Growth and Morphological Features of NiO Crystals

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(Received June 14, 1975)

Abstract

NiO crystals are grown by a closed-tube chemical transport method using HCl gas as transport agent. Whiskers, needles, thin blades and platelets are obtained and their morphological features are studied. Whiskers are single crystals with the growth direction parallel to one of ⟨001⟩, ⟨110⟩ and ⟨111⟩ axes. Both needles and thin blades are bicrystals in such a manner that they are composed of two crystals with their lattices mutually rotating by a certain angle around a common [111] axis. In most of the thin blades, the rotation angle is either 22° or 28°, while the needles have always the angle of about 8°. Platelets consist of more than three twin lamellae.

1. Introduction

Stolpe[1], and Emmenegger and Petermann[2] reported, just briefly, that NiO crystals were grown in a closed tube by a chemical transport method with certain halogens and hydrogen halides for the transport agent. They showed that, when HBr and Cl_2 were used, the grown crystals were chiefly single crystals with an octahedral shape. With HCl, Stolpe obtained only polycrystalline aggregates, whereas Emmenegger *et al.* reported that a quartz ampoule was so heavily attacked that the growth experiments could not be performed with any meaningful results.

In contrast with their results, we have found that NiO crystals having several characteristic external forms, such as whiskers, needles, thin blades and platelets, are able to be grown under suitable growth conditions by using the same method with the same transport agent, HCl. A part of these results were already reported elsewhere, chiefly concerned with their growth conditions[3][4]. Here, the morphological features of grown crystals will be reported in detail.

2. Experimental Procedures

Nine kinds of NiO powders, distinct from each other in the starting salts and in the decomposition conditions, were used as raw materials. First, powder (A) was prepared from reagent grade nickel sulfate, by heating it in air at 1200°C for 2 days, as shown in Table 1. Similarly, powders (D), (E), (E′), (F), (F′) and (G) were prepared from four different hydrous salts under the conditions indicated in Table 1. In the case of powder (B), sponge nickel (purity: 4 nines) was dissolved in dilute solution of nitric acid, and nickel hydroxide was deposited from the nitrate

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Table 1. Various kinds of NiO powders used as raw materials.

Kind of powder	Starting salt	Decomposition	
		Temp. (°C)	Time (days)
A	$NiSO_4 \cdot 6H_2O$	1200	2
B	$Ni(OH)_2$	1000	7
C	$[Ni(NH_3)_4(H_2O)_2]\ (NO_3)_2$	1000	7
D	$Ni(NO_3)_2 \cdot 6H_2O$	1000	4
E	$NiC_2O_4 \cdot 2H_2O$	1200	5
E′		1000	5
F	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	1200	6
F′		1000	6
G	$NiCl_2 \cdot 6H_2O$	1000	2

solution by an addition of sodium hydroxide. After filtering, washing and drying, this hydroxide was decomposed in air at 1000 °C. With powder (C), nickel ammoniate was prepared from the sponge nickel and thermally decomposed in almost the same procedures as those with the powder (B).

HCl gas was made by dehydration of hydrochloric acid with concentrated sulfuric acid.

The growth experiments were carried out in quartz glass ampoule, 10 mm in inner diameter and 12 cm in length. A quartz glass tube was charged with a prescribed amount of NiO powder, subsequently evacuated to about 5×10^{-6} Torr and sealed after a desired amount of HCl gas was introduced. The amount of the gas was determined by monitoring filling-gas pressure at room temperature.

The loaded ampoule was placed in a horizontal two-zone furnace operated at 1050–1000 °C. The ampoule was initially set in such a position that the growth region could be heated in the high temperature zone for cleaning. After 20 hours of the heating, the ampoule was moved to a final position for crystal growth where the powder enclosed at one end of the ampoule was placed in the high temperature zone (1050 °C), while the growth region near the opposite end of the ampoule in the low temperature zone (1000 °C). In all the growth runs, the growth time was 50 hours.

Specification of the grown crystals was performed by micrographical observations and by X-ray examinations. Specular reflection obtained by using a laser beam was also employed to determine indices of the external facets of the crystals.

3. Experimental Results

3.1 Growth condition

Four distinct types of NiO crystals were grown when 1 g of the powder (A) was charged with HCl gas at suitable gas pressures. At 10 Torr, a number of whiskers were grown, sometimes together with platelets. These whiskers were found by X-ray examinations to be single crystals with a growth direction parallel to ⟨001⟩ axis. When the gas pressure was raised to about 50 Torr, further, whiskers with ⟨110⟩ growth direction and thin blades were simultaneously grown. It was noted that ⟨001⟩ whiskers were able to be obtained in charging 1 g of the powder (B), (C) or (D) if about 0.5 mg of sulfur was added with HCl gas at 10 Torr.

The platelets were usually grown with any one of the powders (B), (C) and (D), when 1 g of the powder was charged with HCl gas at 10 Torr. In some of these growth runs, needles were simultaneously obtained. The platelets and the needles were also grown, if 0.5 g of the powder (E) or 0.3 g of the powder (E′) was charged with HCl gas at 10 Torr. Some of the growth runs with the latter powder were found to yield whiskers with ⟨111⟩ growth direction instead of platelets and needles.

Lumped crystals of polyhedral forms and aggregates of platelets were predominantly obtained by use of 1 g of the powder (F) or (G) and 10 Torr of HCl gas.

When 1 g of the powder (E′) or (F′) was charged with HCl gas at 10 Torr, any crystals were hardly grown as found by Emmenegger *et al.*[2] The same results were generally found in growth runs using the NiO powders which were prepared from the salts at temperatures below those denoted in Table 1.

3.2 Morphology

(1) ⟨001⟩ *whiskers*

Whiskers of this type were up to ten millimeters in length, and had a thickness ranging from nearly one micron to several hundred microns. Photos. 1(a)-(c) show typical examples of ⟨001⟩ whiskers and their corresponding cross sections obtained by cleavage perpendicular to the growth direction. As seen in Photo. 1(a), ⟨001⟩ whiskers often have a square cross section and are bounded by {100} lateral faces with {111} tip facets. Such a morphology is commonly observed in whiskers of a few microns thick, and occasionally even in whiskers of a few tens of microns thick. ⟨001⟩ whiskers thicker than about ten microns usually have a petalshaped cross section with protrusions along ⟨110⟩ axes (Photo. 1(b)). These whiskers are frequently found to be bounded by {311} facets. It is seen that the grooves have been formed probably as a result of the growth at the edges of {100} lateral faces where the supersaturation may be high. When whiskers grow thicker than several tens of microns, however, the grooves disappear presumably because another thickening process works to fill them up. Their external faces are composed of predominantly {111} facets (Photo. 1(c)), although {100} facets are occasionally observed, too.

(2) ⟨110⟩ *whiskers*

Whiskers with ⟨110⟩ growth direction were similar both in thickness and in

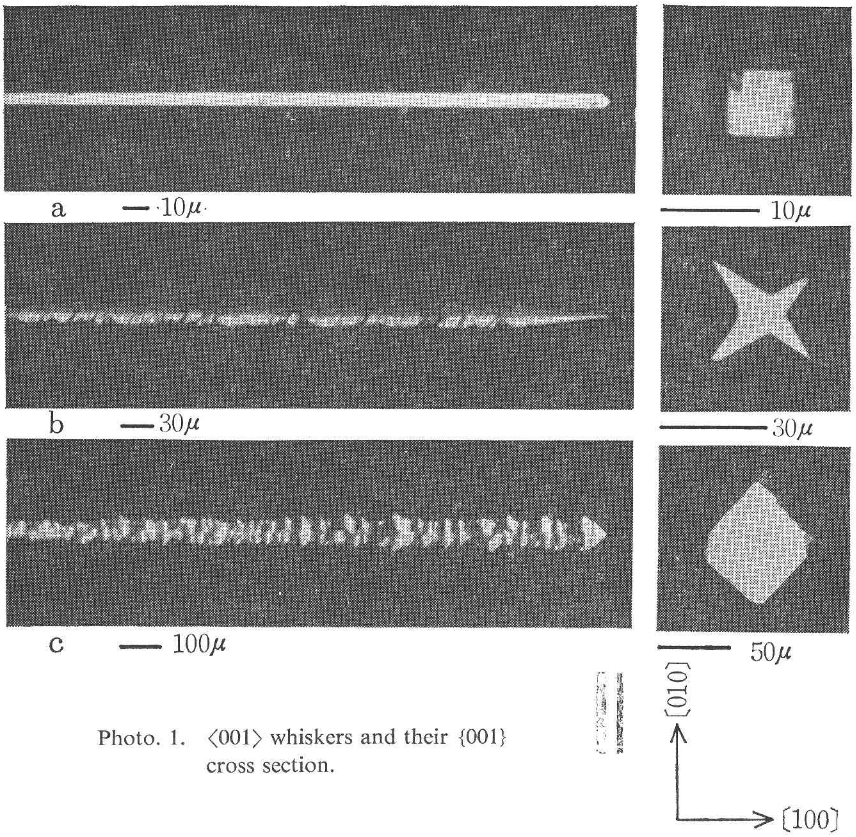

Photo. 1. ⟨001⟩ whiskers and their {001} cross section.

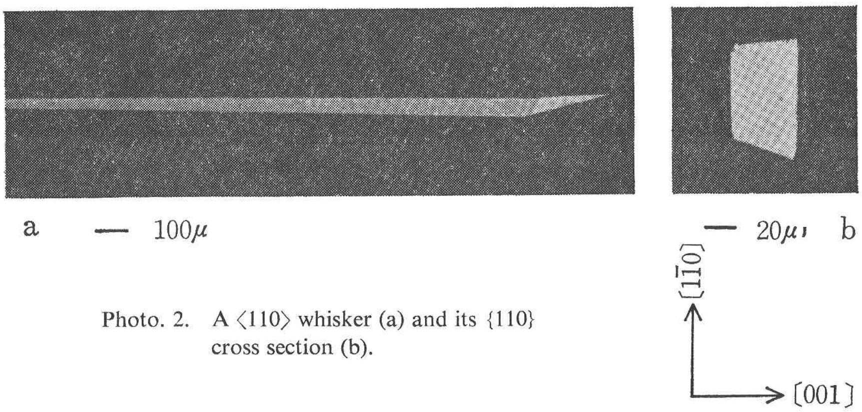

Photo. 2. A ⟨110⟩ whisker (a) and its {110} cross section (b).

length to the ⟨001⟩ whiskers. However, any clear change of morphology due to the thickening growth could not be detected.

⟨110⟩ whiskers frequently have a tapered form such as shown in Photo. 2(a). They are bounded by lateral faces which can be indexed either as {111} or as {311}. Some of the lateral faces are fairly smooth and others have numerous steps. Photo.

2(b) shows a polished cross section of a ⟨110⟩ whisker. As seen in this example, two-fold symmetry is usually lacking from the morphology of ⟨110⟩ whiskers for some reasons.

(3) ⟨111⟩ *whiskers*

Similar to the ⟨001⟩ whiskers and the ⟨110⟩ ones, whiskers with ⟨111⟩ growth direction also had a length up to ten millimeters and a thickness ranging from a few microns to several hundred microns. Photo. 3(a) shows a typical example of ⟨111⟩ whiskers. Their external faces are found to consist of {111} and {311} facets. The cross section is nearly triangular in shape (Photo. 3(b)).

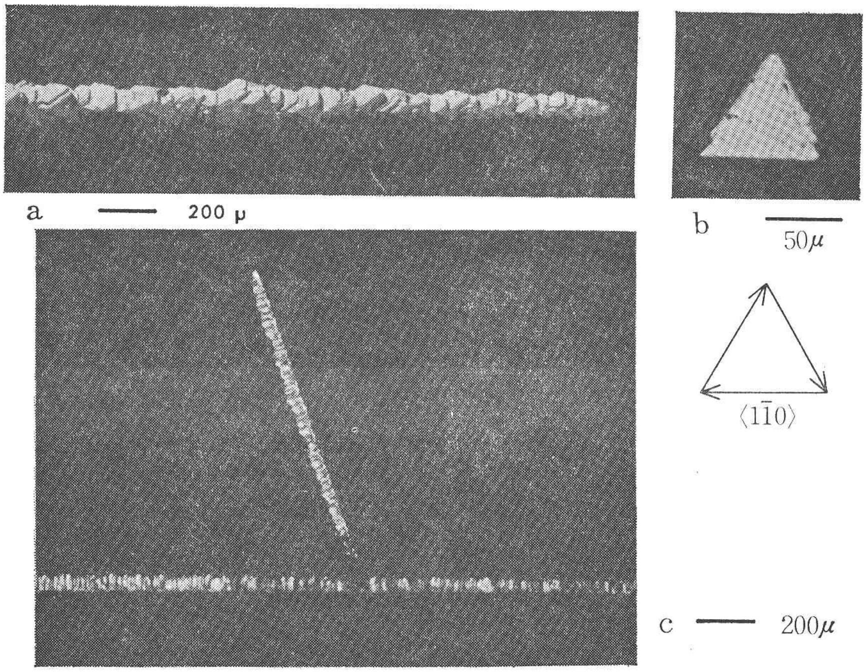

Photo. 3. A ⟨111⟩ whisker (a), its {111} cross section (b), and a branched ⟨111⟩ whisker (c).

For whiskers of this type, it is noted that branching sometimes occurs during their growth as seen in Photo. 3(c). X-ray diffraction shows that branching does not introduce any new crystallographic orientation into them. The branching is considered to be due to the occurrence of growth in two ⟨111⟩ directions brought about by occassional nucleation on a side facet in addition to ordinary nucleation on the top facet. For ⟨111⟩ whiskers, kinking is sometimes observed, too. The X-ray examination reveals that a kinked whisker is also a single crystal with its direction of growth changing from a ⟨111⟩ direction to another equivalent one.

(4) *Needles*

Needle-like crystals were typically several tens of microns to a few millimeters thick and up to ten millimeters long. An example is shown in Photo. 4. In Photo.

5 is reproduced a transmission Laue photograph which indicates that a needle is composed of two crystals mutually rotated in orientation by an angle of about 8° around a common ⟨111⟩ axis perpendicular to the major surface seen in Photo. 4(a). For such needles X-ray and optical observations show that the growth direction is just in between the two corresponding ⟨$\bar{1}10$⟩ axes of the mutually rotating crystals. From the observed rotation angle, therefore, the indices of the growth direction is estimated approximately as ⟨$\overline{13}$ 12 1⟩. Photo. 4(c) shows a cross section of a needle which was obtained by appropriate mechanical polishing and chemical etching. The boundary of the mutually rotating crystals is indicated by an arrow in Photo. 4(c). It is to be noted that the boundary is more or less curved and further seems to have rather high indices. The side faces of needles usually have numerous steps (Photo. 4(b)), since the growth direction deviates definitely from

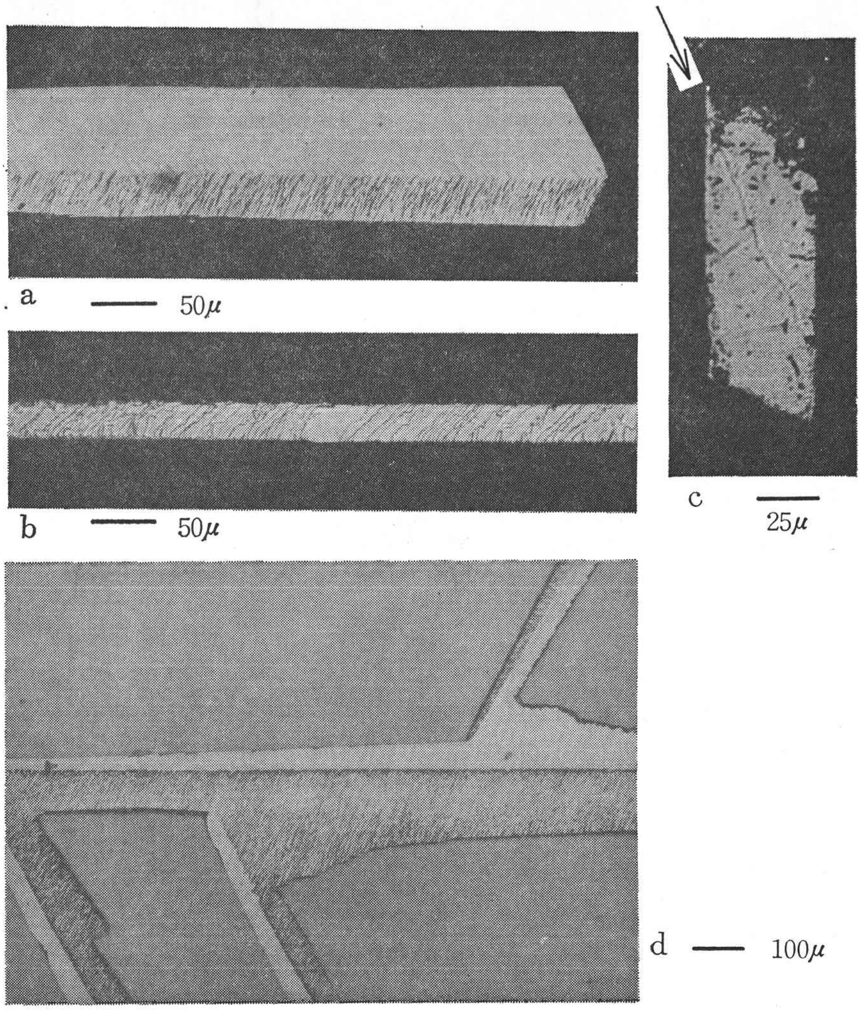

Photo. 4. Major surface (a), side face (b), cross section of a needle (c), and a branched needle (d).

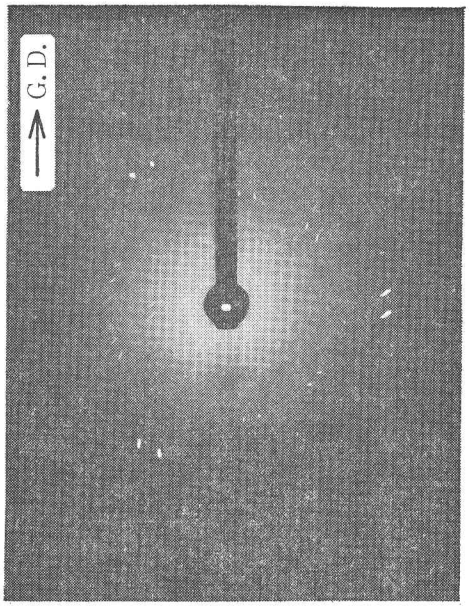

Photo. 5. Laue photograph of a needle. The arrow indicates the growth direction (G.D.).

the $\langle\bar{1}10\rangle$ axis.

As seen in Photo. 4(d), sometimes a number of branches are successively grown from a needle with a fixed angle of about 60°. X-ray diffraction verifies that these branches should have not only the same texture but also the same crystallographic orientation as the stem has.

(5) *Thin blades*

Crystals belonging to this type were as thin as nearly one micron, and had a width of a fraction of millimeter and a length of several millimeters. As seen in Photo. 6, a thin blade consists of a whisker-like axial core and a pair of wings. The wings are narrow near the tip (Photo. 6(b)), indicating that they are grown following the axial growth of the whisker-like core. X-ray examinations indicate that the paired wings on both sides of the core are single crystals, but their lattices are mutually rotated by a certain angle around a common $\langle 111\rangle$ axis perpendicular to the major surface. Therefore, each thin blade is a bicrystal and the boundary which separates component crystals in the blade must lie within the axial core. The rotation angle is found to be either 22° or 28° for most blades. These values are much larger than the value of 8° found for the needles. Since the direction of axial core bisects the two corresponding $\langle\bar{1}10\rangle$ axes of the component crystals, its indices can be estimated as $\langle\bar{4}31\rangle$ for those blades with the 28° rotation and as $\langle\bar{5}41\rangle$ for the blades with the 22° rotation.

Blades are found to have the bounding edges parallel to either $\langle 110\rangle$ or $\langle 211\rangle$ axes. The thin side faces are identified by specular reflection as either

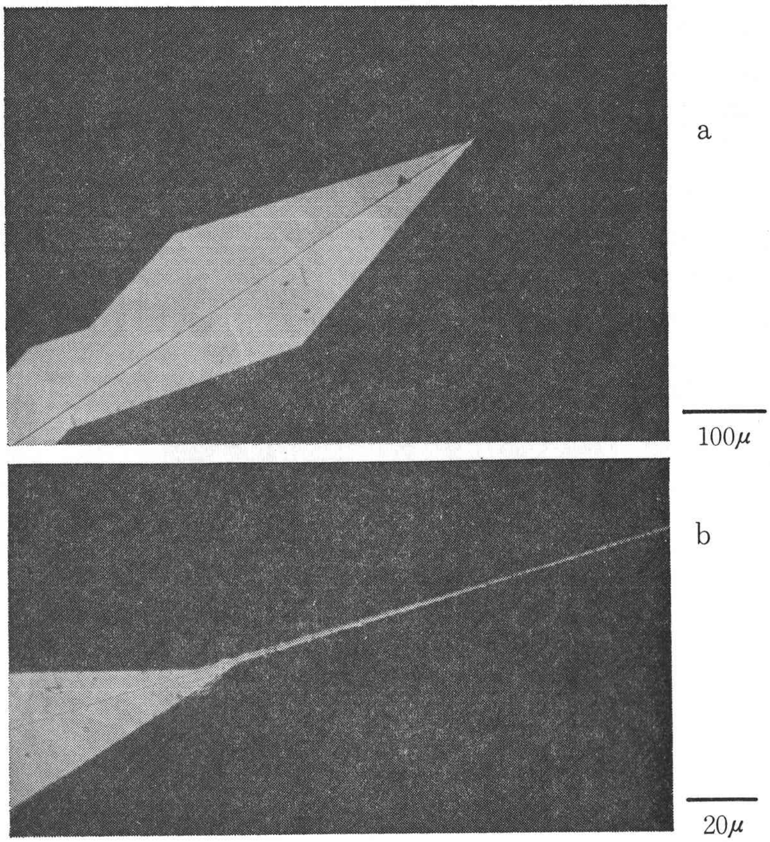

Photo. 6. A thin blade (a) and its tip part (b).

{111} or {311} planes.

(6) *Platelets*

Plate-like crystals had a thickness ranging from several tens of microns to several hundred microns, and a surface up to 50 square millimeters. Photo. 7(a) shows one of these platelets. The platelets are characterized by a fact that they are always composed of multiple lamellae twinned with respect to each other successively on {111} planes parallel to the major surface.

As described in our previous paper[3], the presence of such twinning is confirmed by X-ray observations. The Laue patterns taken with the incidence normal to the major surface exhibit a six-fold symmetry (Photo. 8). But the rotation photographs indicate that the platelets should have the ordinary NaCl-type structure of NiO crystal, leading to a conclusion that the symmetry of Laue photographs is only an apparent one due to twinning. The orientation of twin planes and the number of twin lamellae can be determined by observing the side faces and the cross sections of platelets with a microscope. The platelets usually contain more than three twin lamellae, as seen in Photo. 7(b). From measurements by specular reflection, it is confirmed that the side faces of platelets are indexed as {111} in most cases, and

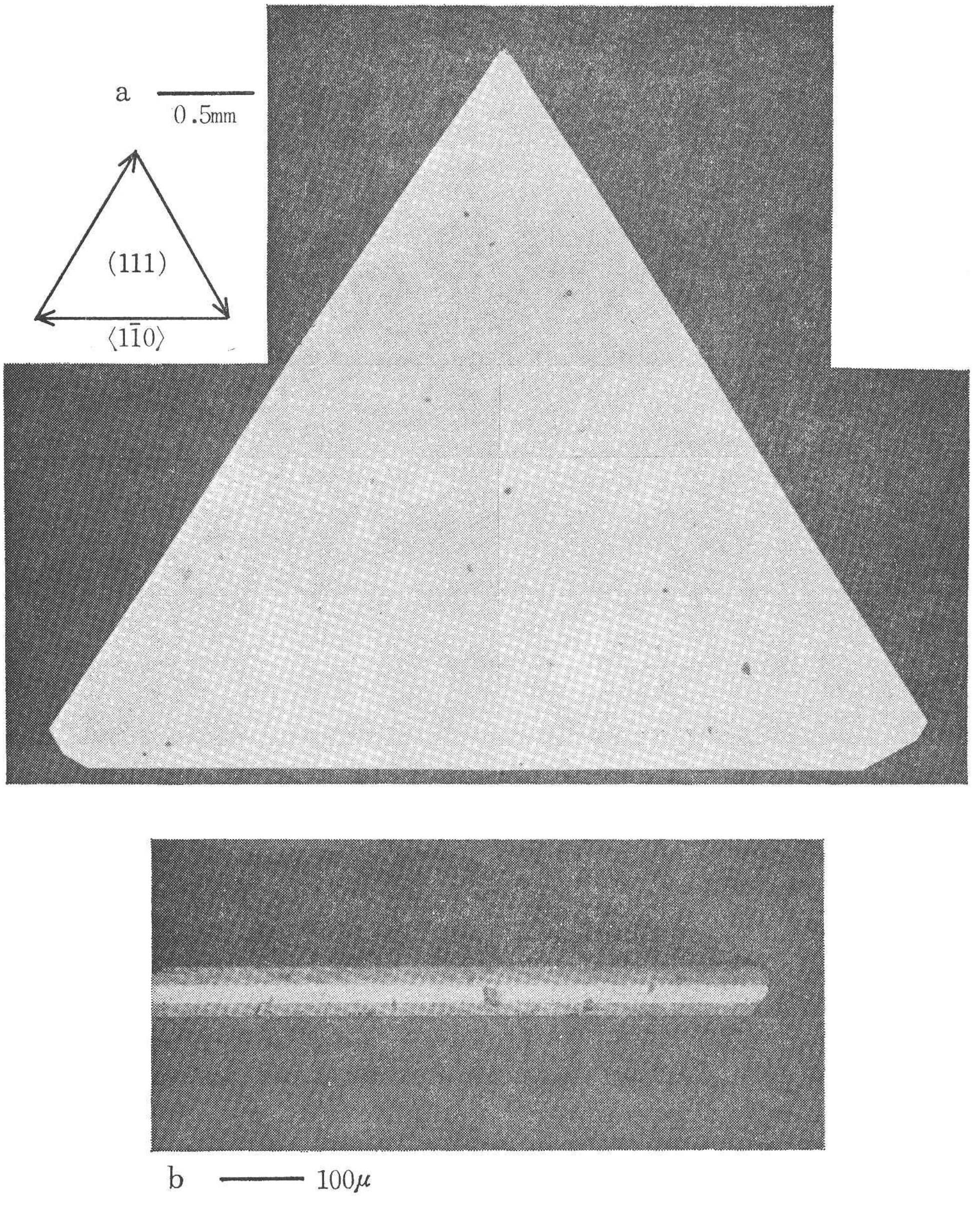

Photo. 7. A platelet (a) and a {111} side face showing two twin planes (b).

occasionally as {311}.

4. Discussion and Conclusion

NiO crystals grown by the closed-tube chemical transport method were studied from a morphological point of view. As shown in the preceding section, X-ray diffraction and micrographical examinations clarify that the grown crystals can be classified into six types, except for tiny single crystals of octahedral shape and some

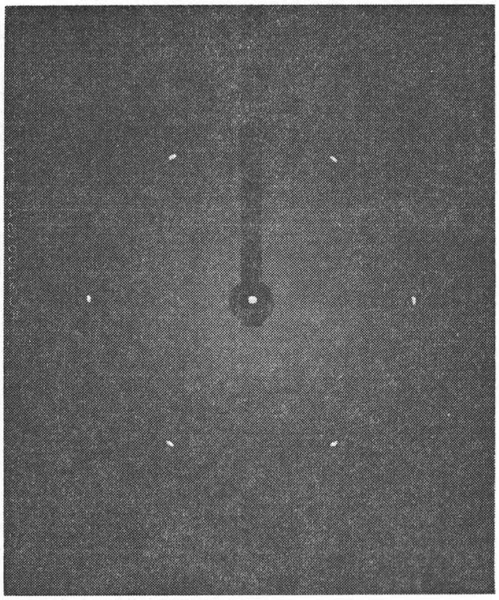

Photo. 8. Laue photograph of a platelet.

complex polycrystalline aggregations. The whiskers are found to be classified into three types and are identified as single crystals with the growth direction, respectively, along either of ⟨001⟩, ⟨110⟩ or ⟨111⟩ axis. On the other hand, the thin blades and needles are found to be bicrystals, and the platelets consist of twin lamellae to be described as "spinel twins".

The growth of dendrites or platelets containing multiple lamellae of {111} twins has been well known in many semiconducting substances of diamond and zinc-blende structures, and explained on the basis of the so-called re-entrant edge mechanism proposed by Wagner and others[5)~9)]. In view of the morphological similarity to these platelets, the growth of the present NiO platelets is also considered to be based on the same mechanism. It may be worth noting, however, that such twinned platelets are rarely grown in ionic substances of NaCl-type structure, in sharp contrast with the semiconducting materials.

As shown before, the blades and needles are composed of two crystals mutually rotated by a certain angle around a common ⟨111⟩ axis. The same orientation relationship has been known to occur for so-called coincidence boundaries obtained in certain fcc metals and alloys during a recrystallization process[10)]. Further, a similar orientation relationship has also been found in vapour-grown dendrites or whiskers of certain hcp metals[11)12)] and solution-grown dendrites of graphite[13)]. In both cases, the observed values of the rotation angle between component crystals coincide with those values obtained for the NiO blades. Some of the previous works suggest that the structures in the hcp and fcc metals should be described as a kind of rotation twins. This suggestion is also applicable to the present NiO bicrystals.

Price[11] indicated for Cd dendrites that the formation of re-entrant edges at a boundary of the rotation twins leads to the dendritic growth of plate-like Cd crystals. A similar mechanism is considered to work at least for the growth of axial cores of NiO thin blades and for that of NiO needles, although there is little similarity in full appearance between the NiO bicrystals and the Cd dendrites.

It has recently been reported that NiO whiskers with the growth direction parallel to ⟨001⟩, ⟨110⟩ or ⟨111⟩ axis can be grown from thin NiO single crystals heated under appropriate conditions[14]. For these whiskers, branching and kinking are found often to occur as in our ⟨111⟩ whiskers. Their growth is explained on the basis of a VLS mechanism which works under the presence of Pt metal. The NiO whiskers obtained in the present experiment are considered to have a somewhat different growth mechanism, in view of differences in growth temperature and in impurity effect. It should be pointed out that the presence of sulfur plays an important role in the growth of the present whiskers[4]. Detailed effects of sulfur on the growth of NiO whiskers will be reported elsewhere.

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