ELECTRON MICROSCOPIC INVESTIGATION OF SODIUM CHLORIDE WHISKERS*

By

B. JESZENSZKY and E. HARTMANN

Department of Experimental Physics, Technical University, Budapest

(Received December 15, 1971)

Presented by Prof. Dr. J. MÁTRAI-ZEMPLÉN

Introduction

Whiskers are single crystals, one dimension of which is much larger than the two others; they are usually a few microns thick. The whiskers have been known for some hundred years [1], but the filamentary forms of materials became the subject of an extensive programme of scientific investigation only in the last two decades when it was revealed that the physical properties of the whiskers are in many respects quite different from those of the bulk single crystals. It was Prof. Z. GYULAI, our late master, who first demonstrated in 1954, that the mechanical strength of whiskers depends on their thickness, and the strength of thin whiskers is hundred times greater than that of the large bulk crystals, approaching in some cases the theoretical strength of perfect crystals [2].

The whiskers are of great industrial importance. Recently some whiskers are used as the main part of some composite materials. The advantage of these materials is the high strength at a low weight. The whiskers have also provided extremely useful single-crystal specimens for the study of the general physical properties of solids. An excellent survey has been published on this subject recently [1]. In the last ten years we also published several reports about investigations concerning the growth and mechanical properties of sodium chloride whiskers [3—11]. In this paper results of electron microscopic investigations concerning the surface structure of NaCl whiskers are reported.

Experimental technique

The investigated whiskers were grown by three methods. In the first method a small piece of sodium chloride crystal (with dimensions of a few millimeters) was put into the middle of a flat Petri-dish, which contained

* Presented at the International Conference on Electron Microscopy held in Varna, Bulgaria, October, 1971.

saturated aqueous solution of NaCl dopped with 0.03% polyvinyl alcohol as a poison. Having covered the dish and kept it at room temperature, the growth of very fine whiskers on the sides of the seed crystal could be observed. Within a few days bundles of whiskers with a length of a few cm-s have grown on each of the four sides of the seed crystal. After drying them they could be cut with a razor-blade and used as samples. They could be caught by a forceps as a thin plate, because the whiskers joined to a kind of a felt. The second method for growing whiskers was that published earlier by us [4], i.e. to grow them on a cellophane membrane from pure saturated solution of sodium chloride. In the third growing method the whiskers were gained by growing on ceramic materials according to the well-known GYULAI-method [2].

The sodium chloride whiskers are not suitable for direct observation in an electron microscope. The thicker crystals are not transparent to the electron beam, the thinner ones, however, quickly evaporate in it. For this reason the carbon replica method [12] and the so-called gold decoration technique elaborated by BASSETT, [13] BETHGE and others [14, 15] have been applied. The procedure of the gold decoration method consists in evaporating in high vacuum a very small quantity of gold onto the surface of the sample heated to 150—200 °C. Under these conditions the gold does not form a continuous layer. The gold atoms don't lose their kinetic energies at once, they are migrating on the surface, and where the conditions are advantageous to nucleate, they form a small gold particle. Such places are the surface steps, the surface defects and the impurities on the surface. The arrangement of gold particles is fixed by a layer of carbon deposited on top of the gold layer. The carbon replica with the embedded gold particles was then taken off by dissolving the whiskers in water, and fished onto a microgrid they were examined in the electron microscope. It was demonstrated by BASSETT [13] and BETHGE [14, 15], that the gold decoration traces out the relief of surface in atomic dimensions. It shows steps with height of 2.81 Å, although the lateral resolution of our electron microscope is only 25 Å. This is the main advantage of the gold decoration technique.

The gold decoration was carried out in a Balzers type Microba-3 vacuum apparatus at 10^{-5} torr. The samples were taken into a microfurnace built in the vacuum chamber. Before decoration, the samples were heat-treated at different temperatures, — as high as 500 °C — for 5 to 90 minutes to remove impurities from the surface and in order to build down thermically the surface. The decoration was usually made at 150—180 °C.

The microscopic investigations were carried out in a KEM-1-1 type electron microscope made in the G.D.R. Its resolution reached 25 Å, its highest operating voltage was 60 kvolt. The magnifications were up to 30 000×.

Results

The application of thin replicas enables us to see both sides of a whisker at the same time, because after dissolving the sodium chloride the thin carbon layer covering both sides of the whisker is stretched into one plane by the surface tension of the water (Fig. 1).

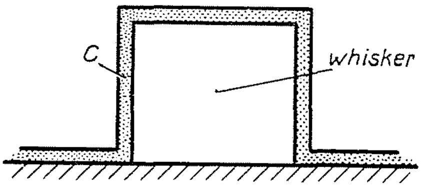

Fig. 1

Table I

Time and temperature of the heat treatment of the samples in Figs 2 to 14

Fig. No.	Time min	Temperature °C
2	—	25
3	60	380
4	5	400
5	90	380
6	60	380
7	60	380
8	10	400
9	30	500
10	60	300
11	10	400
12	10	500
13	5	420
14	10	200

Fig. 2 shows an overgrowth on the side-edge of a whisker. This kind of overgrowth was already observed by us in on optical microscope too [5]. The structure of the side-edge may be better observed by applying the decoration method. In Fig. 3 a thick band appears to consist of several lines which show the side-edge of a whisker built down thermally.

The decoration method makes possible to reveal even the finer overgrowths on the edge of the whisker, because the structure of overgrowths is

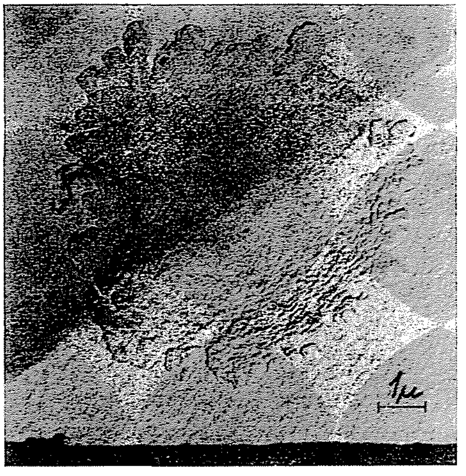

Fig. 2

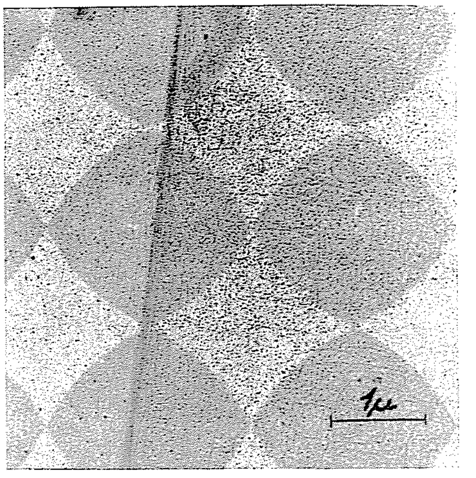

Fig. 3

quite different from that of the other part of the whisker. In Fig. 4 one may observe quite well that the steps on the two parts of the whisker lie orthogonally to each other.

In some cases the side faces of the whiskers thermally built down exhibit patterns referring to screw and edge dislocation, respectively. A two lamellar system belonging to two opposite screw dislocations is seen in Fig. 5. The distance of the two dislocations is about 0.5 μ, and the width of layers on the surface built down is about 0.2 μ. As BETHGE has shown [14, 15], the decorating particles indicate atomic steps as high as $\frac{a}{2}$ (i.e. the half value of the identity distance).

Fig. 6 shows a lamellar system belonging to screw dislocations in the same sense. The cores of the screw dislocations are spaced about 1.8 μ from each other. (The lower part of Fig. 6 is a picture of a carbon sheet belonging to another whisker.) In some cases lamella series consisting of concentric circles adhering to the thermally built down whisker surfaces are seen (Fig. 7). According to Bethge's explanation these lamellar systems form around the emergent points of dislocations which have Burgers vectors parallel to the crystal surface. Recently, this lamellar system was interpreted by SERNA and BRU [16] so that it had been formed by the slip of a screw dislocation. In our opinion, in our case the explanation by BETHGE is correct. Namely it is improbable that more screw dislocations would have slipped together at the same time during the heat treatment, and the heating would have stopped just at the time when the middle circles of the lamellar system had not disappeared yet. The explanation of the origin of the observed dislocations (at growth or

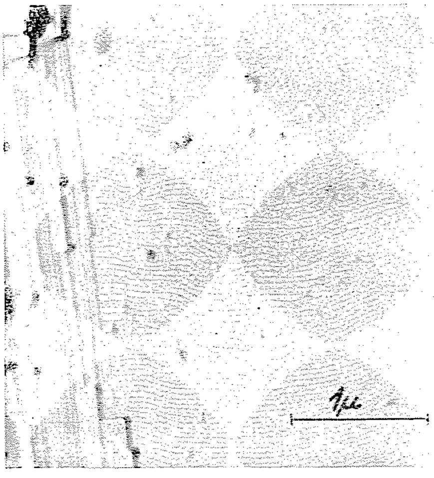

Fig. 4

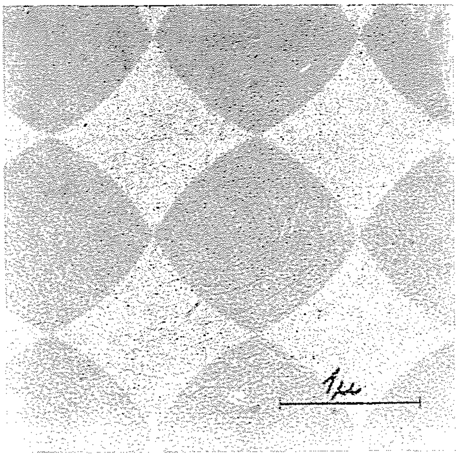

Fig. 5

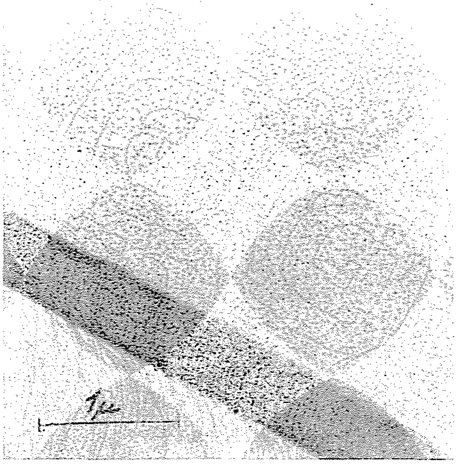

Fig. 6

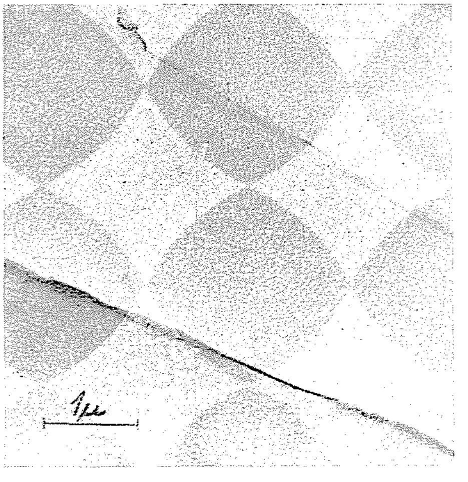

Fig. 7

by handling) will be the subject of further investigations. It is certain, however, that in the case of whiskers grown from a solution dopped with polyvinyl alcohol, the screw dislocations took part in the formation of overgrowths, as it is seen in Fig. 8, demonstrating a decorated picture of overgrowths formed along a whisker's side-edge.

The evaporation of whiskers proceeds by formation of hole seeds (German: Lochkeime). The nearly rectangular spots outlined by the decorating gold particles are in general different in size; they may be too small to be identified else than by the four gold particles situated in corners of the small area (Fig. 9).

In our previous paper it has been demonstrated that during the growth of NaCl whiskers from a solution poisoned with polyvinyl alcohol [7—8], the poison (i.e. PVA) builds in into the whiskers.

The effect of the incorporated poisons appears in three different ways in the decoration method. If the surface contamination is too heavy, the surface steps are not decorated. If the surface contamination is reduced by heating the whiskers to a higher temperature where most of the contaminations burn and leave for the vacuum space, decoration is produced, some part of

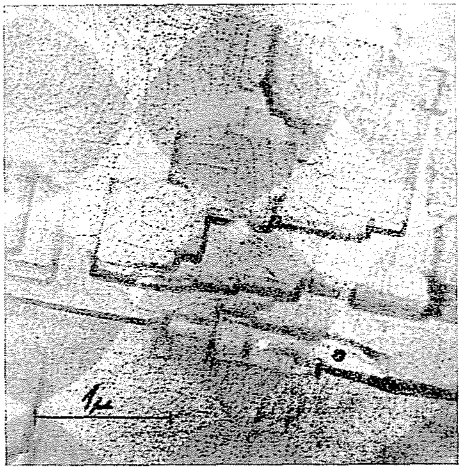

Fig. 8

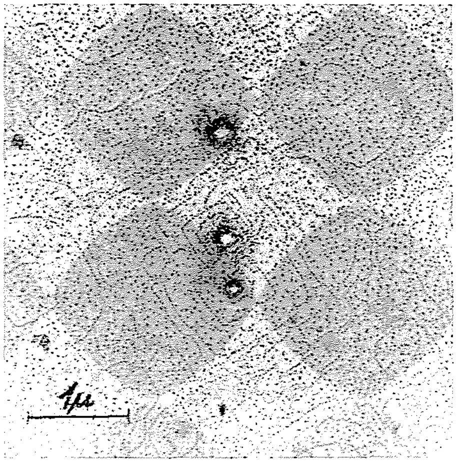

Fig. 9

the surface being covered by spots consisting of small gold particles. These spots (Figs 9—10) indicate the parts of the surface covered by the remained contaminations. The third form of the effect of contaminations manifests itself by the saw-toothed form of the steps: namely the contaminations hinder uniform step-formation (see right side in Fig. 4).

In the middle of the whisker's face generally a pattern indicating lamellar growth is found. These patterns are related to the crystallization of a drop of solution remaining on the surface, and to the emerging points of a channel running in the whisker along its axis. In certain cases quadratic holes have been seen on the carbon replica (Figs 9 and 11). On these parts of the whisker surface probably secondary whiskers occurred which had stabbed the carbon replica.

We have studied several plastically deformed whiskers too. Fig. 12 shows the sides of a plastically bent whisker. The whisker was heated to 500 °C for 5 min in vacuum as high as $2.5 \cdot 10^{-5}$ torr before the deposition of carbon.

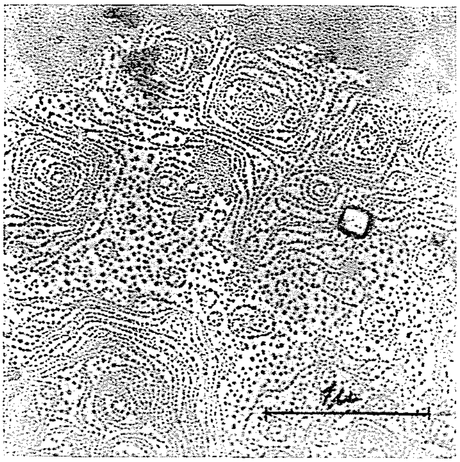

Fig. 10

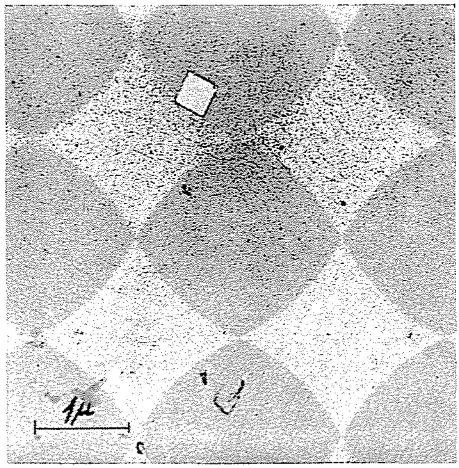

Fig. 11

On the deformed places the whisker was built down strongly and thus the neutral zone clearly appeared, where no stress in the whisker acted (Fig. 12). The slip bands were made visible by simple carbon replica, the finer slip lines, however, by the gold decoration technique (Figs 13 and 14). The slip steps are straight in general, but sometimes one may observe cross-slip as well.

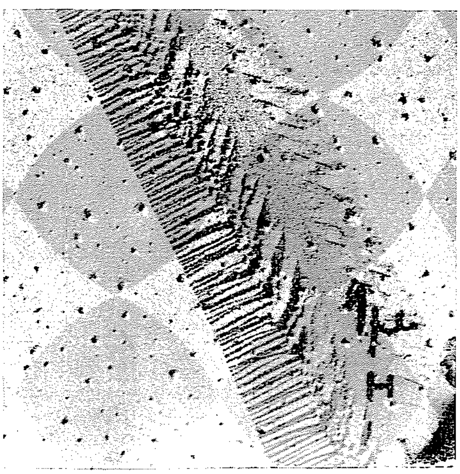

Fig. 12

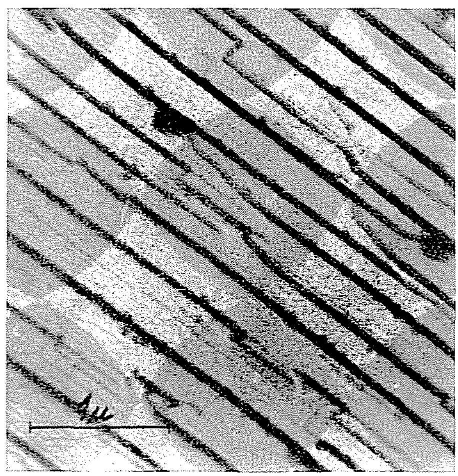

Fig. 13

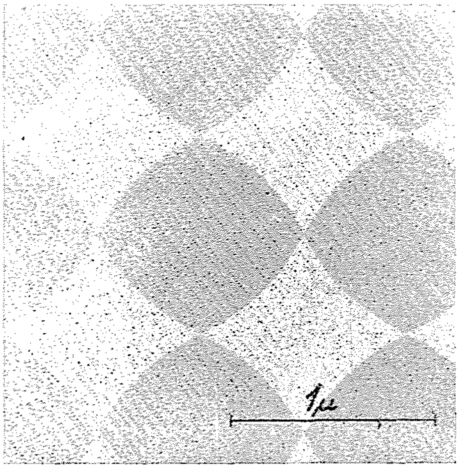

Fig. 14

We are grateful to Mrs. BÖSZÖRMÉNYI-NAGY for aid in the preparative work.

Summary

The surface structure of NaCl whiskers has been studied by electron microscopy using carbon replica and gold decoration technique. The evaporation processes of the whiskers are interpreted; some plastically deformed NaCl-whiskers are examined.

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Béla JESZENSZKY
Dr. Ervin HARTMANN
Budapest XI., Budafoki út 8, Hungary