A HREM Study of Nonbasal Twinning and Superlattices in Ilmenite

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Abstract

The microstructures of natural ilmenite found in Panzhihua district, China, were examined by high-resolution electron microscopy (HREM). The \([12\bar{1}0]\) structural images showed clearly the \((10\bar{1}1)\) nonbasal twinning which seems to be coincident with the \([\bar{1}012]\) rotation twinning. The superlattices with periodicities of 16.8 and 12.6 Å, respectively, as well as the unit-cell twinning related to the ordering of \((10\bar{1}1)\) multiple twinnings were observed. The superlattice resulting from the ordering arrangement of \((10\bar{1}1)\) stacking faults related to the slip systems suggested by Heuer [Philos. Mag. (1966), 13, 379–893] were also detected. Possible genetic aspects are considered.

1. Introduction

The twins of ilmenite (\(\text{FeTiO}_3\)) as well as corundum can occur on the basal and the \{10\bar{1}1\} planes, either as growth twins (Epple, 1964) or as mechanical deformation twins which were first reported by Mugge (1886). The latter is the primary mode of plastic deformation at room temperature when single crystals are subjected to hydrostatic stresses (Kronberg, 1961). Kronberg (1957) suggested atom movements for the \((0001)\) twinning plane based upon the idea of synchronized displacement of quarter/partial basal dislocation. In the case of rhombohedral twinning, Tertsch (1949) quoted \(K_1 = (10\bar{1}1), K_2 = (\bar{1}012)\) and \(S = 0.202\) which were confirmed later by Dugdale (1965) and Heuer (1966). Heuer (1966) also showed that deformation markings can be tentatively attributed to basal twinning. Kronberg (1964; unpublished work, see Heuer, 1966) also pointed out that, when considering only the nearly h.c.p framework of oxygen in ilmenite or corundum, this twinning is equivalent to the \((1\bar{2}2)\) twinning found in some metals with a hexagonal lattice. Shock can produce deformation in ilmenite by twinning initially on \((0001)\) and, in the latter stages, at higher temperature, by twinning on \{10\bar{1}1\} planes (Sclar, Bauer, Pickart & Alperin, 1973).

2. Experimental

The possible slip systems found in ilmenite or corundum were listed by Heuer, Firestone, Snow & Tullis (1971) and Snow & Heuer (1973) and the dislocation networks in them related to these slip systems have also been observed. Philibert (1983) has reviewed these defects recently.

HREM is a suitable means to study the fine structure of materials at the unit cell or even at the atomic level and this paper presents the microstructures of \((10\bar{1}1)\) twinning and domain structure in ilmenite at the subcell level. The arrangement of Fe cations was revealed and some superlattices resulted from the ordering arrangement of rhombohedral twinnings and nonbasal shear slip on the \((10\bar{1}1)\) plane have also been observed.

3. Results and discussion

3.1. \((10\bar{1}1)\) nonbasal twinning

The structure of ilmenite (\(\text{FeTiO}_3\)) was first analyzed by Barth & Posnijk (1934). They showed that ilmenite has a close relationship to corundum...
with \( a = 5.082 \), \( c = 14.026 \) Å and space group \( R3 \).

Fig. 1(a) shows the projected structure of ilmenite viewed down the [1210] axis, in which the O atoms are arranged approximately in a hexagonal close-packed structure, the Fe atoms located between the two layers of O atoms and the Ti atoms in between these two atomic layers. The cations lie on alternate planes at approximately one-third and two-thirds of the distance between the oxygen layers. Fig. 1(b) shows the simulated image calculated for a thickness of 80 Å and defocus value of -700 Å based upon the distance between the oxygen layers. Fig. 1(b) shows the simulated image calculated for a thickness of 80 Å and defocus value of -700 Å based upon the multislice program written by Ishizuka (1982). By comparison with the projected structure of ilmenite, it is shown that under the Scherzer condition pairs of Fe atoms will be imaged as bright dots in the high-resolution image, and therefore a direct relation between the high-resolution image and the structure of ilmenite can be observed under suitable conditions. Fig. 2(a) is an observed image showing the (10\( ^{1} \)) nonbasal twinning which is confirmed by the inserted electron diffraction pattern (EDP). Although such twinning has been shown unambiguously by experiment, it is difficult to derive the structural model from the simple plastic deformation based upon the slip system suggested by Heuer (1966). A possible configuration of (10\( ^{1} \)) nonbasal twinning of ilmenite is shown in Fig. 2(b) constructed by rotating one part of the crystal through 180° around the [\( 010 \)] axis that passes through the O atoms at height 20 as shown in Fig. 1(a). The pairs of Fe atoms of the two variants near to the twin interface are too close to be resolved so that they will be imaged as larger bright dots compared with those in the matrix. In this configuration the height of the atoms in the twin variant is changed relative to those atoms in the matrix. It is noted that in Fig. 2(a) the dots at the interface appear to be larger than those in the twin variants, which agree with the possible structure model (Fig. 2b). It should be pointed out that in Fig. 2(b) the twin interface is a nonconservative one because the ratio of cation to anions deviates from the ratio in ilmenite and such a twin

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\begin{align*}
\text{Fig. 1. (a) The projected structure of ilmenite viewed down the} \\
\text{[1210] axis; the large, medium and small circles represent O, Ti} \\
\text{and Fe atoms, respectively. The dashed line indicates the} \\
\text{possible (10\( ^{1} \)) nonbasal twin plane. The heights of the} \\
\text{atoms above the (1210) plane are indicated by numbers, where the} \\
\text{length of the (1210) axis is 100. (b) Simulated image in the same} \\
\text{direction as (a), calculated for a thickness of 80 Å and a defocus} \\
\text{of -700 Å, where the bright contrast corresponds to the} \\
\text{Fe-atom pairs.}
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 2. (a) [1210] structural image showing the (10\( ^{1} \)) nonbasal} \\
\text{twinning where the dots on the interface seem to be larger than} \\
\text{those in the twin variants. (b) A possible structure model of the} \\
\text{[1012] rotation twinning where the dashed line is the rotation} \\
\text{axis passing through the O atoms at height 20 (see Fig. 1a) and} \\
\text{the groups of Fe atoms at the interface were imaged as bigger} \\
\text{dots in the high-resolution image [see (a)]. The different circles} \\
\text{have the same meaning as in Fig. 1(a) and the height of the} \\
\text{atoms is omitted for clarity.}
\end{align*}
\]
interface corresponds to a deficit of anions or an excess of cations. This ratio would be difficult to obtain by a simple shear slip according to the slip system suggested by Heuer (1966). On the other hand, the rhombohedral (1011) plane is the secondary slip plane (Snow & Heuer, 1973); therefore, the (1011) mechanical deformation twinning would be the result of multiple shear slip and the movement of atoms in such a case could also be complicated. In our observation the multiple shear slip is not obvious although single (1011) nonbasal slip has been found. It is possible to derive the reflection twinning from Fig. 2(b) if the relaxation of atoms and large distortion at the interface can be accommodated. The change of ratio of cations and anions at the interface shown in Fig. 2(b) is actually related to the fluctuation of cations or anions, where the excess of cations is more probable because the octahedral coordinated positions are one-third vacant and so available for cations to occupy. Thus cations have some freedom to occupy these vacancies in ilmenite if the fluctuation of cations occurred when there was a fluctuation of environment temperature or activity of anions, especially in the initial stage of nucleation of a crystal, and this could be maintained in the growth process. As a result, the nonstoichiometric structure may be caused by the presence of such (1011) twinning. This is different from the (0001) basal twinning, in which the twin interface is a conservative one and the chemical composition is the same as the matrix (Kronberg, 1957).

3.2. (10T1) nonbasal domains

Domain structures have been widely found in many minerals (Buseck, 1981) and alloys (Ye, Li & Kuo, 1985). Fig. 3(a) shows the (10T1) domain structure in ilmenite, where the two domain variants having the (10T1) twin orientation relationship are confirmed by the inserted EDP. It should be pointed out that the two variants are not located at the exact twin positions but have a relative displacement along the [1012] direction at the domain boundary after the [1012] 180° rotation as shown in Fig. 2(a). The magnitude of this displacement is about 1/8 of the [1012] vector, and the distance of two rows of image dots at the interface becomes narrow (about 5/7 of that in the matrix). Therefore, they are the (1011) twin-domain structure with a (10T1) twin-like orientation and a translation with respect to each other. Fig. 3(b) shows a possible arrangement of the atoms in such a domain structure, where the two variants have a relative displacement in the [1210] direction. The domain boundary is also a non-conservative one because the ratio of cation and anion here is also different from the matrix of ilmenite, that is corresponding to the excess of cations similar to the (10T1) twin as shown in Fig. 2(b). The balance of electrical charge may be kept either by changing the nature of the chemical bond or the valence of Fe atoms near the interface. The presence of this kind of domain structure can also cause nonstoichiometry in the matrix of ilmenite in the same way as (10T1) twinning. This domain configuration is also difficult to derive from the shear slip of the atoms according to the slip systems listed by Snow & Heuer (1973). It therefore may be the result of the fluctuation of cations that may correspond to either a reduced or an oxidized atmosphere in the nascent nucleation and the configuration was kept in the process of crystal growth. Such phenomena have also been observed in other minerals (Wang, Ye & Kuo, 1988).
3.3. Superlattices and unit-cell twinnings

If multiple twinning happens periodically in a crystal, a superlattice with long periodicity normal to the twin plane should result. For example, orthorhombic enstatite is constructed by twinned monoclinic enstatite, and so-called unit-cell twinning is formed (Iijima & Buseck, 1976). Fig. 4(a) (top part) shows a general view of the multiple (10T1) twinning, where the laths with different contrast are in a (10T1) twin orientation known from the inset EDP (upper left corner). In the S areas the ordered twinnings can be found, and as a result the twinned slabs form a modulation wave normal to the (10T1) plane. Therefore, the wavelength of this modulation wave is equal to the period of the superlattice produced by the twinned slabs as shown in the schematic diagram (Fig. 4b). In this case the wavelength as well as the repeat period of the superlattice must be a common multiple of the (10T1) plane distance and this period can be examined directly in the enlarged image of the S area (lower part of Fig. 4a) where the major repeat period is 16-8 Å (4 × d10T1). This is also confirmed by the inset optical diffraction pattern (ODP) of this area (bottom left corner of Fig. 4a), in which there are three extra spots indicated by arrows between the two basic spots in the direction normal to the (10T1) plane. In the same area there is also a slab with a repeat period of 12-6 Å (3 × d10T1), thus two kinds of superlattice have been found. It is different from the basal-twinning modulation because the latter only causes the long period along the c axis of ilmenite, i.e. nH polytypes could be constructed but the Bravais lattices should remain the same as ilmenite. In contrast, the nonbasal-twinning modulation causes a change in the Bravais lattice of the superlattice. For instance, for the 4 × d10T1 superlattice, the Bravais lattice changes into orthorhombic (Fig. 4) and for the case of the 3 × d10T1 superlattice the Bravais lattice becomes monoclinic. The lattice parameters of these superstructures can be deduced based upon the schematic diagram (Fig. 4b) as follows: \( a = 16.80 \), \( b = 9.76 \), \( c = 5.08 Å, \alpha = \beta = \gamma = 90° \) for the 4 × d10T1-type superlattice; \( a = 12.83, b = 9.76, c = 5.08 Å, \alpha = \beta = 90, \gamma = 95.5° \), for the 3 × d10T1-type superlattice; where the repeat period along the [012] direction is actually 2/3 of the value of the [1012] vector, which is known from Fig. 1(a) and therefore the length of the b axis becomes 9.76 Å instead of 14.64 Å.

If the atomic arrangement of ordered (10T1) nonbasal twinning is coincident with the proposed structural model (Fig. 2b), the superlattices here are also the nonstoichiometric structures resulting from the fluctuation of cations in the initial stage of nucleation of a crystal. In other words, the fluctuation of cations is an original activity in the formation of nonstoichiometry in ilmenite or other minerals.

3.4. Superlattices related to the slip systems

The ordered (10T1) planar faults may also cause a superlattice as shown in Fig. 5(a), in which there are some diffuse rows of dots that appear so that after every two sharp rows there are alternately one or two diffuse rows. The periodic existence of rows also forms a modulation wave with an average wavelength of 16-8 or 12-6 Å. The diffuse image dots in Fig. 5(a) may be caused by the movement of atoms in the (10T1) plane. The possible slip systems related
to the (10\overline{1}1) plane listed by Snow & Heuer (1973) are the following:

<table>
<thead>
<tr>
<th>possible slip plane</th>
<th>possible Burgers vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10\overline{1}1)</td>
<td>2/3 [\overline{1}2T0]</td>
</tr>
<tr>
<td>(10\overline{1}1)</td>
<td>2/3 [\overline{1}T11]</td>
</tr>
</tbody>
</table>

Bayer & Cooper (1967) have suggested another slip system, (10\overline{1}1) [\overline{1}012], which is in agreement with Heuer's result. Although these slip systems are all possible in ilmenite, the most probable slip system is (10\overline{1}1), 2/3[T2T0]. Because in this case the direction of motion of the atoms is parallel to the incidence beam as shown in Fig. 5(b), the projected positions of dots in the image may be not changed. On the other hand, the dots may become smeared because of the movement of the atoms. These dots could be smeared more seriously by intentionally deviating the incident beam slightly from the exact [T2T0] orientation. In this slip system the Burgers vector is also a basal one and has a smaller value than the other two, and any change of the Burgers vector means that these stacking faults were produced at a different temperature range, i.e. the larger the Burgers vector the higher the temperature at which the stacking fault was produced.

In our study a superlattice related to the (10\overline{1}1) slip systems has been suggested, and this superlattice as well as the ordered twinning-modulation superstructure introduce new Bravais lattices. Although they have the same repeat period normal to the (10\overline{1}1) plane, which has been proved by ODP or structural images, respectively, the arrangements of the atoms in these new cells are different from each other and thus the symmetries for these superlattices are also different. It is important to note that the ratio of the cations to anions at the slip plane remains the same as that in the matrix so that the superlattice caused by shear slip of the atoms in the above systems leaves the chemical composition unchanged, i.e. they are stoichiometric structures. In other words, this is in principle different from the unit-cell twinning-modulation superstructure.

4. Concluding remarks

By comparing the observations and the above discussion, the following conclusions can be drawn. The [\overline{1}012] rotation twinning and the (10\overline{1}1) twin domain structure are revealed at subcell level and they seem to be coincident with the suggested structural models. The (10\overline{1}1) unit-cell twinnings as well as the superlattices resulting from the ordered (10\overline{1}1) multiple twinnings, with repeat periods of 16.8 and 12.6 A, respectively, are found together. The (10\overline{1}1) stacking faults possibly related to the (10\overline{1}1) 2/3[T2T0] slip system and modulated structures related to the ordering arrangement of these stacking faults are determined as well.

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References


