Growth mechanism of helicoidal nickel whiskers

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SYNOPSIS

From a study of the growth of nickel whiskers by reduction of the iodide of the metal, these whiskers have been classified into two categories :

—rectilinear whiskers,
—helicoidal whiskers,

Whether rectilinear or helicoidal the whiskers are always formed by a stacking of idiomorphic crystals. The conditions governing the growth of rectilinear whiskers have been established earlier. The present work relates to helicoidal whiskers. On the basis of the mechanism described by Amelinckx, the paper explains the formation of a helical dislocation and how the climb of this dislocation brings about a periodic change of the direction of growth ; this periodic change is responsible for the preferential development of the planes III according to a certain sequence. The depth of the loop and the rate of growth are directly correlated to the number of vacancies or point defects captivated. The formation of open loops or closed loops is therefore a direct function of the experimental conditions and particularly of the reduction temperature of the nickel iodide. This explains the formation of imbricated helicoidal whiskers.

NICKEL whiskers obtained by reduction of the iodide of the metal can be classified into two categories :

(i) rectilinear whiskers
(ii) helicoidal whiskers

In general, these whiskers are formed by a stacking of small idiomorphic crystals. The law governing such stackings was determined theoretically in a previous investigation.[1,2] It was shown that they were formed from nickel iodide in fusion and that the theory of dendritic growth was quite true for rectilinear whiskers ; the axes of growth are of low indices (<111>, <100>) and the conditions required for dendritic growth as described by Papapetrou[3] are fulfilled.

Rectilinear whiskers without branches are obtained, because one of the directions of dendritic growth is favoured and the development takes place only in that direction.

This paper presents a study of the growth mechanisms of helicoidal whiskers.

Preparation of whiskers

The whiskers are obtained by hot reduction of nickel iodide. Decomposition of iodide takes place according to the following two reactions :

By hydrogen :

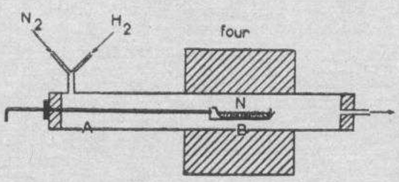
$$I_2Ni + H_2 = Ni + 2I\,H$$

By heat only

$$I_2Ni = Ni + I_2 \text{ (equilibrium of dissociation)}$$

The experiment is carried out between 900° and 980°C depending on the requirements.

The resistance furnace (Fig. 1) is mounted on a silica tube of 35 mm diameter. The tube is closed on both ends by brass stoppers provided with holes. One of these holes is used for the manipulation of the boat by means of a stainless steel rod ; the hole on the other side serves for the evacuation of gases. All removable



1 *Diagram of the set up for preparation of whiskers*

A : cold zone
B : reduction zone
C : boat containing the iodide

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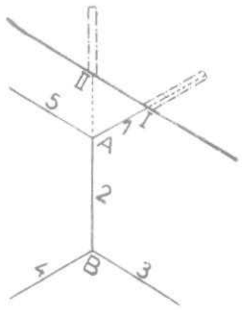


2 *Frank's network near the surface*

4 *Helicoidal nickel whisker* ×500

parts as well as the passages are provided with toric joints in order to avoid pollution of gases.

Reduction of nickel iodide is carried out in a biscuit boat.

The nitrogen used for purging as well as the hydrogen meant for the reduction is of the purest grade available in the market.

Growth mechanism

General

It is known that a helical dislocation[4] can be formed from a mixed dislocation mainly of screw type, anchored at two points (these two points could be, for example, nodes of the network of Frank). The edge portions of the dislocation rise and drag the screw portions, which cause a curvature of the line and the formation of the helix.

This mechanism based on the climb of dislocations and the diffusion of point defects therefore involves a phenomenon activated thermally.

Figure 2 is a diagram representing the network of dislocations near the surface. If it is assumed that these dislocations are mainly of the screw type, the mechanism described above may play a role in the process.

All these dislocations are anchored at two points; this is true even for dislocation 1 if the concept of image force is considered.

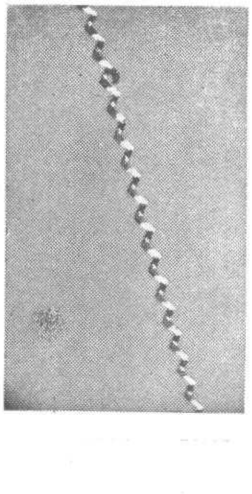
Whereas dislocations 3 and 5 are not well oriented with respect to the surface, the orientation of dislocations 1 and 2 is favourable to the formation of a whisker on the surface of the metal. The metal forming the whisker can be provided either by compression (squeeze whiskers) or by chemical reaction at high temperature (chemical whiskers); the latter case will be considered in this study.

Two growth processes are possible at this stage;[5] a whisker could be produded by the dislocation 1 and it could grow in an oblique direction with respect to the surface, in the direction of its Burgers' vector, at I on the diagram of Fig. 2. Another whisker could also develop at II if the forces between the loops of the helix formed by 2 become sufficiently high to enable these loops to move towards the surface in the direction of Burgers' vector.

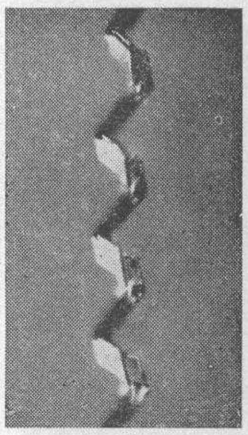
Application to nickel whiskers

Papapetrou's theory which is perfectly applicable to rectilinear whiskers does not explain the regular and systematic change of direction of growth of helicoidal whiskers. The climb of the helical dislocations formed will explain these changes in the direction of growth if we assume the presence of a network of disloca-

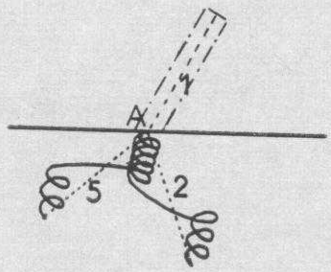
3 *Crystal which could have been at the origin of the whisker of Fig. 4* ×1000



5 *Helicoidal nickel whisker* ×200



6 *Helicoidal nickel whisker ×500*

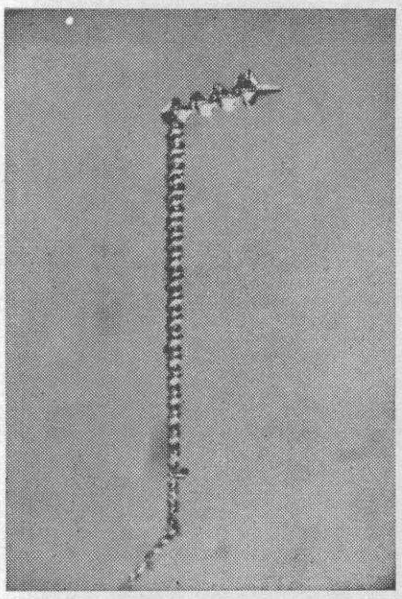


8 *Diagram of the formation of the whisker of Fig. 7*

tions in the substratum formed by the nascent nickel lining the boats.

In fact, the growth of whiskers is effected by provision of metal at their tops. The helicoidal morphology would be a direct consequence of the rotation of the point of emergence of the dislocation along the helix. The growth step, which is a consequence of the prismatic slip of the screw dislocation, will also describe this helix, and due to the crystalline system of nickel, this will lead to the formation of close packed planes {111} limiting the lateral faces of the whisker. For a given concentration of vacancies there is a minimal radius of curvature of the dislocation line ; this is one of the factors which determine the shape of the helix. Webb has discussed in the case of palladium[6] the various factors influencing the shape of helices.

The helicoidal dislocation which will produce the whisker could be contained in one of the small crystals present in a large number on the walls of the boats (Fig. 3). During its growth the whisker will preserve crystalline faces of the same index as that of the initial crystal (Fig. 4).



7 *Whisker consisting of two parts : one helicoidal (top) and the other imbricated helicoidal ×200*

Numerous possible forms are found amongst nickel whiskers (Figs. 5 and 6), but the indices of the faces of crystals forming these whiskers are always low and the axes of growth are axes <111> or <100>.

The development of imbricated whiskers can be explained by this mechanism based on the climb of helical dislocations.

On Fig. 7 it may be noted in particular, that the whisker is formed by two rectilinear parts : at the top is seen a helical growth of the type that has been described whereas at the base two helical whiskers are imbricated.

If we consider again the diagram (Fig. 8) of Fig. 2, we may assume that dislocation 1 has formed a whisker (corresponding to the top of the whisker of Fig. 7).

Let us consider dislocation 2 : its climb will produce not one helical dislocation but two such dislocations separated by an edge type dislocation. The same is true for dislocation 5. If it is assumed that both climb simultaneously, there would be formation, from A, of two imbricated helices which in their turn can lead to the formation of a whisker consisting of two imbricated helices. In Fig. 7 the angle between the two parts of the whisker can also be explained by the theory.

Such plaits of whiskers have already been observed on copper.[7]

Conclusion

Papapetrou's theory explains very satisfactorily the piling up of crystals forming rectilinear or helical whiskers. With particular reference to the latter, the theory does not account for the regular change in the direction of growth. In this respect, the theory based on the climb of helical dislocations completes Papapetrou's theory.

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