Cathodic Reduction of Some Oxidizing Reagents on Passivated Fe, Cr and Fe-20 wt% Cr Alloy in a Borate Buffer Solution

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1 INTRODUCTION

On corrosion study, quite few works have been done on cathodic reactions. In many cases, cathodic reactions take place on passive films formed on metals and alloys. It is therefore necessary that the electrochemical nature of the passive film and their effect on the cathodic reaction occurring on them must be more clarified. It has been reported that passive films possess semiconductive properties. The authors have studied on oxygen reduction on passive stainless steels and revealed that the reaction was chemically controlled and semiconductive properties give strong effect on cathodic reaction of oxygen¹⁾. In order to know more about them, the cathodic reduction of some oxidizing reagents is carried out on passivated Fe, Cr and Fe-20wt%Cr alloy and relation between electronic properties and the structure of their passive films is examined.

2 EXPERIMENTAL

Disk electrodes of pure iron, chromium and Fe-20wt%Cr alloy were employed as samples ($7.1 \times 10^{-6} \text{ m}^2$). The pH 8.4 borate buffer solution dissolving potassium bichromate or potassium ferricyanide as oxidizing reagents were used. They were deaerated by bubbling pure nitrogen gas. The samples were abraded with # 1,500 energy paper and degreased by trichlorethylene.

10 minute cathodic prepolarization at -1.5 V (vs. SCE) was carried out to reduce an air-formed oxide film and then 30 minute passivation was made at 0.4 V . After changing to the solution containing an oxidizing reagent, the disk samples were stepwisely polarized for 2 minutes each in the cathodic direction. Ac impedance measurement was carried out at several constant potentials with a frequency response analyzer.

3 RESULTS AND DISCUSSION

3.1 Polarization curves of passivated Fe, Cr and Fe-20wt% Cr alloy in $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{K}_3\text{Fe}(\text{CN})_6$ containing solutions

Figure 1 shows the potentiostatic polarization curves for passivated Cr, Fe and Fe-20wt%Cr alloy in $0.1 \text{ M } \text{K}_2\text{Cr}_2\text{O}_7$ or $0.05 \text{ M } \text{K}_3\text{Fe}(\text{CN})_6/0.1 \text{ M } \text{K}_4\text{Fe}(\text{CN})_6$ solution and indicates current limitation due to chemical reaction control. Concerning Cr, it is observed that the limiting current for the $\text{Cr}_2\text{O}_7^{2-}$ reduction is much larger than that for $\text{Fe}(\text{CN})_6^{3-}$ and that a rather sharp current peak appears at around 0.05 V on both polarization curves. On the other hand, as for Fe, a reverse relation on limiting current can be observed and a current peak can be seen at around -0.3 V . It is thus found that strong metal selectivity to cathodic reaction exists and a current peak or knick appears at a certain potential, E_p depending on metals. In the case of Fe-20wt%Cr alloy, for the $\text{Cr}_2\text{O}_7^{2-}$ reduction, a current peak appears nearly at E_p observed on Cr and for the $\text{Fe}(\text{CN})_6^{3-}$ reduction, that appears nearly at E_p observed on Fe. These results seem to be attributable to

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change in semiconductive properties of the passive films.

3.2 Impedance measurement for film capacitance during $\text{Cr}_2\text{O}_7^{2-}$ or $\text{Fe}(\text{CN})_6^{3-}$ reduction

Ac impedance measurement of passivated Cr, Fe and Fe-20wt%Cr alloy was carried out at around E_p during cathodic reduction of $\text{Cr}_2\text{O}_7^{2-}$ or $\text{Fe}(\text{CN})_6^{3-}$ in the pH 8.4 borate solution. The measured impedances could be almost explained by equivalent circuits composing a RC cascade connection of a couple of a film capacitance and a film resistance (probably influenced by adsorption) and that of an electric double layer capacitance and a faraday resistance. The capacitance of passive films was estimated by curve fitting. The Mott-Schottky plot for film capacitance is exhibited in Fig. 2. A nearly triangle-shape relation can be seen with an apex existing at around E_p on the cathodic polarization curve. The linear relation with negative slope means n-type semiconductivity and that with a positive

slope means p-type one. The reciprocal slope values are proportional to the carrier density in the passive films²⁾. It can be found that the larger the limiting current is, the larger the carrier concentration is in both cases. If it is assumed that the carrier density is in proportion to adsorption quantity, this phenomenon seems to be reasonable. Concerning Fe-20wt%Cr alloy, a triangle type relation can be also obtained (Fig. 2). It is found that for the $\text{Cr}_2\text{O}_7^{2-}$ reduction, an apex of the triangle relation selectively exists near E_p observed on Cr and that for the $\text{Fe}(\text{CN})_6^{3-}$ reduction, it exists near E_p observed on Fe. This means that these two reductions favourably occur on the different components. This seems to support that the structure of the passive films consists of a mixture of iron oxides and chromium oxide.

3.3 Change in structure of passive films on Fe, and Cr during cathodic reduction

As mentioned above, at around E_p , the semiconductivity of the passive film changes from p-type to n-type. According to study on electrochemical formation and reduction of passive

Fig. 1 Cathodic polarization curves of passivated Cr, Fe and Fe-20wt% Cr alloy in pH 8.4 borate solution with 0.1 M $\text{Cr}_2\text{O}_7^{2-}$ (open marks) or 0.05 M $\text{Fe}(\text{CN})_6^{3-}$ (solid marks)
○●: Cr, △▲: Fe, □■: Fe-20wt% Cr

Fig. 2 Mott-Schottky plot for film capacitance of Cr, Fe and Fe-20wt% Cr during cathodic reduction of $\text{Cr}_2\text{O}_7^{2-}$ or $\text{Fe}(\text{CN})_6^{3-}$. Number is the magnitude of the ordinate and marks the same as in Fig. 1.

films on Fe^{3+} and Cr^{4+} , it has been reported that as for Cr, $\text{Cr}^{3+}_{2-2x}\text{Cr}^{6+x}\text{O}_3$ is reduced to Cr_2O_3 at around 0.05 V and as for Fe, excess oxygen is reduced at around -0.3 V. These potentials correspond to the observed E_p . Since the oxidants are possibly considered to be p-type semiconductors and the reductants to be n-type ones, the observed Mott-Schottky relations can be understood.

According to the adsorption theory on the surface of semiconductors⁵⁾, adsorption quantity of anions on n-type semiconductors is limited as called "depletion adsorption" and that on p-type semiconductors increases as called "accumulative adsorption". Passing E_p in cathodic polarization, semiconductivity of passive films changes from

p-type to n-type, which reduces quantity of adsorbants. Assuming that limiting current depends on quantity of adsorbants, limiting current seems to reduce below E_p . It seems to be understood that this phenomenon causes a current peak or a knick.

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