The Effect of Temperature on the Growth of the Multi-atomic Oxide Layer on a Smooth Platinum Anode in an Acid Solution

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It is well known that the oxide formed on a platinum anode under ordinary conditions does not grow beyond a monolayer.[1,4] However, it has recently been reported[5-8] that the oxide grows into the inside of the platinum electrode when the electrode is anodically polarized at a high potential or at a high current density.

It is the purpose of this communication to report some findings on the effect of temperature on the anodic growth of the multi-atomic oxide layer in an acid solution under galvanostatic conditions.

Experimental

The anodic oxidations of the electrode were carried out in an all-glass cell consisting of a large central compartment and two smaller sections separated from the main section by fine-pore-fritted glass disks. The middle compartment served as the test electrode section; both the side compartments contained a platinum sheet, 2 cm^2 in area, which served as a counter electrode. The cell was mounted in a thermostatic water bath which controlled the temperature to ±0.01°C within the 15—30°C range.

The electrolytic solution used for this work was a 0.5 M sulfuric acid solution which had been prepared from sulfuric acid of the GR grade and from conductivity water triply-redistilled using a quartz still.

Test electrodes, smooth platinum foils 0.5 cm^2 in area, were spot-welded to platinum wire, which was then sealed in glass supports. They were cleaned by successive washings with hot chromic acid, hot dilute nitric acid, and, most throughly, with conductivity water. The cleaned electrodes were then heated to redness in a gas flame and, after cooling, cathodically polarized to the hydrogen evolution potential using a current of 60 μA/cm^2 in an oxygen-free solution in order to remove the oxide film formed during the heating.

The electrode was oxidized by anodic polarization in an air-saturated solution at different temperatures but with a constant current of 200 mA/cm^2. The extent of the oxidation of the electrode was estimated from the cathodic charging curve (the potential-time curve), which was taken with a current of 60 μA/cm^2 at 25°C in another cell containing the solution freed from dissolved oxygen by passing purified nitrogen gas through. A pen recorder with a high-impedance input preamplifier (50 MΩ) was used to record the charging curves.

The potentials reported here are referred to a normal hydrogen electrode, although the work carried out with a $Hg/Hg_2SO_4/0.5$ M H_2SO_4 reference electrode.

Results and Discussion

The curves II—V shown in Fig. 1 are the cathodic charging curves for the electrodes preanodized at different temperatures but with the same current density and for the same length of time. For temperatures lower than 22°C, curves similar to the curve II were obtained. The plateau at 0.62 V may be ascribed to the reduction step of the monolayer oxide on the surface. The rapidly-falling region following this plateau, however,

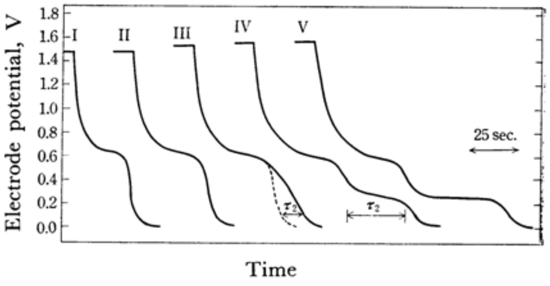

Fig. 1. Cathodic charging curves for the electrode pre-anodized at various temperature.
i_c=60 μA/cm^2
I: Temperature=17°C, time=60 min, current=600 mA/cm^2
II: Temperature=22°C, time=30 min, current=200 mA/cm^2
III: Temperature=24°C, time=30 min, current=200 mA/cm^2
IV: Temperature=26°C, time=30 min, current=200 mA/cm^2
V: Temperature=28°C, time=30 min, current=200 mA/cm^2

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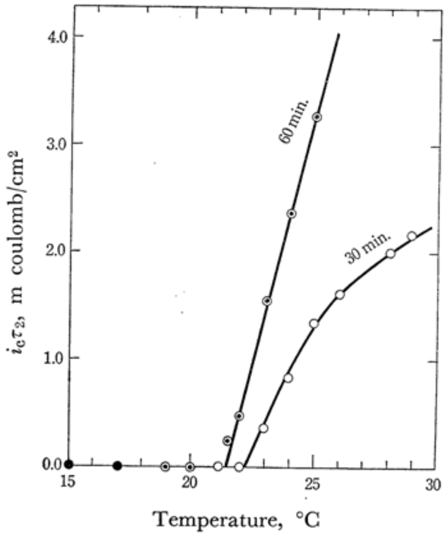

Fig. 2. Quantity of electricity required for the second plateau as a function of the temperature in the pre-anodization.

●, Pre-anodization current=600 mA/cm^2, time=60 min
⊙, Pre-anodization current=200 mA/cm^2, time=60 min
○, Pre-anodization current=200 mA/cm^2, time=30 min

becomes less steep at 24°C (curve III). This sloping region is transformed to the second plateau at a higher temperature (curve IV); this perfectly-leveled plateau increases in area with the transition time with an increase in the temperature (curve V). It should be noted that, regardless of the appearance of the lengthening second plateau, the transition time of the first plateau maintains a constant value, one which is equal to that of the plateau of the curve II for 22°C. This suggests that the first plateau is the reduction step of the outermost monolayer of the oxide. The charge required for the second plateau increased extensively with an increase in the temperature. Such a large charge cannot be accommodated by any reasonable oxidation state of surface atoms alone. The fact that oxygen atoms readily reach positions below the surface has been demonstrated by low-energy electron diffraction.[9] Consequently, the second plateau may be ascribed to the reduction of the multi-atomic layer of the oxide grown into the inside of the metal.

When the electrode is oxidized for 60 min under the same current, the inner oxide begins to form at 22°C; its quantity linearly increases with an increase in the temperature (Fis. 2), but at 21°C and below the inner oxide is never formed, even at a large current density, as may be seen from the curve I in Fig. 1.

It may be concluded from the above results that the oxide film formed at temperatures lower than the critical temperature of 22°C has a tight structure and protects the growth of the oxide into the inside of the metal. At temperatures higher than 22°C, however, the oxide grows to the multi-atomic layer, which has a well-defined phase property.

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