

## Electrolytic Micromachining of Iron Whisker Surfaces

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### ABSTRACT

An electron microscopic study of etch patterns of iron whiskers suggests that contamination films which were formed on the whisker edges during the growth process can be removed effectively by hydrochloric acid solutions (pH 0.2-2.0), resulting in the formation of a highly active and smooth surface. At higher pH, however, such a surface cannot be produced. This may be either a result of the insolubility of the original film or the formation of a new protective film on removal of the original film from the whisker surface. Additives such as chromic acid, cupric chloride, ferric chloride, and nitrate ions, present in appropriate concentrations in hydrochloric acid solutions, are found to produce a very smooth surface with pointed tips. Based on the above experimental results a growth mechanism for metal whiskers has been suggested.

Investigations on the physical properties and crystallographic structure of metal whiskers have been conducted by various workers (1, 2). However, very few studies have been reported on the chemical properties of whiskers, especially on the activity of their surfaces in a corrosive environment. This is important since the sides of whiskers are supposed to consist of faces of high density and low surface energy and to be free from dislocations (1, 2). Since different faces of a single crystal possess widely different activities in a corrosive liquid or gas (3, 4), it is also desirable to give due allowance to the orientation of crystal faces developed at the sides of a whisker with respect to its fiber axis. In order to test the reactivity of whisker surfaces, some dissolu-

tion experiments in acid solutions were carried out with iron whiskers. Electron micrographs were taken to study the smoothness of whisker surfaces resulting from etching. Since dissolution processes are often a measure of growth processes in reverse, the present investigation sheds some light on the mechanism of whisker formation itself.

### Experimental

The iron whiskers, prepared by reduction of halide vapors with hydrogen in the usual way (1, 2, 5, 6), were 5-10 $\mu$  in diameter and 10-12 mm in length. They were carefully spot-welded on 4-mil tungsten loops for ease of handling during etching. Electrolytic etching was conducted at 25°C in HCl solutions

Table I. Summary of electrolytic micromachining results

Nature of corrosive medium	pH of the medium	Impressed voltage, a.c.	Remarks about surface after etching	Electron micrograph, 5000X
Conc. HCl diluted 10 times	0.15	6-0.1	Irregular surface and no sharp tip	Fig. 1
Conc. HCl diluted 20 times	0.4	0.1-0.2	Smooth surface	Fig. 2
Conc. HCl diluted 30 times	0.5	0.2	Smooth surface and sharp tip	Same as Fig. 2
Conc. HCl diluted 40 times	1.0	0.4	Smooth surface and sharp tip	Same as Fig. 2
Conc. HCl diluted 80 times	2.0	0.6	Tolerably smooth surface with extremely sharp tip	Fig. 3
Conc. HCl diluted 120 times	3.0	0.8	Poor tip and surface starts showing unevenness	Fig. 4
Conc. HCl diluted 150 times	4.0	1.2	Poor tip and the surface is rough	Fig. 5
Conc. HCl + conc. HNO <sub>3</sub> (3:1), saturated with CuCl <sub>2</sub>	<0.1	0.8	Tolerably sharp tip but surface is rather rough	Fig. 6
Conc. HCl + conc. HNO <sub>3</sub> (3:1), diluted one time, and saturated with FeCl <sub>3</sub>	<0.1	0.6	Tolerably smooth surface but no sharp tip	Fig. 7
Conc. HCl + conc. HNO <sub>3</sub> (1:10), diluted one time	<2.1	0.4	Growth of spiral showing crossed screw dislocation, which on further etching gives tolerably smooth tip surfaces	Fig. 8, 9
Conc. HCl diluted 10 times with 0.05% chromic acid	<0.2	0.6	Tolerably smooth surface	Same as Fig. 3
Conc. HCl diluted 10 times with 0.1% chromic acid	<0.2	0.6	Rough surface	Same as Fig. 5

of pH values ranging from 0.1 to 4 at externally impressed voltages (a.c.) of 0-1.2, in general. Some runs were conducted at pH 5 and externally impressed voltages up to 8. The acid, of A. R. grade, was diluted with distilled water to give the desired pH conditions. The solutions were held in a 50 ml Pyrex beaker open to the atmosphere. A carbon rod was used as the cathode during dissolution experiments. The electrolytic etching was carried out for a few seconds at an angle with the normal to the liquid surface, since, in general, vertical immersion did not lead to a sharp tip. The angle of inclination for etching was not very critical, any value ranging from 15° to 60° leading to satisfactory results. This procedure was found to give a whisker tip of radius 10<sup>-4</sup> to 10<sup>-5</sup> cm, which is suitable for use in field emitters. The electron micrographs were taken at a magnification of 5000X. Results are summarized briefly in Table I.

#### Results and Discussion

It is seen from the electron micrographs that acid solutions of pH values from 0.2 to 2, with an appropriate externally applied voltage on the whiskers, favor a smooth surface with a pointed tip. At a pH of 3, a rather uneven surface is obtained, even when using higher anode voltages during etching. At a pH of 4, it is difficult to etch a tolerably smooth surface even at voltages between 1.2 and 3.0. At still higher pH values, the whisker retains its original cylindrical filamentary structure, even at impressed voltages up to 8. The behavior at or below a pH of 3 may be attributed to the dissolution of a protective coating on the original whisker surface, followed by progressive dissolution of metal. The insolubility of the original protective film or the instantaneous formation of a highly protective coating on the

whisker surface after dissolution of the original film may lead to progressive resistance to corrosion of whisker surfaces at higher pH conditions. When the HCl solution is too highly acidic, the dissolution of the original film as well as the metal is very fast and this leads to an irregular type of surface, as can be seen from Fig. 1. It is also possible that such a rough surface may result due to the more pronounced interaction of whisker surfaces with impurities present in higher concentration in more concentrated acid solutions.

It is noted from Table I that iron whiskers (insoluble in conc. HNO<sub>3</sub>) are soluble at impressed voltages of 0.6-0.8, when 3 parts by volume of conc. HCl are added to 1 part by volume of conc. HNO<sub>3</sub> and the resulting solution is saturated either with cupric or ferric chloride at room temperature. The result is a tolerably good surface, as can be seen from Fig. 6 and 7. The above mixture of acids, in the absence of cupric or ferric chloride, results in an immeasurably fast dissolution rate, which does not favor a controlled action. Cupric or ferric ions present in appropriate amounts in acid solutions tend to suppress the hydrogen discharge reaction at cathodic sites of the whisker surface, thereby controlling the rate of dissolution of metal which leads to an effective micromachining of the surface.

By comparing Fig. 3 with Fig. 5, it is seen that addition of chromic acid in appropriate amounts to conc. HCl solution leads to smooth micromachining, whereas additions in too high a concentration result in roughness of the whisker surfaces. This result probably can be attributed to adsorption of chromic acid at various active sites on the surface and its subsequent desorption by chloride ions as discussed in previous communications (7, 8).

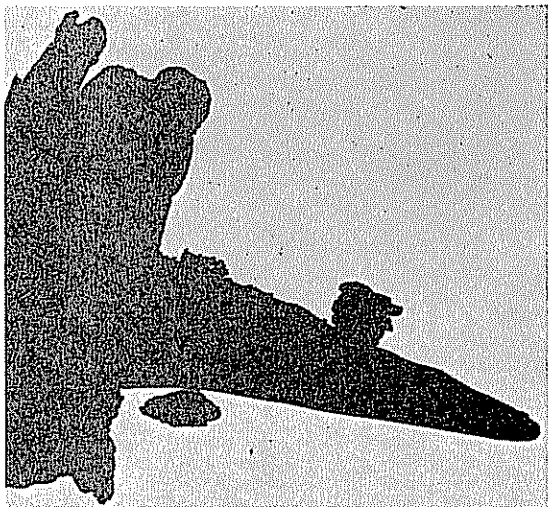


Fig. 1

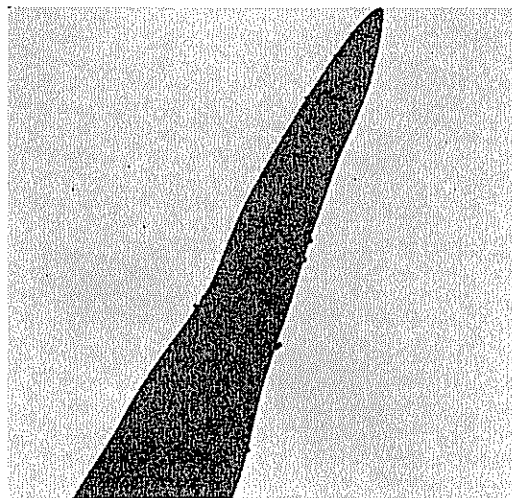


Fig. 4

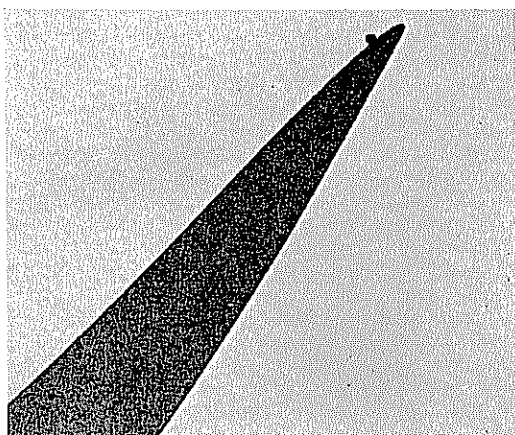


Fig. 2

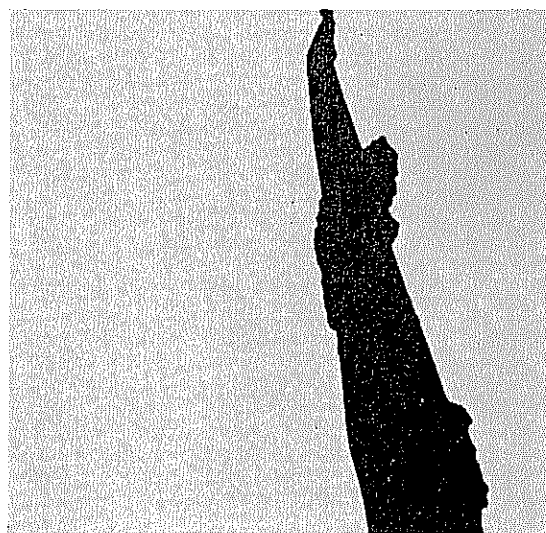


Fig. 5

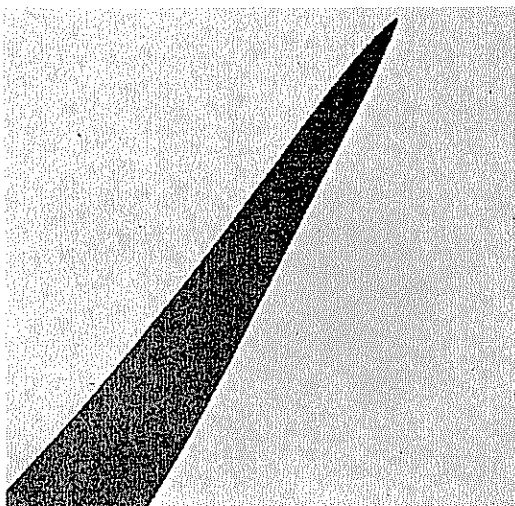


Fig. 3

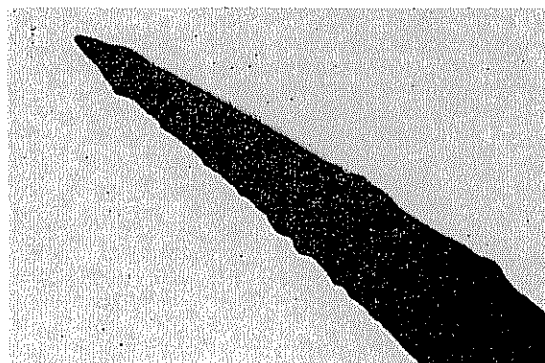


Fig. 6

Etching of an iron whisker at 25°C and 0.4 v from a twice diluted solution consisting initially of conc. HNO<sub>3</sub> and conc. HCl in a proportion of 10 to 1 reveals a crossed screw type of dislocation (Fig. 8). This surface on subsequent etching, however, becomes moderately smooth and possesses a sharp tip. This can be seen from Fig. 9. Such a dislocation results from a twist grain boundary when two whiskers, most probably originating from two adjacent sites in a parent whisker, cross each other at an angle.

This is a direct verification of the presence of axial screw dislocations in iron whiskers (9). However, this phenomenon is not general and was found only in a few isolated whisker samples.

Freshly etched whisker surfaces when preserved under vacuo ( $10^{-3}$  mm Hg) or kept in a desiccator containing dry air for a few hours become highly inert to the corrosive solutions from which they were etched previously. The whiskers do go into solution at considerably higher voltages but a smooth surface and pointed tip is not obtained. This finding shows that the whisker surfaces are very active, picking up contaminants after etching (probably from vac-

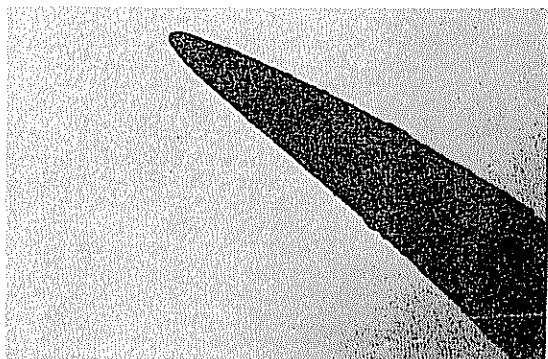


Fig. 7

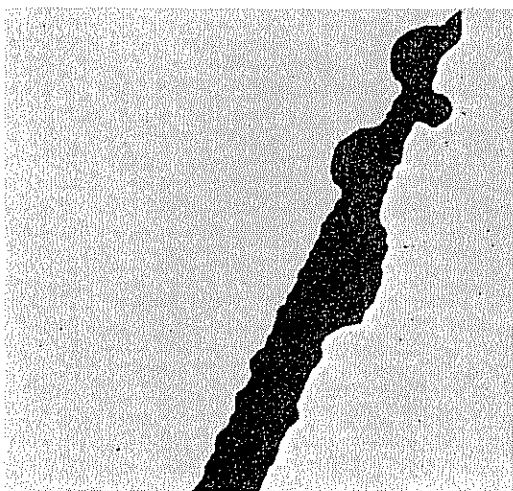


Fig. 8

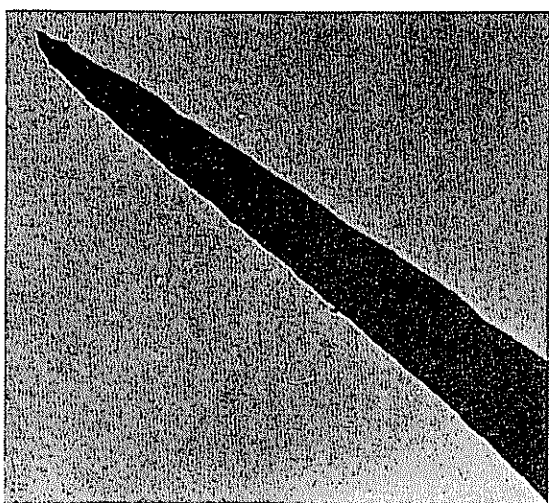


Fig. 9

uum pump oil or residual oxygen when they are preserved under vacuo or oxygen from the air when kept in a desiccator) to give a highly homogeneous and protective coating. This leads to the conclusion that the iron whisker surfaces were very active during formation and quickly picked up contaminants (2, 10). The adsorption of contaminants at the sides of whiskers during their formation might suppress all the active centers which contribute to their lateral spread, resulting in subsequent inertness to corrosive environments. This reasoning is in substantial agreement with the results of Van der Meulen and Linstrom (11) and Coleman and Sears

(10). Probably the conclusion of Green and Wolf (12) that silver whiskers are comparatively inert in nitric acid solution is a result of the inability of nitric acid to remove quickly the homogeneous contaminating film formed on the silver surface during the growth process.

Our present knowledge of the mechanism of metal deposition on unclean surfaces either by electrodeposition or by reduction of halide vapors by hydrogen is inadequate to explain satisfactorily whisker formation. It has been suggested that the active centers for deposition of metal atoms or ions on the sides of a whisker might be blocked by contaminants, saturating the surface forces which would have otherwise contributed to lateral spread of the whisker (11, 13, 14). As a result, metal atoms or ions will have an unusually high mobility on such surfaces, since the weak Van de Waals' forces are incapable of incorporating them into the lattice from the sides of a whisker. The atoms, consequently, will be incorporated into the crystal lattice only after reaching the bare surface at the tip, where, probably owing to the higher rate of condensation of metal atoms, contaminants cannot spread during the growth process. Termination of growth should occur only when the rate of condensation of metal atoms on the tip is slow compared with the rate of spread of impurities on the whisker surface. Our experiments which show the high activity of whisker surfaces in suitable etching media, after the initial protective film is removed by dissolution, thus partly explains the mechanism of whisker formation.

#### Acknowledgment

The authors are indebted to the Physics Dept., The Pennsylvania State University for supplying the iron whiskers. This work, in part, has been supported by the Atomic Energy Commission, Contract No. AT(30-1)-1710.

Manuscript received May 26, 1960.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1961 JOURNAL.

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