LETTERS TO THE EDITORS

Preferential Etching of Dislocation-pits of Nickel

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The method in use for preferential etching of crystal defects of a metal is primarily based on many empirical observations, but it does not necessarily represent the best desired etching. Recently, however, it has been suggested that in the case of stainless steel, an electrochemical approach by means of a potentiostat permits a quantitative study of etching⁽¹⁾⁽²⁾, where the potential of a metal immersed in an electrolyte can be maintained constant with the aid of a potentiostat. There is, in general, a simple relationship between the electrode potential and the dissolution rate of a metal. Fig. 1 shows

Fig. 1 Relation between the electrode potential and stationary anodic dissolution current on nickel in 1 N H₂SO₄ at 25°C.

the curve obtained with nickel in 1 N H₂SO₄ at 25°C⁽³⁾. At lower potentials (+0.0 to +0.4 V in standard hydrogen-electrode scale), nickel is in the so-called active state and the dissolution rate increases with the potential up to 200 mA/cm² in equivalent dissolution current density. At intermediate potentials (0.5 to +1.0 V) nickel becomes passive and becomes difficult to dissolve into the solution owing to the formation of a very thin oxide film on the surface. For higher potentials (+1.0 to +1.5 V), the anodic dissolution again takes place exhibiting an trans-passive state where the dissolution kinetics clearly differs from that in the active state⁽³⁾⁽⁴⁾.

The difference in the microstructure between the surface etched at the active state and that etched at the over-passive state has also been found on the nickel by an electron-microscopic investigation. The specimen was prepared by melting electrolytic nickel of 99.97% purity and casting in vacuum. Then, it was cold-rolled into a plate and subsequently annealed at 800°C for 10 min. After polishing the surface, the specimen was electrolytically etched in either the active state or in the trans-passive state in 1 N H₂SO₄ using a potentiostat of the Gerischer type⁽³⁾.

Photo. 1 shows a microstructure of the surface etched

Photo. 1 Microstructure of nickel etched potentiostatically in the active state in 1 N H₂SO₄; +0.18 V × 2 hrs. × 6300

in the active state. It is seen that the etch-structure differs with in different grains. It has been revealed in a previous paper⁽⁴⁾ that, in the active state, nickel dissolves from the bare surface by consecutive reactions consisting of the surface reaction producing the soluble nickel-complex ion of NiOH⁺ and the dissociation reaction of the complex ion in the solution-layer just over the surface. Since, in the stationary anodic dissolution, the rate of the over-all reaction is controlled by the dissociation reaction in the vicinity of the surface⁽⁴⁾, the surface reaction should be in quasi-equilibrium condition, making nickel ions on the surface readily migrate between the metal and the solution. Thus, the etch-figure

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- (2) N. Ito and G. Okamoto : Trans. of Japan Inst. Metals, 2 (1961), 120.
- (3) N. Sato and G. Okamoto : J. Electrochem. Soc., 110 (1963), 605.
- (4) N. Sato and G. Okamoto : J. Electrochem. Soc., 111 (1964), 897.

Photo. 2 Microstructure of nickel etched potentiostatically in the overpassive state in 1 N H_2SO_4 ; +1.35 V $\times 6.5$ hrs. $\times 6300$

characteristic for each of grains is expected to appear in the microstructure as shown in Photo. 1.

Photo. 2 is a microstructure of the surface etched in

the over-passive state. No particular etch-structures, except the dislocation etch-pits along sub-boundaries, can be seen in the interior of grains. This may be understood from the fact that in the trans-passive state the surface of nickel is covered with a thin oxide film through which the dissolution is taking place. Therefore, there is no free-movement of nickel ions on the surface and the crystallographic orientation of the grains has no effect on the etch-structure. The crystal imperfections such as dislocations and grain boundaries, however, would affect the surface oxide film to produce etch-pits, since the free energy of the formation of crystal imperfections is generally much higher than the energy-difference between different crystal planes.

It is stressed that by potentiostatic electrolysis in H_2SO_4 , the dislocation etch-pits were preferentially formed at potentials in the trans-passive state where nickel dissolved through the surface oxide film. The same technique to obtain dislocation etch-pits could also be applied to other metals. The detail will be reported elsewhere.

By Norio Sato*

* Physical chemistry and Electrochemistry Laboratory, Faculty of Engineering, Hokkaido University, Sapporo, Japan.