METALLURGY

Desorption of Tritiated Bound-water from the Passive Film Formed on Stainless Steels

IT has been admitted by a number of workers that the passivity of metals is caused by a formation of passive films as a result of electrochemical reactions between metals and their environment. The passive film has been assumed to be a sort of hydrous oxide which has more or less colloidal character.

Rhodin[1] appears to be the first to find the existence of bound water in the passive film of stainless steel by using chemical analysis of the film stripped from the surface. We have measured, by means of a microthermogravimetric technique, the amount and the characteristics of bound water in the passive film on the surface of stainless steel without stripping the film[2].

In the work recorded here, the rate of desorption of the bound water in the passive film formed on stainless steel in 1 N sulphuric acid at various potentials was measured using tritium as a tracer. For the measurement of tritium in the form of tritiated water, a coincidence liquid scintillation counting system was used.

A thin foil specimen of 304 type stainless steel (25 mm × 15 mm × 0·02 mm) was etched in a mixture of dilute hydrochloric, nitric and hydrofluoric acids, followed by washing with re-distilled water, and it was immersed in sulphuric acid solution for passivation. The solution was 1 N sulphuric acid tagged with tritium of about 75 mc./ml. Before the passivation the specimen was prepolarized at −250 mV (in saturated calomel electrode scale) for 1 h, the solution being stirred with a purified nitrogen gas to activate the surface completely. The specimen was then passivated in the solution of 25° C using a potentiostat at various potentials in the passive potential region for two different periods of time of 60 min and 1,000 min. After completion of the passivation treatment, the specimen was removed from the solution, rinsed in re-distilled water, and dried with filter paper. The tritiated specimen was then introduced into a vial of 20 ml. capacity containing scintillating solution, which had been prepared by dissolving 4 g of PPO and 0·05 g of POPOP into 1 l. of dioxane free from oxygen. The vial was set in the counter kept at a constant temperature of 18° C.

Fig. 1 shows a typical example of the time variation of the counting rate. There is no change of the counting rate with time before the immersion of the specimen in the scintillating solution, even if the scintillating vial is exposed to room light; at point A in Fig. 1 the vial was out of the counter for 15 min, being exposed to light. The counting rate, however, increased with time after the tritiated specimen was introduced into the scintillating vial at point B. These facts indicate that the increase of
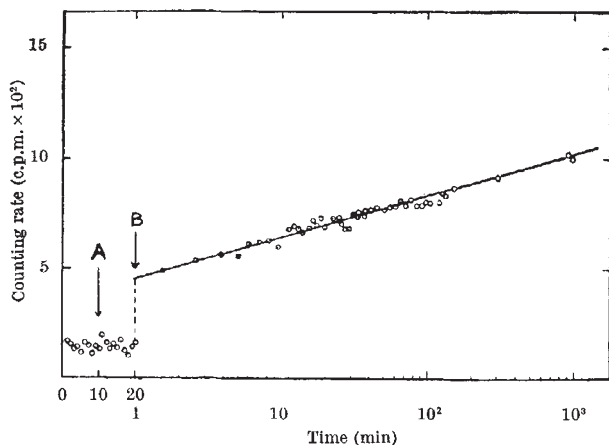

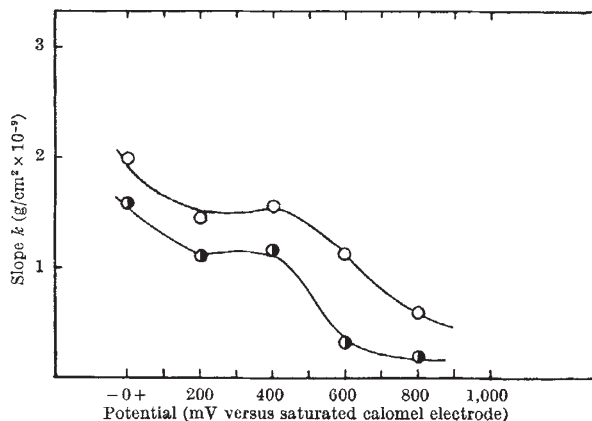Fig. 1. Typical change of counting rate with time

Fig. 2. Slope of desorption—log time curve against passivation potential. O, Passivation for 60 min; ◑, passivation for 1,000 min

the counting rate with time is not attributed to the excitation of the scintillator by light, but to the desorption of tritiated water from the surface into the dioxane scintillating solution. Since the passive film itself may act as an absorbant of β-radioactivity of tritium, the emission directly arising from the tritium included in the film would scarcely affect the counting rates observed.

From the result shown in Fig. 1, the amount of tritiated water desorbed from the surface film is found to increase with time according to the following empirical equation:

$$q = k \log t + \text{const} \qquad (1)$$

For the specimens passivated under various conditions, the same logarithmic relationships were observed and the slope k was determined from the observed results using equation (1). The dependence of the slope k on the potential and the period of time of passivation is shown in Fig. 2. It can be seen that the value of the slope k becomes smaller, as the potential is more noble and the period of time is longer.

A comparison between the foregoing results, and the previous experiments dealing with the dependence of the amount of bound water on the potential and on the period of time of passivation[3], leads to a conclusion that the desorption rate constant k increases with increasing the bound water existing in the passive film.

It is an interesting fact that the value of the slope k begins to decrease abruptly at a potential of around 0·5 V, above which activation of passivated stainless steels in sulphuric acid solution has been known to become difficult[4]. This suggests that the bound water in the film plays an important part in the stability of the passive film against corrosion.

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[1] Rhodin, T. N., Ann. N.Y. Acad. Sci., 58, 855 (1954).
[2] Okamoto, G., Shibata, T., Ishikawa, T., and Nagayama, M., Extended Abstrs., Second Intern. Cong. Metallic Corrosion, New York, 50 (1963).
[3] Unpublished results.
[4] Carius, C., Arch. Eisenhüttenwes., 27, 401 (1956).

Oxidation of Vanadium in Dry and Moist Oxygen–Argon Mixtures

VANADIUM is notable for its very rapid rate of oxidation at temperatures above 675° C, at which temperature the main oxidation product, V_2O_5, melts. The presence of V_2O_5 in the oxide scale of other metals, either through the presence of vanadium as an alloying constituent, or through its introduction from furnace ash, may also cause rapid attack (so-called catastrophic oxidation), usually above about 650° C. This is usually ascribed to the fluxing action of the molten V_2O_5 on the oxide of the basis metal[1].