INFLUENCE OF MACHINING ON HYDROGEN-EVOLUTION OVERVOLTAGE AT NICKEL

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UDC 620.193.41

It is known that the rate of spontaneous corrosion and the corrosion potential can depend on the treatment to which an electrode is subjected [1]. Polishing of the electrode has been found [2] to affect one of the coupled reactions in the steady-state corrosion of nickel, hydrogen evolution, and the hydrogen overvoltage at a polished nickel electrode has been shown to be less than at a similar electrode preliminarily subjected to alternating (anodic–cathodic) polarization.

The present investigation was an attempt to make a more unambiguous determination of the factors leading to the aforementioned change in hydrogen-evolution overvoltage.

The electrodes were fabricated from electron-beam smelted nickel. Before the measurements, they were treated with hot concentrated alkali and rinsed with redistilled water. The electrolyte was 0.1 N H_2SO_4. The hydrogen-overvoltage curves were determined potentiostatically in an argon atmosphere (from 0 to −300 mV with respect to a hydrogen electrode in the same solution). Before the measurements, the electrode was held at the free-corrosion potential for 15 min. Each point on the overvoltage curve corresponded to holding for 3 min at the potential in question.

The currents at $\varphi = -300$ mV for a freshly polished nickel electrode and for the same electrode held at this potential for 30 min were 0.018 and 0.017 A/cm^2 respectively, while that after anodic etching was 0.001 A/cm^2.

Hence it can be seen that the change in current resulting solely from prolonged cathodic polarization was slight.

It should be noted that the largest change in the overvoltage was observed after prolonged etching of a polished electrode at the potential of the maximum solution current, $\varphi = 0.1$ V (Fig. 1).

It was also found that polishing with different grades of abrasive* or preliminary surface treatment after polishing (rinsing in hot or cold alkali and washing with alcohol or redistilled water) had no effect on the observed change in overvoltage.

A substantial amount of nickel ions appeared in the electrolyte during prolonged anodic solution. Experiments involving addition of nickel sulfate to the electrolyte before anodic etching of the electrode surface showed that nickel ions did not affect the hydrogen-evolution overvoltage at a polished electrode.

We investigated the increase in overvoltage as a function of the anodic solution potential of the polished electrode and the anodic-solution time. The results of these experiments enable us to state that the increase in overvoltage during anodic etching is independent of the etching potential and is governed by the amount of nickel that dissolves out of the electrode surface.

The time at which the overvoltage reached its maximum (maximum *a* in Fig. 2) corresponded to solution of 10^4 single layers or a nickel layer with a thickness of 1 μm.

*Polishing with No. M24 emery paper, Alundum powder, and powdered magnesium oxide.

L. Ya. Karpov Scientific-Research Physicochemical Institute. Translated from Zashchita Metallov, Vol. 7, No. 4, pp. 471-472, July-August, 1971. Original article submitted March 19, 1970.

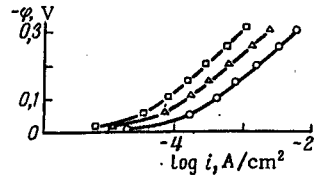

Fig. 1

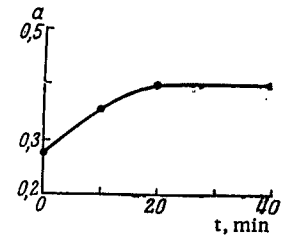

Fig. 2

Fig. 1. Curves representing hydrogen-evolution overvoltage at nickel. ○) At polished electrode; △) at polished electrode after etching for 10 min at potential of 110 mV; □) the same, after 40 min.

Fig. 2. Curves representing constant a in Taffel equation as a function of solution time for nickel electrode, $i = 3.5 \cdot 10^{-3}$ A/cm^2.

We measured the double-layer capacitance after polishing of the electrode and after anodic etching, * in order to determine the role of the change in surface geometry during etching.

The capacitance was reduced by a factor of 1.3-1.5 after etching, which, although it indicates some surface smoothing, does not permit explanation of the observed increase in overvoltage, which causes the hydrogen-overvoltage current to vary by a factor of 5-10.

Electrolytic nickel deposited on a standard specimen also exhibited a decrease in overvoltage after polishing and an increase after anodic solution, although these effects were less pronounced and less reproducible.

One conclusion to be drawn from our experiments is that surface machining leads to a decrease in hydrogen-evolution overvoltage as a result of development of a superficial energy nonuniformity greater than that for electrochemically treated specimens.

The increase in overvoltage after solution of nickel is apparently due to removal of the surface layer, which is distorted by machining; the maximum effect is produced by removal of a definite amount of nickel and not by increasing total etching time. This enables us to state that the increase in overvoltage is caused not by slow adsorptive phenomena but by solution of deformed metal crystals.

LITERATURE CITED

1. G. Ulig, Corrosion of Metals [Russian translation], Metallurgiya (1968), p. 51; U. R. Evans, Corrosion and Oxidation of Metals [Russian translation], Mashgiz (1962), p. 354.
2. N. Ya. Buné, Zashchita Metallov, 1, 168 (1965); 3, 50 (1967).

*The capacitance measurements were made with the pulsed potentiostatic method.