The Etched and Corroded Surfaces of Iron Single Crystal as Revealed by Means of Electron Microscopy and Diffraction

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The electron microscopic observation of the etched surface of iron single crystal made it possible to assign the crystallographic axes of iron single crystal. The corrosion of iron was here investigated with an iron single crystal thus oriented. The most inactive surface plane of ferritic crystals was the (110) plane consisting of the closest packed atoms. The Fe_3O_4 crystals formed on the etched surface of iron single crystal were oriented by microscopy and diffraction. It was explained atomistically through the results obtained that the Fe_3O_4 formed on Fe substrate might protect the substrate from corrosion.

Experimental

The single crystal used in the present study was a piece of wire (diameter: 2 mm., length: 10 mm.). This specimen was etched with an etching solution (ethanol-bromine 10:1 by vol.) for 10-30 seconds. Many etching grooves running parallel to each other were recognized by the naked eye on the side face of specimen. The oxide replica of this side face was prepared by the procedures described in the previous paper(1), and it was stripped from the substrate by Mahla-Nielsen's method(2). The electron micrograph obtained is shown in Fig. 1, in which there are octahedral crystals (size: 50-300 mμ) oriented parallel to each other. All octahedrons found in Fig. 1 are inclined by 22° regarding the (001) planes to the replica film, as is illustrated in Fig. 2. The (111) planes of these octahedrons are inclined by 32° to the replica film (*vid.* Fig. 2). The other octahedral planes $(\bar{1}11)$, $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}1)$ planes are inclined by 56°, 56° and 70° to the replica film respectively. These inclination angles are larger than 32°. (The inclination angles given here are not strict, but within the limits of error ±5°.)

The electron beam running parallel to the etching grooves of specimen gave a diffraction pattern of Fig. 3. Fig. 3 verifies the existence of α-iron single crystal, whose (001) planes are inclined by 29° to the macroscopic surface of specimen given by shadow edge in diffraction pattern. This fact is in accordance with the results obtained in microscopy (29°≈22°). It is concluded in this way that the etched face of iron single crystal was composed of the (111) and its equivalent planes, as is shown in Fig. 2.

The electron beam running vertical to the replica film of Fig. 1 gave a diffraction pattern of Fig. 4, which verified the existence of oriented Fe_3O_4 crystals. It was comprehended through Fig. 4 that the incident beam was parallel to one of the principal axes of Fe_3O_4 crystal. When c-axis of Fe_3O_4 crystal was selected as this principal axis, the (102) plane of Fe_3O_4 was approximately parallel to the (111) plane of Fe substrate; because the angle between the (102) and the (001) planes of Fe_3O_4 was 27°, and that between the (111) planes of Fe and the replica film (*vid.* Fig. 2) was 32°, *i. e.*, 27°≈32° (*vid.* Fig. 5a). The equivalent planes of (111) shown in Fig. 2 were so steep inclined by 56° and 70° to the replica plane or macroscopic plane of specimen, that these planes were opaque for electrons (*vid.* Fig. 1). Therefore, the diffraction pattern of Fig. 4 had to be given only by the replica part of the (111) faces of Fe

(1) S. Yamaguchi, *J. Appl. Phys.*, **22**, 680 (1951).
(2) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 873 (1948).

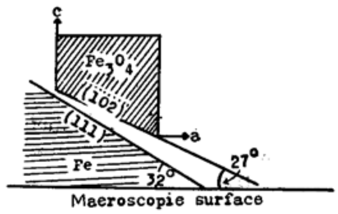


Fig. 5a.

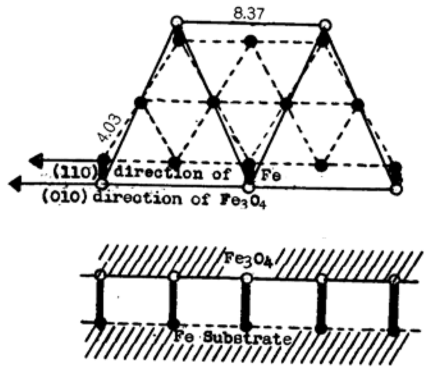


Fig. 5b.

substrate inclined by 32° to the macroscopic face of specimen. The relation between the (102) plane of Fe_3O_4 and the (111) plane of Fe substrate is shown atomistically in Fig. 5b by taking into consideration the etching grooves directed in Figs. 1, 2, 3 and 4. (The (010) direction of Fe_3O_4 was parallel to the (110) direction of Fe substrate, because the etching grooves were parallel to the (010) direction to Fe_3O_4 and to the (110) one of Fe.)

Discussion

Activity of Metal Faces.—According to the previous report of the present author(3), the corrosion rate of metal crystals depended on the activities of boundary lattice planes of crystals. So far as the cubic face-centred metal crystals were concerned, the (111) planes, which consist of the closest packed atoms, was most inert among the lattice planes. The (110) plane with coarse atom density was most active among the principal planes. In the cubic body-centred metal crystals there was a relation between the activities and the indices of lattice planes, which was quite similar to the case of cubic face-centred metal.

The (110) faces of cubic body-centred metal, whose atomic density is largest among the lattice planes, was most inert among the surface lattices of this metal. The etched surface of Fe-Cr alloy (Cr: 13 %) was composed of the dodecahedral (110) and its equivalent planes (*vid.* Fig. 6)(4), so that it was considerably corrosion-resisting. (The specimen of Fig. 6 was a rolled plate. Etchant: methanol-bromine, 100:1 by vol.) On the contrary, iron single crystal composed of the (111) and its equivalent planes, which were shown in Fig. 1, became mat more rapidly in the air at room temperature than Fe-Cr alloy of Fig. 6.

According to the theory of ionization series, Cr is by no means more inactive than Fe. Nevertheless, Fe-Cr alloy is more corrosion-resisting than pure Fe. This is due to the fact that there are the dodecahedral planes of cubic body-centred crystal on the substrate surface. The Cr in Fe-Cr alloy gives rise to the (110) planes on the etched surface of ferritic crystal.

Nature of Protective Film. — It was reported by Nelson that the ($\sqrt{2}\,\bar{1}\,0$) direction of Fe_3O_4 formed on iron was parallel to the (111) direction of substrate(5). The results obtained in the present study did not agree with those of Nelson.

The (102) plane of Fe_3O_4 is composed of Fe^{++} only. It is possible that these Fe^{++} ions and the Fe atoms of α-iron combine chemically with each other by exchanging their valency electrons. In cosequence of this, the Fe_3O_4 crystals can adhere solid to the metal substrate. Metal substrate is protected from further corrosion by being masked with the corrosion products, especially when the corrosion products are not only stable, but also adhere to the substrate under the given conditions. One of the Fe^{++}-Fe^{++} distances in the (102) plane of Fe_3O_4 is 8.37 Å. and the Fe-Fe distance in the (111) plane of iron is 4.03 Å. $8.37 \approx 4.03 \times 2$. It is, therefore, plausible to give a boundary structure between oxide and metal, as is shown in Fig. 5b. The experimental results on the corrosion products of metals and alloys might be referred to the previous papers of the present author(6).

Steps of Corrosion.—The corrosion of metals should be divided into the following two steps: In the first step of corrosion the rate depends on the indices of surface lattices, *i. e.*, here this is determined by the activities of the surface lattice planes. (The rate will be expressed in a form of $e^{-E/kT}$ in this case.) In the second step of corrosion the rate depends on the properties of the corrosion products

(3) S. Yamaguchi, This Bulletin, **24**, 122 (1951).

(4) The angles measured in a (110) plane in Fig. 6 coincided approximately with those of a geometrically exact dodecahedron.

(5) H. R. Nelson, *J. Chem. Phys.*, **5**, 252 (1937).

(6) S. Yamaguchi, This Bulletin, **18**, 53 (1943); S. Yamaguchi, T. Nakayama and T. Katsurai, J. Electrochem. Soc., **95**, 21 (1949).

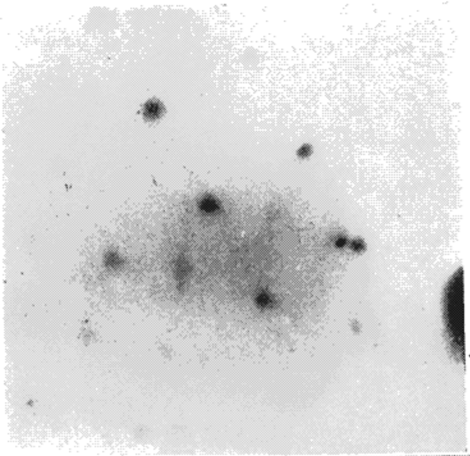
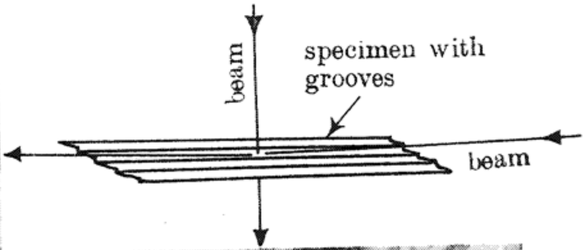


Fig. 3.



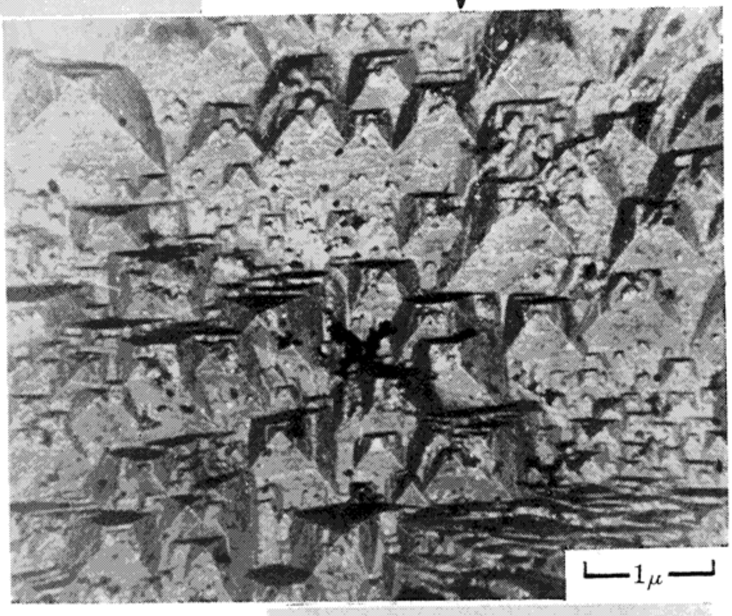


Fig. 1.

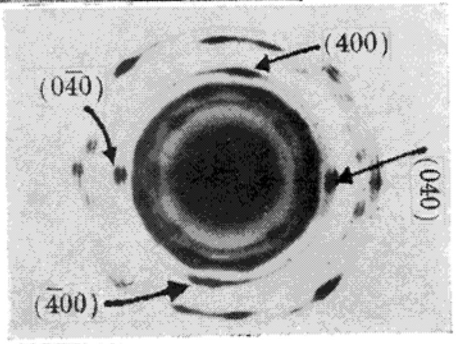


Fig. 4.

Fig. 1.—A magnified image of oxide replica formed on the etched surface of iron single crystal.

Fig. 3.—A reflection pattern obtained with the beam running parallel to the etching grooves of specimen.

Fig. 4.—A diffraction pattern obtained with the beam running perpendicular to the replica film of Fig. 1.

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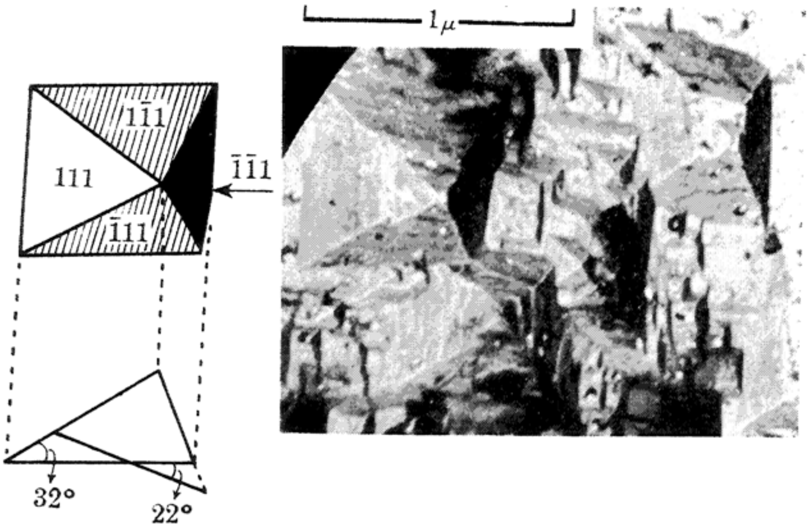

Fig. 2.—The etched surface of iron single crystal: the inclination angle between the (001) plane of octahedron and the replica film is shown schematically.

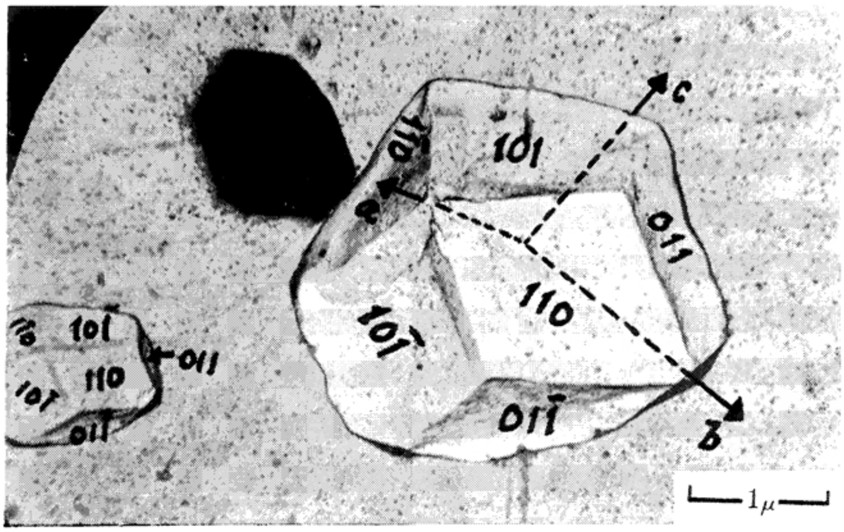

Fig. 6.—The etched surfaee of ferritic Fe-Cr alloy composed of the dodecahedral (110) and its equivalent planes.

formed over the metal surface. When the corrosion products on metals are exfoliated from the substrate ("erosion"), the corrosion of the first step takes place again. The dissolution of sodium in water is the typical corrosion, in which the first step is held until the end of corrosion. The formation of passive state, which is realizable on iron in nitric acid, is the typical corrosion of the second step.

Summary

1. It has been demonstrated in the present study that the single crystal of pure iron can be oriented by means of electron microscopy and diffraction in order to cut the single crystal along the desired planes. The single crystal of iron was oriented hitherto only by x-ray and optically[7].

2. The (110) faces of the cubic body-centred ferritic alloys was most inert among their surface lattices. Chromiun in 13 Cr stainless steel should be added to iron in order to give rise to the inert (110) planes on the substrate surface.

3. The etched surface of iron single crystal was composed of the (111) and its equivalent planes. The (102) planes of Fe_3O_4 crystals formed on this surface were parallel to the (111) planes of substrate. And the (010) direction of the former was parallel to the (110) direction of the latter. This fact signified that the (102) planes composed of Fe^{++} might be soldered to the (111) planes of iron by exchanging of residual valency electrons. As a matter of fact, the Fe_3O_4 film formed on iron under the given conditions serves as protective coating for substrate.

4. The corrosion of metals depends either on the activities of surface lattice planes of metals or on the properties of the corrosion products formed on surfaces.

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(7) J. G. Walker, H. J. Williams and R. M. Bozorth, *Rev. Sci. Instr.*, **20**, 947 (1949).