Oxide Formation on Iron Surface Corroded in Non-Oxidizing Acids

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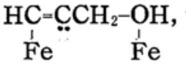
On corroding an iron specimen in hydrochloric acid solution with an inhibitor, such as propargyl alcohol, it is possible to observe the formation of ferrous oxide on its surface by means of electron diffraction with good reproducibility of results. The propargyl alcohol is known to be an efficient inhibitor for steel against hydrochloric acid solution(1). Yamamoto(2) assumed that the propargyl alcohol is able to inhibit the dissolution of iron, since it is adsorbed onto the iron surface with its triple bond. A formation of complex compound, such as  $\underset{\underset{\textstyle Fe}{|}}{HC}=\underset{\cdot\cdot}{C}CH_2-\underset{\underset{\textstyle Fe}{|}}{O}H$, was also suggested by Lüthringhous and Goetz(3). In their suggestion, they pointed out the effect of hydrochloric acid from the stand point of the organic chemistry. It is of interest, therefore, to examine experimentally whether their assumptions are true or not.

In this investigation the determination of the corrosion products was carried out by means of electron diffraction. The mechanically polished specimens (5×5 mm.) were immersed in 2 N HCl solution with or without propargyl alcohol about 4 hr. at 70°C. The concentration of propargyl alcohol added was about 10 mM. After the corrosion test, the specimens were washed with distilled water, ethanol and petroleum ether successively, and then immediately examined in an electron

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1) J. W. Reppe, "Acetylene Chemistry", Charles A. Meyer & Co., Inc., New York (1949), p. 96.

2) K. Yamamoto, This Bulletin, **27**, 379 (1954).

3) A. Lüthringhous and H. Goetze, *Angew. Chem.*, **64**, 661 (1952).

diffraction camera working with 50 kV. electrons. The lattice parameters of the oxide film were determined in reference to those of gold foil. The reflection pattern obtained from the specimen corroded in 2 N HCl solution containing the propargyl alcohol is shown in Fig. 1.

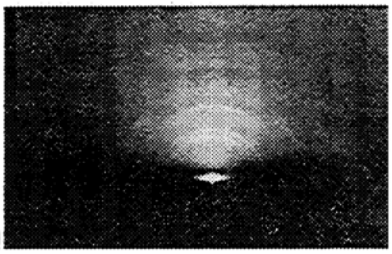

Fig. 1. Diffraction pattern from the iron specimen corroded in 2 N HCl solution containing the propargyl alcohol.
Temperature: 70°C, Immersion time: 4 hr.

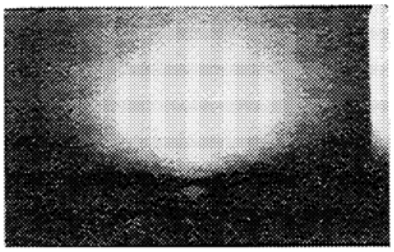

Fig. 2. Diffraction pattern from the iron specimen corroded in 2 N HCl solution containing the propargyl alcohol.
Temperature: 70°C, Immersion time: 8 hr. at 70°C and thereafter 12 hr. at room temperature.

When the specimen was corroded for longer time (about 8 hr.) followed by standing for 12 hr. at room temperature, its surface was coated by Fe_3O_4 (or γ-Fe_2O_3). (See Fig. 2.)

Only the iron pattern was observed on the surface of the specimen exposed to 2 N HCl without the propargyl alcohol.

The inhibition mechanism of propargyl alcohol may be explained by considering that oxide films formed on iron surface are protected by the adsorbed propargyl alcohol from a further attack of acid. The oxide films may be always created on the iron surface by dissolved oxygen or OH ions formed at the iron dissolution[4].

In the present investigation the oxide film formation is experimentally observed with the electron diffraction (reflection method). From these results, it is suggested that the oxidation of iron is carried out at the dissolution even in the non-oxidizing acid, such as hydrochloric acid.

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[4] K. F. Bonhoeffer and K. E. Heusler, *Z. Elektrochem.* **61**, 122 (1957).