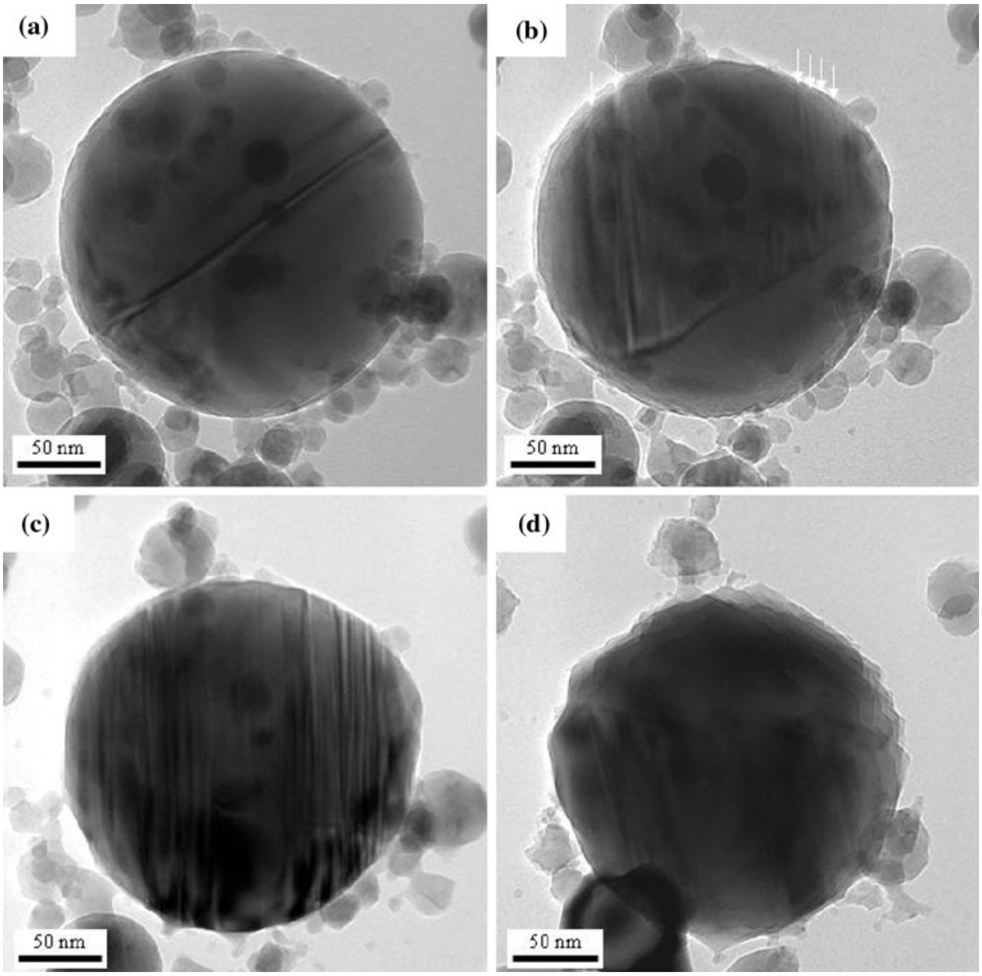

Fig. 8 In situ observation of twin formation in a big anatase particle heated at 700 °C: **a** 13 min, **b** 32 min, **c** 40 min, and **d** 91 min. The *arrows* indicate the twin planes

addition, it was surrounded by the low-energy surfaces of {110}, {101}, and {011}. The electron diffractions of Fig. 9 shows that the growth direction is related to a {101} twin. From the directions of terraces and surfaces, it is clear that the rutile particle grows along a $\langle 1\bar{2}1 \rangle$ direction on the {101}-twin plane.

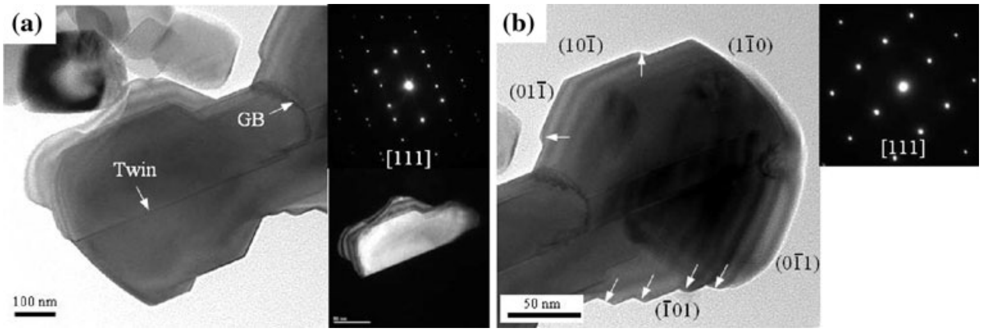

Fig. 9 TEM micrographs showing twins and grain boundaries in the grown rutile particle. The *insets* of each picture show the electron diffraction patterns and dark field image. The electron diffraction pattern and dark field image in the *insets* of (**a**) confirm that a rutile particle has {101} twin and grain boundaries. The picture of (**b**) shows that a rutile particle has {101}, {110}, and {011} surfaces with a lot of terraces indicated with *arrows*. The electron diffraction pattern in the *inset* of (**b**) certifies that a rutile particle is a single crystal

Discussion

As shown in Fig. 2a, the phase transformation temperature of nanocrystalline titania powders, 650 °C, was lower than the known one of titania, 750 °C [22]. This is consistent with the results that the phase transformation temperature is lowered as the particle size is reduced. In this study, however, the critical size for phase transformation is much bigger than reported [7–9]. This bigger critical size in the defect-free nanocrystalline titania powders can be explained in terms of the deficiency of nucleation sites of rutile.

The heating temperature is an important factor to determine the rates of growth and phase transformation of rutile. As shown in Fig. 2a, the nucleation of rutile is promoted more strongly at the higher temperature because the probability to form the amorphous interfaces between anatase particles, which behave as the nucleation sites, increases with heating temperature. The higher temperature may give the larger energy for rotation and coalescence to the anatase particles. This is supported by the fact that, when the heating time was changed at the fixed temperature, the anatase particles could not grow bigger than ~ 37 nm as shown in Fig. 2b. In addition, the smaller particle size of rutile in the beginning stage of heating process of Fig. 1a and b supports that the nucleation of rutile at the amorphous interfaces between anatase particles, which will be called "interface nucleation" in this report, is dominant in the nanocrystalline titania powders.

Figures 3f and 5f show that the interface between anatase particles can be amorphized by severe shear strains during heating process. It corresponds to the fact that the partial amorphous region between particles, which is formed by the amorphization process involving surface diffusion under the influence of the capillarity effect, can help the rotation of particles by shear stress [23, 24]. Therefore, it can be thought that the anatase particles rotate and coalesce with the help of the amorphous interfaces between them. If temperature is high enough for anatase particles to overcome the energy barrier for the phase transformation, however, the amorphous interfaces between the anatase particles behave as the nucleation sites of rutile. From Fig. 7a and b, it was confirmed that rutile is formed at the amorphous interface between small anatase particles heated at 500 and 600 °C for 4 h. The Moiré fringes of Fig. 7b are the evidence that the rutile nucleation occurs on the anatase surface by the shear strains of coalescence. However, this nucleation on the surface corresponds to that at the interface because it started from the interface between the small anatase particles indicated with "A" in Fig. 7b. It can be thought that the nucleation of rutile on the surface of anatase, which was suggested as a nucleation mechanism of rutile [14, 16], is induced by coalescence as well.

In addition to the interface nucleation, the anatase-to-rutile phase transformation can occur through martensitic transformation. It has been reported that the twins play an important role for the nucleation of rutile in the anatase powders heated hydrothermally [13]. As the twins were observed only in the powders heated to 700 °C and cooled immediately as shown in Fig. 7c, it is believed that the twin formation is dominant in the beginning stage of heating process and does not result from the cooling process. Figure 8 also clarifies that twins are formed during heating process, not cooling. Therefore, these twins are regarded as the transformation twins. It is thought that, once rutile nucleates on the surface of an anatase particle, it generates twins and grows along the direction parallel to the twin planes. However, after the region of rutile reaches to the opposite surface of the particle, it expands along the direction normal to the twin planes absorbing the nearest anatase region. This martensitic transformation of nanocrystalline titania powders was observed in other oxide systems as well [25, 26].

It has been known that the intrinsic and extrinsic defects are the origination sites for twins [23, 27]. The "intrinsic" represents the pre-existing defect. On the other hand, the "extrinsic" is the defect to be generated by external change like strains. As the nanocrystalline titania particles are defect-free, it can be thought that the extrinsic defects like Hertzian contact, which can be formed by shear strains of coalescence, behave as the origination sites for twins in this system [27]. The amorphous interfaces between anatase particles can be regarded as the extrinsic defects generated by shear strains of coalescence. In addition, thermal expansion anisotropy of rutile can be a driving force for the growth of twins [28, 29]. Therefore, the extrinsic defects induced by the coalescence of anatase particles cause the origination of twins and rutile with a form of twin grows by help of thermal expansion anisotropy of rutile. However, the martensitic transformation was observed only in the anatase particles larger than ~25 nm. Although the nanocrystalline titania particles are defect-free, the intrinsic defects may exist in the large anatase particles and cause the twin formation as shown in Fig. 8. Therefore, the fact that the critical size of anatase particles for the phase transformation depends on the production methods is closely related to the presence of the intrinsic or extrinsic defects. The critical size in this study is bigger than that reported in other articles, because the physical vapor synthesis can produce the defect-free anatase particle despite of bigger particle size. In conclusion, the nanocrystalline titania powders will show the different critical size, transformation temperature, and transformation mechanisms according to the presence of defects, which depends on the production methods.

The grown rutile particles contain twins or grain boundaries with the low-energy interfaces as shown in Fig. 9. It should be noted that the twins observed in big rutile particles may or may not be the same twins as those formed in the martensitic transformation because the twins can be formed by coalescence of rutile particles [26]. Figure 9a shows that a rutile particle has a {101} twin and a grain boundary as indicated by arrows. The dark field image and electron diffraction in the insets of Fig. 9a confirm the existence of twin and grain boundary. In Fig. 9b, it is shown that a rutile particle is surrounded by the surfaces of {110}, {101}, and {011}. These surfaces have been known as the low-energy surfaces to determine the crystal shape of rutile [30]. The electron diffraction in the inset of Fig. 9b shows that this particle is a single crystal of rutile. Moreover, a rutile particle has a lot of terraces on the surfaces. From the directions of terraces and surfaces, it is concluded that a rutile particle grows along a $\langle 1\bar{2}1 \rangle$ direction on the {101}-twin plane. It is consistent with the growth direction of titania nanowires produced from titania clusters [21]. Therefore, it can be thought that twins affect the growth direction of rutile particles.

Conclusions

The mechanisms for the growth and phase transformation of the nanocrystalline titania powders were suggested through ex situ and in situ TEM observation. The growth of anatase particles results from coalescence and once rutile nucleates the rutile particles grow at the expense of the nearest anatase particles. After the phase transformation is completed, the rutile particles grow through coalescence. The nucleation mechanisms of rutile are classified into interface nucleation and martensitic transformation. The interface nucleation of rutile occurs when the amorphous interface is formed between the small anatase particles by shear strains of coalescence. On the other hand, the martensitic transformation is caused by the intrinsic defects in a big anatase particle or at the extrinsic defects like the amorphous interfaces between anatase particles in the beginning stage of heating process. Therefore, the presence of the intrinsic or extrinsic defects influences the critical size, transformation temperature, and transformation mechanisms depending on the production methods of nanocrystalline titania powders. The growth direction of rutile particles has a close relationship with the orientation of twins. A rutile particle grows along a $\langle 1\bar{2}1 \rangle$ direction on the (101)-twin plane and is surrounded by the low-energy surfaces of {110}, {101}, and {011}.

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