

Semiconductor Properties of Passive Film on Fe-18Cr Alloy Formed in Acid and Neutral Solution

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Passive films on Fe-Cr alloys have been analysed in detail using the UHV surface analysis techniques to reveal their layered structure (1), which plays important role for corrosion resistance. On the other hand, measurements of electronic properties of passive film by an impedance spectroscopy and photo electrochemical response some time give arise contradict results. In this presentation, we describe such apparently inconsistent behaviour is to be fairly explained by introduction of duplex semiconductor structure, the property of which is highly influenced by pH. Moreover, the difference of corrosion behaviour, including film growth kinetics, between passive films formed in neutral and acid solution will be also described.

It has been widely acknowledged that passive films on Fe and Fe-Cr alloys exhibit n-type semiconductor property, mainly based on the results obtained by the electrochemical impedance spectroscopy. On the other hand, the photo electrochemical response reveals positive and/or negative photo current depending on the applied potential and pH (2). For example, Mott-Schottky plot of capacitance measured for passive film formed on Cr and Fe-Cr alloys in an acid solution clearly shows n-type semiconductor behaviour, whereas photo current is basically negative value for most of potentials in passive region, which apparently implies p-type semiconductor behaviour.

The authors introduced duplex semiconductor layers model in order to describe the electronic properties of passive films on Cr and Fe-Cr alloys in an acid solution (3). As shown in Fig.1(a), a passive film formed in acid solution is composed of inner oxide layer and outer hydroxide layer with p and n type semiconductor characteristics, respectively. The photo electrochemical response mainly arises in the inner oxide layer, which is in a depleted state, to generate a negative photo current, the absolute value of which decreases with increasing applied potential. This is typical behaviour of p-type semiconductor. The photo excitation in the outer hydroxide layer, which has smaller energy band gap (~2.5 eV) compared to that of the inner oxide layer (3.6~3.7 eV), actually gives a small positive photo current at some noble potentials with a specific photon energy region. On the other hand, the capacitance of space charge layer arises in outer hydroxide layer, which reveals n-type semiconductor behaviour in a noble potential region in the passive state, because at noble potentials the space charge layer of the inner oxide layer becomes very thin to generate larger capacitance. Therefore, the smaller capacitance generated in the outer hydroxide layer is observed. Details have been described elsewhere (1).

In neutral solution, on the other hand, both the inner oxide and outer hydroxide layer reveal n-type semiconductor properties, as shown in Fig.1(b). In the neutral solution, Fe-18Cr alloy exhibits a typical positive photo current, which increases with increasing applied potential, and Mott-Schottky plot shows positive slope.

The flat band potentials obtained in both measurements are approximately equivalent. Therefore, it is assumed that both internal oxide and outer hydroxide layers are in depleted states.

Such difference in the electronic structure may result in a variety of corrosion resistance and also the passive film growth kinetics. The property for the energy band structure to note is that the energy band slope in the inner oxide layer is negative and positive toward film/solution interface for the passive film formed in the acid and the neutral solution, respectively (see figure). For positive slope, *i.e.* in neutral solution, it is possible for a cation to migrate outer ward or for an anion inner ward resulting in growth of the film. On the other hand, for a negative slope generated in the film formed in the acid, a film growth by ions migration along the potential gradient is impossible. Kirchheim described that the growth of a film continued for a long period in a neutral solution, but the growth of the film terminated in few minutes to remain almost constant in the acid (4). Such behaviour is coinciding with the above mentioned potential gradient in the passive film. We also reported that a positive photo current (positive slope in the film) was observed for Fe-18Cr alloy in acid solution during the very initial period of passivation, which means that film may grow in the early stage in the passivation (5).

The correlation between the corrosion behaviour and the electronic structure in passive films will be described.

References

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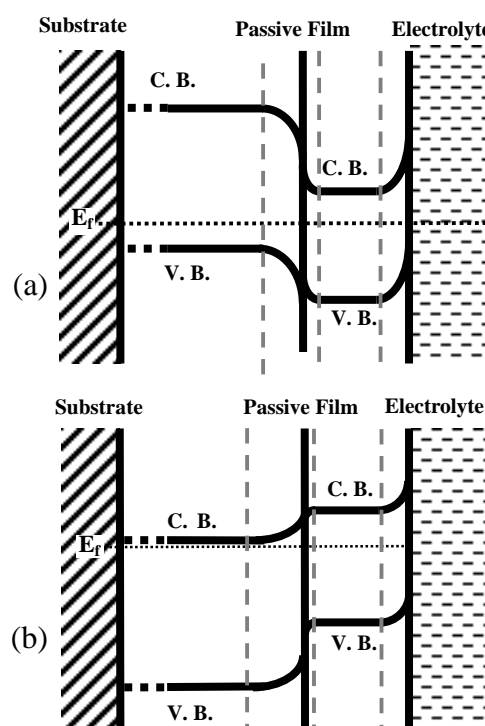


Fig.1 A schematic presentation of the electronic band structure of passive films formed on Fe-Cr alloys in (a) acid and (b) neutral solution.