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GROWTH HISTORY OF HEMATITE

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ABSTRACT

On one crystal of hematite from Japan, the whole final history of growth, from two-dimensional nucleation to spiral growth and the movement of dislocations after growth has ceased, is observed. The end growth history is explained.

Measurements of the step heights made with precision multiple-beam interference show the existence of a growth island formed by two-dimensional nucleation. This has a height of a few units plus a fraction of the unit cell. The step of a spiral growth layer is shown to be a half unit cell. This is a rare feature in crystal growth. The mechanism of the formation of growth islands is also discussed.

INTRODUCTION

Since F. C. Frank (3) proposed the screw dislocation theory of crystal growth, much support for his theory has been reported. Most of the studies were mainly concerened with the spiral itself, its structure and its movement, and did not treat of spirals as a phenomenon during the whole history of growth.

Crystals, especially in nature, rarely grow under definite and unchanged conditions, for the growth conditions may well change either gradually or even suddenly during the course of crystallization. It is not unlikely that natural crystals, at the early stage of growth, may grow under higher supersaturation conditions than the 25% which Frank and others estimated as the critical value for two-dimensional nucleation.

Therefore, in the early stages of growth under high supersaturation conditions, two-dimensional nucleation may well occur without the need for screw dislocations. At the later stage when the condition of supersaturation no longer obtains, then a screw dislocation may form. A spiral growth front can then spread away from the screw dislocation, overlapping and possibly engulfing the nucleation region. But some nucleation regions may still remain uncovered on some crystals.

In this report an account is given of studies on the microsurface structures of the basal plane of a hematite crystal from Japan from which a good deal of the end-growth history can be derived. Further evidence of movement of dislocations after the cessation of growth has also been observed on this crystal. Special attention will be drawn to differences of thickness of the growth layers between two-dimensional nucleation and spiral growth.

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Observation of the Surface Structures on the (0001) Face

The hematite crystal under study is of hexagonal habit, found at Saganoshima, Japan. It occurs in cavities of a basaltic lava. From the mode of occurrence, it is considered that the crystal grew by a reaction between iron chloride gas, which migrated from the magma reservoir as a post-volcanic action, and underground water, etc. The temperature of crystallization is estimated to be rather high, say above 800° C.

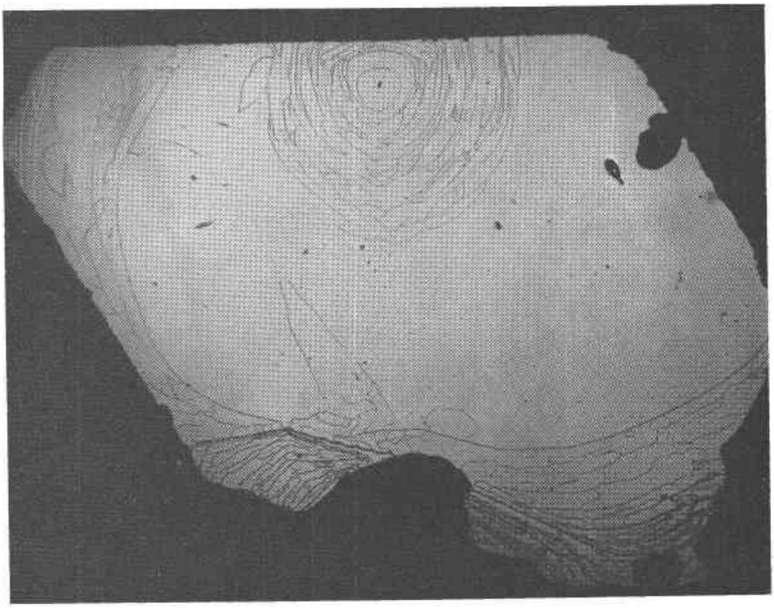

Fig. 1. Ordinary photomicrograph of (0001) face of the crystal about ×10.

Observations of the surface structures were made mainly with a phase-contrast microscope. As this microscope has already revealed growth layers of height 2.3 Å (4) (the shortest distance between two successive oxygen layers in the structure of hematite, and $\frac{1}{6}$ of the unit cell height), the sensitivity is adequate to reveal the existence of spiral patterns.

Figure 1 shows a low magnification photomicrograph of a basal plane of the crystal. Only thick growth layers are visible. Most of the surface other than the marginal and central areas is flat. The thick layers have irregular or circular form.

Over a hundred phase-contrast photomicrographs of this fairly flat area were taken and reconstructed. Two special features appeared, spiral patterns, and triangular islands and tongue-like terraces.

Spiral patterns

Most of the fairly flat area is covered with spiral patterns originating from two screw dislocations of opposite sign. At the origin, the spiral is a triangle, but after a few turns the corners of the triangle tend to round off, and the final pattern is triangular but with curved corners.

In accordance with Frank's explanation (3), the spirals originate from two screw dislocations of opposite sign to form a loop. In the case of two spirals of the same sign originating from one point, the growth fronts do not interfere, but the spacings of the successive layers become narrower.

Several cases occur in which a new spiral joins the main spiral en route. In such cases, the new spirals do not appear in the usual spiral pattern, but form a growth front parallel to that of the original one after a half turn.

At all the screw dislocation points observed, a straight line, which starts from a dislocation and crosses the growth fronts in a short distance has been observed. These lines disappear either at the edge of the thick layers or at some point on the surface. On either side of the line, the level is different. Viewing from the start (screw dislocation point), the right side is higher in the case of the line originating from a left handed spiral, and vice versa. This relation dan be explained as follows. The sign of a spiral originating from a screw dislocation of which the left side is an elevation will be right handed, and vice versa. Therefore, if the dislocation moves after completion of the spiral pattern, the straight line of which the left side is elevated will be observed on right handed spirals, and the right side elevated line will appear from the left handed spiral. At the points where these lines cross the spiral growth fronts, no kinks or disturbance of growth front are observed at all. No evidence of spiral growth has been observed at the other ends of these lines. These facts clearly show that the straight lines are the traces of the movement of dislocations after the completion of the spiral pattern.

B) Triangular islands and tongue-like terraces

The spacing between successive layers from a screw dislocation is usually regular, and their growth fronts are smooth lines. But, as shown in Fig. 2, at some places on the spiral pattern, several tongue-like terraces appear. These terraces clearly have thicker height than the spiral growth layers, because the latter are intercepted by the terraces. At first glance, it would appear that the upper surface of a terrace is combining with a spiral growth layer to form a common surface. But closer examination reveals that there is a very faint discontinuity boundary, which is shown by an arrow in Fig. 3, between these two. This shows that the height of

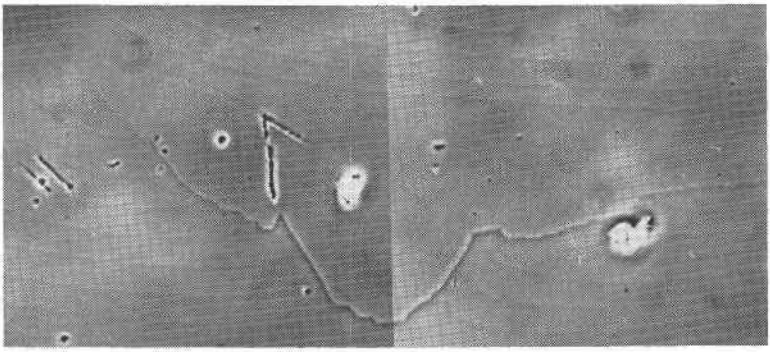

Fig. 2. The tongue-like terrace. Positive phase contrast. ×125

the terrace is not an exact multiple of the height of the spiral growth layers. Numbers of the spiral growth layers which are intercepted by the terrace are exactly the same at both sides of the terrace.

Around the marginal region of the spiral pattern, there are a few relatively thick triangular growth islands which have zig-zag corners, a good

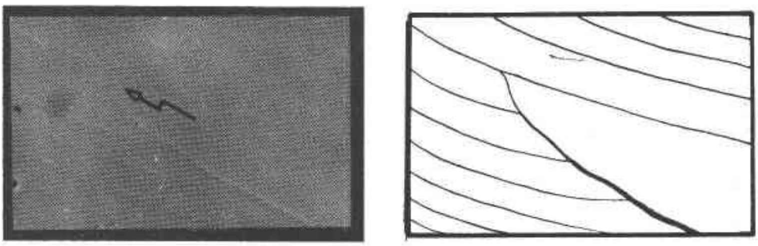

Fig. 3. Example of boundary discontinuity line between the tongue-like terrace and the spiral growth layers. The boundary line is shown by an arrow in the photograph, and schematically drawn on the right. Positive phase contrast. ×135.

example being that shown in Fig. 4. When the growth fronts of spiral arrive at such islands, the spreading of the spiral layers is intercepted by the island with the result that the growth fronts take on a curved shape and avoid the islands. The spiral growth layers surrounding the lower triangular island in Fig. 4 represent an early stage of this interception, and the upper show a succeeding stage.

If the triangular islands are compared with the tongue-like terraces, one finds similarity in their orientations and outer forms. These two are evidently different stages of the same feature. Thus, if the spiral growth proceeds from the stage of Fig. 4, and the total height of the piling of the spiral growth layers reaches to nearly same height as the triangular islands, then these two will combine and form almost a common surface. (As the height of the islands are not exact multiples of the height of the spiral growth layers, the surface is not quite smooth and plane. But the difference is less than the height of one growth layer, it appears nearly like one level.) The succeeding spiral growth fronts are not intercepted

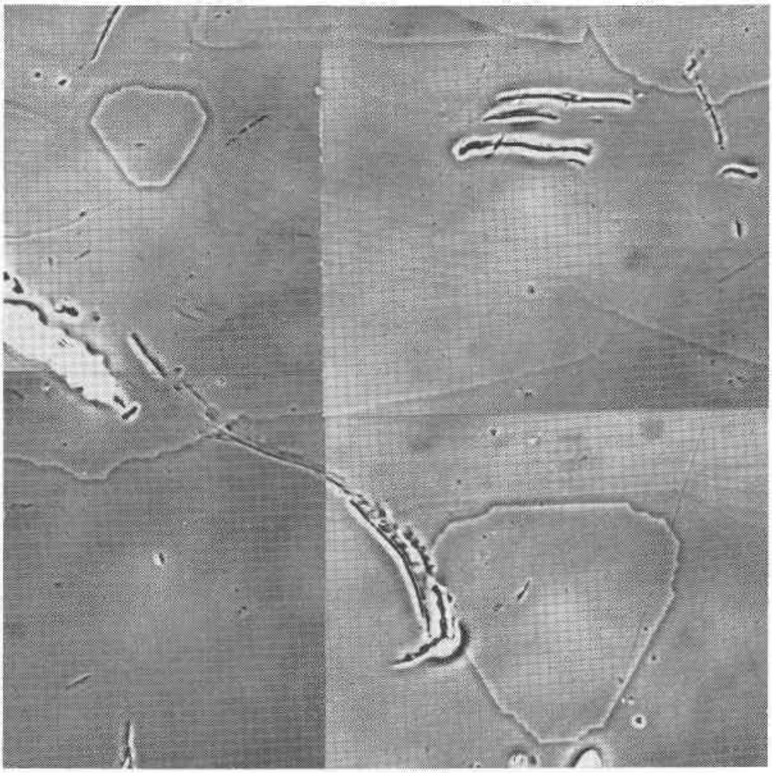

FIG. 4. The triangular growth islands. Irregular black lines and white patches on the islands are artificial scratches. Positive phase contrast. ×135

by the islands, but continue spreading without any interference. As a result of this process, the tongue-like terraces are formed.

It has been observed that the central part of the spiral is completely free from triangular islands and tongue-like terraces. Moving towards the lower part the latter are observed; the complete triangular islands appear only near the margin of the spiral pattern. From this fact, and the fact that the spiral growth fronts are intercepted by the latter structures, it is safe to conclude that the triangular islands and tongue-like terraces exist before the formation of the spiral pattern.

Both the triangular islands and the terraces are definitely elevations. Their surfaces are molecularly flat and no micro-structures can be seen on them other than scratches or percussion marks (Fig. 4). From the high resolution of the microscope used, we can safely conclude that no spiral growths take place on these islands and terraces. They are formed by a three-dimensional nucleation without the help of any screw dislocations.

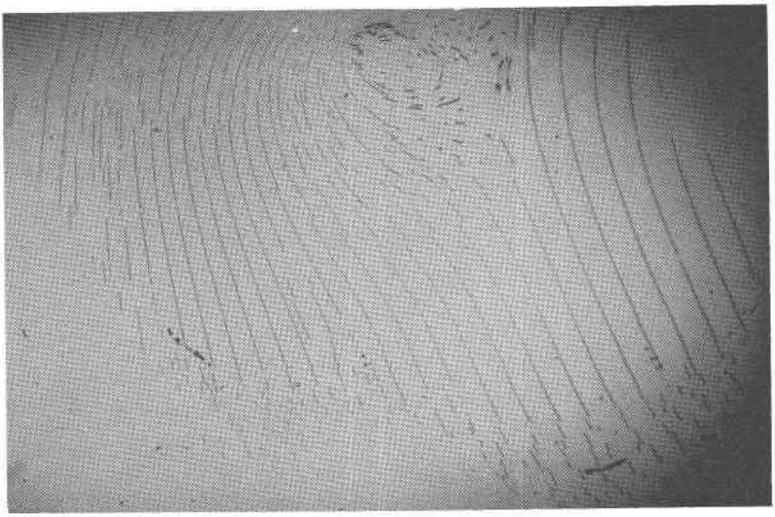

FIG. 5. Low magnification multiple-beam interferogram of the crystal. The same face and the same magnification of Fig. 1. Notice that no shift on the fringes is observed in the flat area.

No fine structures can be seen at the edges of the islands or the terraces. This suggests that these features were formed as separate entities and not by the piling of thinner layers.

Measurements of the Thicknesses of the Growth Layers

Multiple-beam interferometry (5) has been applied to the measurement of the thicknesses of the growth layers.

Even with a fairly highly dispersed interferogram, it was very difficult to secure distinguishable shifts of the fringes at the edges of the spiral growth layers (Fig. 5-6). Fortunately, the tongue-like terraces and the triangular islands have reasonable thickness which give clearly distinguishable shifts of the fringes, and we can count the number of the spiral growth layers which are intercepted by a terrace. This will give the average height of a spiral growth layer. Table 1 shows the results obtained by this method. Fig. 6 is an example of the multiple-beam interferogram.

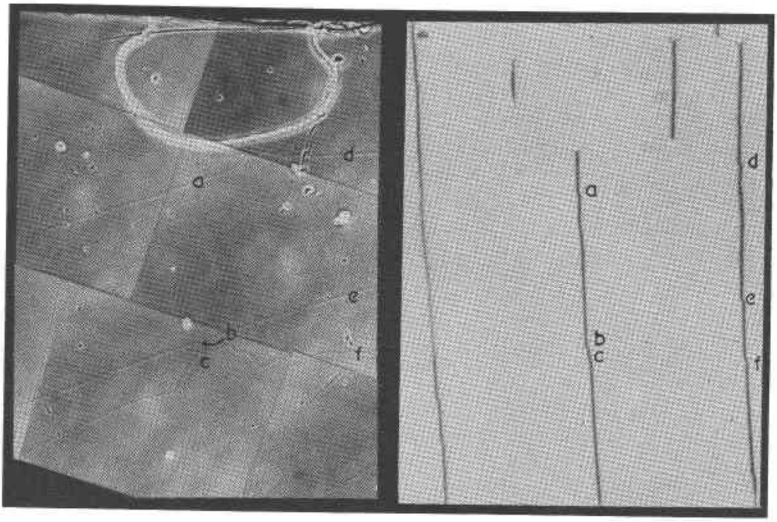

FIG. 6. High dispersion multiple-beam interferogram and a positive phase contrast photomicrograph of the same area. a, b, c—shows the corresponding positions. Notice that only at the edge of the tongue-like terraces, distinguishable shift of the fringe is observable. ×57

TABLE 1. HEIGHT OF SPIRAL GROWTH LAYERS INTERCEPTED BY A TERRACE

Measured height	Number of layers	Average height	Measured height	Number of layers	Average height
12.9 Å	2	6.4 Å	30.5 Å	5	6.1 Å
13.7	2	6.8	31.6	6	5.3
15.1	2	7.4	32.9	5	6.6
17.9	4	4.5	34.2	6	5.7
19.9	3	6.6	36.6	6	6.1
23.9	5	4.8	39.0	5	7.8
28.0	6	4.7	41.8	6	6.9
28.8	4	7.2	46.0	7	6.6
29.2	5	5.8	63.2	7	9.0
29.6	4	7.4			

Average height of a spiral growth layer—6.4 Å

The derived height of a spiral growth layer ranges from 4.5 Å to 9.0 Å, and averages 6.4 Å. It is certainly not 14 Å, which is the height of the unit cell of hematite (more exactly 13.73 Å). The height of a spiral growth layer, namely the Burger's vector of the screw dislocation, is clearly not a unit cell, but a half of this within experimental error. Most measurements of spiral height made so far show that the step height of a spiral is one unit cell height or a small rational multiple of a unit cell, but there are a very few observations of spirals with steps less than a unit cell. For example, S. Amelinckx has observed a spiral of a half unit cell on SiC (1), and on long chain compounds (2). The writer has also reported a 2.3 Å spiral (4), which is $\frac{1}{6}$ of the unit cell, on natural hematite. The spiral described here is one other example of a spiral with step less than a unit cell. And, it seems to the writer that the spirals with step less than a unit cell are possibly fairly common phenomena on natural hematite. It is intended to discuss this in more detail elsewhere.

The height of the tongue-like terraces ranges from about 20 Å to 70 Å (Table 2). As already indicated, it is clear that their heights are not exact but fractional multiples of the height of a spiral growth layer. Observed numbers of the spiral growth layers which are intercepted by the terraces, and calculated heights of the terraces are shown in Table 2. The heights of the triangular islands are about 40 Å.

TABLE 2. HEIGHT OF TONGUE-LIKE TERRACES

Number of layers	3	4	5	6	7	8	10
Number of instances	1	1	2	2	5	1	1
Calculated height of the terraces	20.7 Å+X	27.6 Å+X	34.5 Å+X	41.4 Å+X	48.3 Å+X	55.2 Å+X	69.0 Å+X

$0\,\text{Å} < X < 6.9\,\text{Å}$

SUMMARY

From the above observations, we can summarize as follows.

1. The triangular islands and the tongue-like terraces are originally similar, and clearly existed before the formation of spiral patterns.
2. These structures have the thickness of several plus a fraction of the unit cell of hematite. No spiral patterns are observed on their surfaces, which shows that these islands were formed by three-dimensional nucleation.
3. The fact that the edges of these structures are not composed through the piling of thinner layers suggests that the islands were formed as a single growth feature and not by successive piling of thinner layers.

4. Any spirals on the crystal were certainly formed later than the above structures. As no structures were observed on the spiral patterns, they were clearly formed at the latest stage of growth.

5. The height of the spiral growth layers is a half unit cell. The successive stages of interaction between the growth fronts of the spiral and the pre-existing triangular growth islands have been clearly observed on the crystal.

6. A straight line which starts from a screw dislocation and intersects spiral growth fronts without any effect on the fronts is accounted for by the movement of the dislocation, after the end of crystallization.

Conclusions

The end growth history of the crystal can therefore be inferred as follows.

At the early stage of crystallization, when both temperature and supersaturation condition are high, growth islands form without the help of screw dislocation, at random points on the surface. These islands are considered to arise from the precipitation, adsorption and crystallization of particles of aggregates of atoms or molecules, not by the piling of the thin growth layers.

After the formation of these islands, and if both temperature and supersaturation rates drop, spiral growth fronts spread out from the dislocation points. These can meet with other spirals of the opposite sign with resulting formation of loops. While spreading, when these fronts arrive at the pre-existing growth islands, interception occurs with the result that the front takes on a curved shape, avoiding the island. But, finally piling of the spiral layers reaches a height similar to that of the islands, and the next growth front spreads over the surface of the island and forms a tongue-like terrace.

After the end of crystallization, due to some stress, these screw dislocations can move and if they do they form the straight lines which start from dislocations and intersect the growth fronts with no effects on the fronts.

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References

1. Amelinckx, S., Growth mechanism of carborundum crystals: *Nature*, **168**, 431 (1951).
2. ———, Growth features on crystal of long-chain compounds; I, II, III: *Acta Cryst.* **8**, 530 (1955); **9**, 16, 217 (1956).
3. Frank, F. C., The influence of dislocations on crystal growth: *Disc. Farad. Soc.*, No. 5, p. 48 (1949).
4. Sunagawa, I., Crystal growth of hematite from Ayumikotan, Japan: *Jour. Miner. Soc. of Japan*, **3**, 543 (1958).
5. Tolansky, S., Multiple-beam interferometry, Oxford at the Clarendon Press (1948).

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