High Resolution Electron Microscopic Studies of Crystallographic Shear Structures in Reduced Rutile Crystals

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The crystallographic shear (CS) structures in reduced rutile crystals growing from microcrystallites in vacuum-deposited amorphous films by electron beam heating have been investigated by means of the multi-beam lattice imaging technique and by the image simulation using the multislice method. A new type of the ordered CS structure represented by a (110) CS plane and a [011]/2 shear has been discovered in reduced Ti_nO_{2n-1} crystals with n ≤ 4. A crossed CS structure having the (110) CS planes by the [011]/2 shear and the (110) CS planes by the [011]/2 shear has been found in Ti_{2m}O_{2m-n-n+1} with m = n = 2 and 4. A structure having the crossed CS planes, obtained by two partial CS operations of [011]/3E(110) and [011]/5E(110), has also been found in TiO.

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I. Introduction

The presence of an ordered structure in Ti_nO_{2n-1} with 4 ≤ n ≤ 9 has been revealed using X-ray powder diffraction by Andersson, Collén, Kuylenstierna and Magnéli(1). The crystal structures of these Magnéli phases are described as being derived from the idealized rutile structure by a regular crystallographic shear (CS) operation <011>/2E{121}-(2)-(4). The crystal structures of the family of Ti_nO_{2n-1} with 12 ≤ n ≤ 36, which X-ray diffraction analysis could not clearly reveal, were studied by electron microscopy and electron diffraction(5)(6). The CS planes in the crystals with 12 ≤ n ≤ 36 are aligned parallel to the {132} planes, formed by the same shear vector <011>/2. It was also reported that a smaller degree of reduction (TiO_{1.995}) may introduce disorder shear planes parallel to {132} and {101}. In an intermediate composition range 9 ≤ n ≤ 16, the CS plane rotates continuously from (121) to (132) about [111] axis, producing a continuous series of intermediate CS planes with (hkl) = p(121) + q(011), where p and q are integers(7)(8). Then, all the structures are described as ordered intergrowths of (121) CS and (011) APB (anti-phase boundary) structures with uniform mixing. Thus, the CS planes which have been established in the reduced TiO_2 crystals are only the {121} and {132} planes, and the {101} defect has been regarded as APB.

The geometrical CS structure can be shown up by means of recently developed high resolution electron microscopy (HREM). Bursill and Wood(9) demonstrated that point-to-point resolution better than 0.17 nm was obtained for Ti_bO_{11} using a pole-piece of Cs = 0.7 mm at 100 kV. They also showed that in order to obtain useful defect structure information the resolution is preferred to limit to approximately 0.3 nm so as to use the so-called projected-charge-density approximation. Recently, Yoshida, Yamada, Ota, Bursill and Wood(10) have examined the Ti_8O_7 phase in an annealed TiO evaporated film with a high-voltage EM at a resolution of 0.45 nm. Both (011) twin boundaries and (121) CS intergrowth boundaries were observed, and a new type of (235) intergrowth defect having stoichiometric Ti_5O_9 was found. The present authors have investigated the CS structure in reduced WO_3 crystals, which grew from a vacuum-deposited amorphous film, using the structure imaging...
technique at a resolution of 0.24 nm\(^{11}\). A new family of \(W_nO_{3n-1}\) having an ordered CS structure represented by \([101]/4\cdot(100)\) was discovered in the crystal with the (001) surface. The presence of oxygen walls along the (100) plane and partial CS, both of which were assumed to be followed by the formation of the CS planes, was revealed.

In the present paper, the structure of heavily reduced rutile crystals which were transformed from amorphous TiO\(_2\) by electron beam heating has been investigated by HREM and computer simulation. A new type of the CS structure, \([0\bar{1}1]/2\cdot(110)\) in Ti\(_2\)O\(_3\) and Ti\(_4\)O\(_7\) crystals, is presented. A perpendicularly crossed CS structure which has been found in Ti\(_{16}\)O\(_{25}\) and Ti\(_4\)O\(_5\) crystals, and an obliquely crossed CS structure which has been found in a TiO crystal are revealed.

**II. Experimental**

An amorphous TiO\(_2\) film was prepared by vacuum-evaporation of TiO\(_2\) powder from a tungsten boat onto a cleaved surface of rock salt. The evaporation was carried out at a source temperature of about 1873 K (1600\(^\circ\)C) in a vacuum of 10\(^{-3}\) Pa. The film thickness was controlled to be 10 nm with an oscillating quartz crystal microbalance. After the deposition, the film was wet-stripped from the substrate and mounted on a carbon holey film supported by a standard copper electron microscope grid. The film was then heated by an electron beam irradiation of 1–0.1 A/mm\(^2\), \textit{in situ} in a JEM-6A electron microscope.

The specimen films were observed with a JEM-200CX electron microscope having a high-resolution goniometer stage THG (\(C_s=1.2\ mm\), \(C_c=1.3\ mm\)) operated at 200 kV. HREM images were taken by using the axial beam illumination. Enlarged photographs were printed using the translational multiple exposure processing technique, to eliminate the random noise caused by the granularity of the photographic emulsion and the electron quantum effect.

Multi-beam lattice images were simulated on a computer by the multi-slice method\(^{12}\)\(^{13}\) with a FACOM M-200 computer at the Data Processing Center, Kyoto University.

**III. Results and Discussion**

1. (110) CS structure

An as-deposited amorphous TiO\(_2\) film was composed of micro-crystallites 1 nm in size\(^{14}\)\(^{15}\). As an electron beam of the order of 0.1 A/mm\(^2\) irradiated the film, the micro-crystallites grew to small rutile crystallites about 10 nm in size. A schema of the structure of rutile (tetragonal symmetry, \(D_{4h}^4\cdotP4/mnm\), with \(a=0.4594\) and \(c=0.2958\) nm) and its (001) projection of Ti and O atoms are shown in Figs. 1(a) and (b). Ti and O atoms are denoted

![Schema of the structure of rutile crystal (a) and a (001) projection of its [TiO\(_6\)] octahedra (b).](image-url)
Fig. 2 HREM image of a rutile crystal in the [001] zone axis, and simulated image calculated at $\Delta f = 85$ nm.

by large and small circles, respectively. The filled circles lie on a level ($c=0$) parallel to the (001) plane, and the open ones lie on another level ($c=\frac{1}{2}$). The unit cell is heavily outlined.

Figure 2 shows a multi-beam lattice image of a TiO$_2$ crystal in the [001] zone axis. A simulated image for the perfect rutile crystal is inserted in Fig. 2. The simulated image agrees with the observed one, and it reflects the columns of the [TiO$_6$] octahedra projected along the [001] axis and shown in Fig. 1(b). Hereafter, Figs. 1(b) and 2 may be compared with defect structures presented below.

The image calculation was carried out for a 10 nm thick (001) TiO$_2$ crystal under the following imaging conditions; $C_s=1.2$ mm, $E=200$ kV, a beam divergence of $10^{-4}$ (semi-angle). For the half width of defocus fluctuation of the microscope (mainly caused by energy spread), which acts on the objective-lens envelope function, 10 nm was assumed to be a reasonable value. The other simulations presented in this paper were also made under the same condition. The underfocus value $\Delta f$, which was indicated in each figure caption, was assigned using a manufacturer's figure for the steps of the objective-lens current knob, and the absolute value was determined by the image simulation.

Fig. 3 HREM images of a Ti$_n$O$_{2n-1}$ ($n=4$) crystal with (110) CS planes in the [113] zone axis, which were taken at $\Delta f=65$ nm (a) and $\Delta f=80$ nm (b), as well as the corresponding electron diffraction pattern (c). Simulated images for the CS model shown in Fig. 4 are also presented in (a) and (b).

By further intense electron beam irradiation, the micro-crystallites grew to thin rectangular crystals a few tens nm long and a few nm wide. Figure 3 shows HREM images of a thin crystal and its electron diffraction pattern. From the diffraction pattern it can be seen that the crystal turns out to have the [113] axis parallel to the incident beam. Super-lattice spots of $4 \times (110)$, which appear along the [110]$^*$ reciprocal lattice axis, imply that there are CS planes parallel to the (110) plane. The (001) projection of the structure model, which contains the (110) CS planes for every...
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Fig. 4 (a) The (001) projection of the structure model of Ti₆O₂₅₋₁ (n=4) crystal. (b), (c), and (d) The relative compositions and spacings of atomic planes parallel to (110), (121), and (132) of rutile.

Fig. 5 HREM images of a Ti₆O₂₅₋₁ (n=2) crystal with (110) CS planes in the [001] zone axis, which were taken at Δf=63 nm (a), Δf=77 nm (b) and Δf=91 nm (c). A structure model is shown in (d). The corresponding simulated images are also presented.

Four (110) octahedral layers, is shown in Fig. 4(a). Simulated images for this model are inserted in Figs. 3(a) and (b), and they are in a good agreement with the experimental ones.

Figure 5 shows a through-focal series of HREM images of another crystal with the incident beam parallel to the [001] axis. Simulated images for a structure model containing ordered (110) CS planes shown in (d) are also presented. The images fully explain the experi-
mental images. Hence, the images in Figs. 3 and 4 can be regarded as the (110) CS planes by viewing down the different directions, [113] and [001].

Figures 4(b), (c), and (d) show the relative compositions and spacings of atomic planes parallel to the (110), (121), and (132) planes of rutile, in terms of the illustration Bursill et al. (13) used. The ordered (110) CS structures similar to the others reported so far can be obtained; two O$_{1/2}$ planes are removed for every n TiO planes, and the rutile blocks are closed up so as to eliminate the gaps. Then, the (110) CS structure is represented by the same general formula Ti$_{4n}$O$_{2n-1}$, and it is formed by the same shear vector [011]/2, as easily seen by comparing Fig. 4(a) with Fig. 1(b). The adjacent octahedra across the shear plane share faces. Thus, the compositions of the crystals shown in Figs. 3 and 5 are Ti$_4$O$_7$ for n = 4 and Ti$_2$O$_3$ for n = 2, respectively. These phases may be regarded as having the monoclinic symmetry C$_{2h}$-P2$_1$/m with a = 2.30, b = 0.296, c = 0.650 nm, $\beta$ = 98.1° for Ti$_4$O$_7$ and a = 1.03, b = 0.296, c = 0.650, $\beta$ = 108.4° for Ti$_2$O$_3$. Although the most reduced rutile crystals observed so far were Ti$_4$O$_7$ (1)(16), the present electron beam irradiation on the very thin films made TiO$_2$ much heavily reduced.

The arrangements of [TiO$_6$] octahedra on a (001) layer of the rutile crystals which contain different CS planes are shown in Fig. 6, after Anderson and Hyde (4). Open and filled circles denote O and Ti atoms, respectively. Each CS plane intersects the (001) layer in a line, across which a pair of octahedra share faces. The face-sharing octahedra on different (001) layers make a chain which extends along the [111] direction on the CS plane, connecting one another by sharing their edges, as seen in Fig. 4(a). In different CS structures, the chains are similar but their disposition is different. We can see the dispositions in Fig. 6, in which the edge-sharing squares indicate the intersections of the chains on the (001) layer; the chains parallel to the [111] direction pass obliquely through the (001) layer at the intersections. The intersections are placed on the line parallel to the [u10] axis, where u is 0, 1, 2, and 3 for the (101), (110), (121), and (132) CS plane, respectively. Thus, the different CS structures can systematically be sorted.

The nearest distance between two pairs of face-sharing octahedra, which is placed on different CS planes, or the inter-CS plane distance of the nearest pairs, $D_{hkl}(n)$, was calculated for the (110), (121), and (132) CS structure with different n values, and they are shown in Fig. 7. If the different CS structures are assumed to occur for a given composition with the same n value, then $D_{hkl}$ increases in the sequence $D_{132}$, $D_{121}$, and $D_{110}$. The areal density of the face-sharing octahedra $A_{hkl}$ or the number density of the octahedral chains on the CS plane, which assigns the CS interface energy, increases in the sequence $A_{132}$, $A_{121}$, $A_{110}$ (A$_{132}$: A$_{121}$: A$_{110}$ = 1: 1.4: 2.2). Therefore, in Ti$_n$O$_{2n-1}$ having n larger than 12, the (132) CS planes, on which the interface energy is the smallest, can align with a sufficiently wide spacing. The nearest distances between the two pairs of the facesharing octahedra, which are placed on the different [111] chains
on the same CS plane, or the intra-CS plane distances of the nearest pairs, $\delta_{hkl}$, are also presented in Fig. 7. When $n$ becomes 10 or below, the spacing between the (132) CS planes becomes so small that the repulsion between the adjacent CS planes becomes influential, and then the (121) CS planes, although their interface energy is higher than that of the (132) CS plane, are introduced and extend the CS plane spacing. A value of $n=8$ corresponds to $n$ at which the inter-CS plane distance $D_{132}(n)$ becomes smaller than the intra-CS plane distance $\delta_{132}$. Similarly, the (110) CS planes predominate for the oxides with $n \leq 4$, in which $D_{121} \leq \delta_{121}$.

The {110} CS structure was never reported, although a {101} CS structure was once proposed by Bursill et al. Landuyt and Amelinckx, who observed a hairpin shaped arrangement of defect planes in pairs in reduced rutile crystals, proposed a generation mechanism for the CS planes, a hairpin model. This mechanism depletes one of the defect faces with respect to the stoichiometric composition, whereas the other face is overfilled. The former face can be assumed to be the APB and the latter one is the CS plane. They described that the active area for the formation of the CS planes is clearly the tip of the hairpin where the cations cooperatively jump as well as the interstitial migration occurs. From the illustrations of the model presented in their paper, it can be deduced that the tip of the hairpin is formed by the (110) face, which consists of the CS plane and not of the APB, although they did not point out it. Therefore, it should be emphasized that the (110) CS is not only possible but it may play an essential role for the generation of CS planes. That is, it is assumed that face-sharing octahedra in pairs are actually produced on the (110) face and then are furnished virtually to form a
more stable CS plane. For \( n \leq 4 \), since there is no interface more stable than \((110)\) CS face, the \((110)\) CS plane shows itself.

2. Crossed structure of the \{110\} CS planes

Figures 8(a) and (b) show lattice images of a reduced rutile crystal in nearly [001] zone axis. Crossed broad fringes with 1.15 nm spacing are ascribed to the \((110)\) and \((\bar{1}10)\) CS planes. The \{110\} planes, on which the present CS occurs, have a higher symmetry than the planes on which any other CS occurs, and the present crystals are so thin that they are violently reduced by the intense electron beam irradiation. These are assumed to be reasons why the crossed CS occur on the \{110\} planes. For the convenience of the explanation of image, we assume that the crossed structure results from two independent shearings taking place successively toward two directions. A structure model of the Ti4O7 crystal shown in

\begin{equation}
(a)
\end{equation}

\begin{equation}
(b)
\end{equation}

\begin{equation}
(c)
\end{equation}

Fig. 8  HREM images of a Ti16O25 crystal with crossed \((110)\) CS planes, taken at \(\Delta f = 60\) nm (a) and at \(\Delta f = 125\) nm (b), and the corresponding electron diffraction pattern (c). Simulated images for the structure model shown in Fig. 9(b), at an incident beam direction tilted by 0.063° about [110] and by 0.25° about [1\(\bar{1}\)0] to the [001] direction, are inserted in (a) and (b).

\begin{equation}
(a)
\end{equation}

\begin{equation}
(b)
\end{equation}

\begin{equation}
(c)
\end{equation}

Fig. 9  (a) A structure model of a Ti4O7 crystal with \((110)\) CS planes by \([0\bar{1}1]/2\) shear. (b) and (c) Structure models of Ti16O25 crystal with crossed CS planes of \((110)\) and \((\bar{1}10)\) derived from the Ti4O7.
Fig. 9(a) is the same as that shown in Fig. 4(a); it is obtained by the CS operation [011]/2·(110). A (110) CS plane can be introduced by removing the O-plane either along the P plane passing across the face-sharing octahedra or along the Q plane keeping clear of them. The former’s shear vector is [011]/2 and the latter’s one is [101]/2. The resultant crossed structures have the (110) and (110) CS planes, both of which have the spacing corresponding to \( n = 4 \).

Figures 9(b) and (c) show the structures derived from the above two operations, respectively. In the crossed CS structure Q in Fig. 9(c), four \([\text{TiO}_6]\) octahedra meet on the same level at the crossing of the CS planes by sharing their faces. This seems rather unstable. On the other hand, in the structure P in Fig. 9(b), three face-sharing octahedra are aligned. This configuration is not unnatural, and in fact it exists in the \( \text{Ti}_2\text{O}_3 \) crystal, which has the corundum-type structure. The image simulation was carried out for the model P, and the result is shown in Figs. 8(a) and (b). The incident beam direction therein was tilted by 0.063° about the [110] axis and by -0.25° about the [110] axis to the [001] direction, as presumed from an electron diffraction pattern shown in Fig. 8(c). The simulated images agree substantially with the experimental ones.

Figure 10 shows an image of a crystal having the crossed CS structure, in which the (110) and (110) CS planes having the same spacing corresponding to \( n = 2, \) 0.51 nm, intersect. Its structure model is also presented. This crossed structure enforces each octahedron to be severely distorted, so that it possibly appears only in such a small crystal.

The composition of the crystal having the crossed CS planes can be determined in a similar way to the case of the crystal having single CS planes (Fig. 4). Figure 11(a) shows the relative compositions and spacings of

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**Fig. 10** HREM image of a \( \text{Ti}_4\text{O}_7 \) crystal with crossed (110) CS, taken at \( \Delta f = 65 \) nm, and its structure model.

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**Fig. 11** Relative compositions and spacings of atomic planes parallel to the P plane (in Fig. 9) of \( \text{Ti}_a\text{O}_7 \) (a) and of \( \text{Ti}_b\text{O}_{2n-1} \) (b).
atomic planes parallel to P in the Ti₄O₇ crystal shown in Fig. 9(a). Two types of planes are seen; one has Ti only, the other O only. The atomic planes repeat with a period of 0.322 nm. If we now omit six O₁/₂ planes from an array of eight O₁/₂ planes and close up the rutile blocks so as to eliminate the gaps, we obtain a (110) CS plane in this crystal. Therefore, if they are removed for every four periods, then (110) ordered CS planes with \( n = 4 \) are introduced and thus the crystal has the crossed CS structure shown in Fig. 9(b).

Generally, the atomic planes in the TiₙO₂ₙ₋₁ crystal having the ordered (110) CS plane are arranged as shown in Fig. 11(b). A layer which is composed of \((n-1) \times \) (one Ti plane and two O₁/₂ planes), one Ti plane and \(2n \times O_{1/2} \) planes repeats in the crystal. On removing \(2(n-1) \times O_{1/2} \) planes in the \(2n \times O_{1/2} \) planes for every \(m \) layers and closing the rutile blocks to eliminate the gaps, we obtain a formula, \( m(Ti_{n}O_{2n-1} - 2(n-1)O_{1/2}) = Ti_{mn}O_{2mn-m-n+1} \), for each homologous of the crossed shear structure of (110) and (110) planes. In the case of the crystal shown in Fig. 8, \( n = m = 4 \), and then its composition is Ti₁₆O₂₅ (=TiO₁.₅₆₂₅).

The crystal shown in Fig. 10 is Ti₄O₅ (=TiO₁.₂₅) for \( n = m = 2 \).

3. Obliquely crossed CS structure and partial CS planes

The (110) and (110) CS planes crossed perpendicularly with each other have been described in the above section. The obliquely crossed CS planes, however, were more frequently observed in larger crystals than the crystal shown in Fig. 10. An example of such crystals is shown in Fig. 12, in which the CS planes are crossed at an angle of about 75° with one another. An array of fine bright patches appears in the dark band, which corresponds to the CS plane. From the analysis of the image, a structure model as inserted in Fig. 12(a) is suggested. In order to explain this structure, we at first take a Ti₂O₃ crystal, as shown in Fig. 13(a), with ordered partial (110) CS planes, which are obtained by a displacement of [011]/₃ instead of the perfect CS of [011]/₂. Then, we assume that the other CS planes are formed along Q' plane which corresponds to the Q plane in the perfect CS structure shown in Fig. 9(c), rather than

![Fig. 12 HREM images in a TiO crystal with an obliquely crossed CS structure of [011]/₃· (110) and [011]/₅·(110), taken at \( \Delta f = 65 \) nm (a) and \( \Delta f = 165 \) nm (b). The beam direction is parallel to [001]. Simulated images for the model inserted in (a) are inserted.](image-url)
along the $P'$ plane, taking account of the configuration of the octahedra along the $P'$ and $Q'$ planes. It has been mentioned in §III.2 that the shear vector is $[101]/2$ if the CS planes are formed along the Q plane. However, as we remove oxygen atomic planes parallel to the Q' plane and displace the rutile blocks toward the [011] direction, the angle between the newly introduced CS plane and the existing CS plane becomes larger than 80°, which is the corresponding angle before the displacement, and thereby it does not agree with the observed angle of 75°. A successful operation is a shear of $[0\bar{1}1]/5$ of the rutile blocks, which is possible for the $Ti_2O_3$ crystal by removing two O planes parallel to the Q' plane. If the CS plane is introduced for every two layers of the [TiO$_6$] octahedra, the composition of $Ti_2O_3$ becomes TiO. That is, the crystal is much more reduced than the $Ti_4O_5$ crystal shown in Fig. 9. The structure obtained by this CS operation $[0\bar{1}1]/3\cdot(110)$ and $[0\bar{1}1]/5\cdot(1\bar{1}0)$ is presented in Fig. 13(b), a part of which is inserted in the image shown in Fig. 12(a). Simulated images for this model are shown in Figs. 12(a) and (b). They are in agreement with the observed images and thus the structure model may be regarded as a reasonable one. It may be noted that the [TiO$_6$] octahedra in this structure are deformed unlike those in the ideal rutile, and that the structure is different from the NaCl-type structure of the ordinary TiO crystal.

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