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Abstract

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LAYER-SPIRAL EVAPORATION OF CRYSTALS

(Presented by Academician A. V. Shubnikov, 20 I 1958)

The first direct observation of layer-by-layer dissolution of crystals was carried out by René Marcelin in 1914 on the thinnest (of the order of 1 μ) crystals of paratoluidine floating on the surface of an alcoholic solution (^1). He wrote: "Observing the slight dissolution of finished crystals, it was possible to establish the following: the change proceeds not inward, but along the surface; the substance disappears in successive layers. The thickness of each layer remains constant. This thickness varies from case to case, but may reach a thickness equal to four molecular diameters." At present it is known that four molecular diameters constitute, for paratoluidine, a value equal to the parameter of its elementary cell. Therefore it may be said that the thickness of the evaporating layers reached the elementary value, since René Marcelin observed layer-by-layer dissolution of the (001) face of the crystal.

The results of layer-by-layer dissolution of the basal face of a zinc crystal are described in the work of K. M. Gorbunova and A. N. Zhukova (^2).

Later, the subject of investigation was usually traces of weak dissolution of the crystal surface, the so-called "dissolution figures" or "etch figures." Etch figures are formed during weak dissolution of the crystal surface at the sites where screw dislocations emerge.

In the process of growth it is precisely here that spiral hillocks are formed, which may be regarded as "growth figures." Investigation of the process of formation of spiral-growth centers showed that the center of the spiral is indeed the point of intersection of the dislocation line with the crystal surface (^2).

In the last decade a number of works have appeared whose authors point to the layer-spiral structure of "etch figures." Pandya and Tolansky observed etch figures having a layered structure on the octahedron of diamond (^3). Hewer, Amelinks, and Decaiser investigated by the interferometric method layered etch figures on topaz crystals (^4). Ellis obtained, by slight dissolution, layer-spiral etch figures on germanium crystals (^5), etc.

It follows from the works listed that, near the points where screw dislocations emerge on the crystal surface, growth spirals were observed if a growing crystal surface was investigated, or spiral dissolution figures if a crystal face that had

Figure 1

Figure 1: Figure 1

Figure 3

Figure 2: Figure 3

been subjected to etching was investigated. This makes it necessary to suppose that a growth spiral, in the process of evaporation, must also be transformed into an evaporation spiral.

Experimental investigation of the process of layer-spiral evaporation was the aim of the present work.

In addition, figures formed at various stages of evaporation were studied; knowledge of them is very important for investigation of the morphology of the surface of a crystal subjected to slight evaporation or dissolution.

The use of the apparatus described by us earlier (^2) made it possible to observe not only layer-spiral growth of crystals, but also layer-spiral

Fig. 1

Fig. 3

evaporation of a substance from the surface of crystals. The objects of the investigation were crystals of paratoluidine and naphthalene.

Observation showed that, when a crystal passes from growth to evaporation, the direction of propagation of the layers changes to the opposite one. At the point of equilibrium the layers are immobile. The propagating layers usually do not change their thickness. In addition, it was found that, at the points where screw dislocations emerge on the crystal surface, around which a helicoidal layer develops under growth conditions, weak evaporation causes the spiral to begin "rotating" in the opposite direction. Direct observation of this process is rather difficult because of the low velocity of displacement of the layer fronts both during growth and during evaporation. Therefore we studied these processes by means of time-lapse microcinematography. We filmed the growth and evaporation of a crystal at a magnification of 300 times, at a filming rate of one or three frames per second. Of greatest interest was the study of the morphology of the crystal surface at the moment of transition from crystal growth to its evaporation, i.e., during a nonstationary process.

The transformation of a growth spiral into an evaporation spiral is best observed under very weak evaporation. In this case it is especially easy to notice that the velocity of displacement of the front of the evaporating spiral layer differs depending on its curvature. The most intense evaporation begins at the apex of the helicoidal layer (at the center of the spiral), at places with the smallest radius of curvature. The "rotating" step of the spiral, which encircles the screw dislocation during the process of crystal growth, begins to move rapidly in the opposite direction, forming near the point of emergence of the dislocation an evaporation spiral of the opposite sign. If one looks from above at the face of the crystal, one can see that the spiral layer in the initial stage of evaporation consists of two spirals: at the center there is an evaporation spiral of one sign, and farther out a growth spiral of the other sign.

At the point where these spirals meet, a protrusion is formed (Fig. 1). This protrusion is the transition from the growth spiral, which forms a hill on the crystal surface, to the evaporation spiral, which in the course of further evaporation leads to the formation of a pit. The shape of the protrusion depends on the ratio between the velocity of the reverse motion of the entire spiral layer and the intensity of the evaporation spiral. During evaporation this protrusion does not move along the spiral, but is preserved until it becomes level with the crystal surface. It is displaced by a distance of the order of twice the distance between the turns. This is explained by the difference in the angular velocity of the turns of the growing and evaporating spiral ([6]).

After the angle of dissolution of the cone of the growing spiral reaches 180°, the rapid formation of an evaporation spiral opposite in sign to the growth spiral begins, together with the appearance of a pit on the crystal surface.

Figure 1 shows details of this process, presented as frames from a motion picture (300×). It can be seen (Fig. 1) that in the given case the growth spiral relaxes at the initial stage of evaporation; in the place of one dislocation with a large Burgers vector, a whole group of dislocations is detected. In the course of further evaporation a multi-start evaporation spiral is formed (Fig. 1 ,). After some time through-holes appear at the points where the screw dislocations emerge. The photographs show that two closely adjacent through-holes are formed. Consequently, in the initial stage of growth at least two screw dislocations arose, and only in the course of further growth did one of them, owing to more intensive growth, almost completely eliminate the influence of the second dislocation on the surface relief. The through-holes formed as a result of evaporation grow, while the ends of the spirals continue to move along their edges. Finally, the two holes merge into one large hole. At the edges, however, the terminations of the spiral layers remain (Fig. 1).

Very peculiar figures are also obtained during the evaporation of two

spirals of different signs located at a distance comparable with the distance between successive turns of the spirals. Such spiral layers, joining together in the process of growth, form concentric circles.

The successive stages in the transformation of two closely spaced growth spirals of different signs into evaporation spirals are shown schematically in Fig. 2. The same process is presented in a series of frames from a motion picture taken by us (Fig. 3); nickel sulfate, 300×. It is seen that the initial configuration of the layers is a semicircle formed during growth. The evaporation that has begun is most intense at the places where the curvature of the layers is greatest.

Fig. 2. Scheme of the transformation of two growth spirals of different signs into evaporation spirals

Figure 3: Fig. 2. Scheme of the transformation of two growth spirals of different signs into evaporation spirals

Therefore the steps making up the central part of the spirals, at the ends of the semicircle, move in the opposite direction faster than does the entire spiral layer as a whole. The front of the spiral layers forms "deflections" moving toward one another (Figs. 2 , 3). As soon as these concave parts join with one another, an isolated closed layer is formed (Figs. 2 , 3).

Fig. 2. Scheme of the transformation of two growth spirals of different signs into evaporation spirals

In the course of further evaporation this isolated "nucleus" gradually diminishes until it disappears altogether. As a result, two evaporation spirals of different signs are obtained. Subsequently they produce the same figures as in growth, i.e., successive concentric circles, forming an evaporation pit on the surface.

Investigation of the morphology of the crystal surface at the initial stage of evaporation also makes it possible to notice a number of dislocation outcrops which were inactive during growth and did not produce the characteristic spiral relief. The evaporation that has begun makes them reveal their presence.

In Fig. 1a, at the lower left, a small circular formation was visible. As a result of evaporation it became clear that this formation is a place of accumulation of unlike dislocations, with equal numbers of right- and left-handed dislocations. At first these dislocations formed two small semicircular evaporation layers (Fig. 1). In the course of further evaporation these dislocations produced a relief characteristic of two dislocations of different signs; i.e., the spiral layers produced by these dislocations formed one semicircular layer which, upon further evaporation, gives concentric circles. This suggests that the frequently observed round mounded formations on crystal faces, or round etch figures, are in reality derivatives of an accumulation of dislocations at their center. From the material presented it is also evident that, at an early stage of weak evaporation or dissolution, various dissolution and etching figures are formed.

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