

Semiconductive behavior of passive films formed on Fe-Cr alloy

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Abstract Semiconductive properties of passive films formed on Fe-18Cr alloy in a borate buffer solution were investigated using photoelectrochemical response and electrochemical impedance spectroscopy. Band gap energy of the passive films, E_g , was estimated from a photoelectrochemical spectrum that could consist of two components. E_g s were recognized as approximately 2.4 eV and 3.4 eV, which were mainly derived from Cr hydroxide layer and Cr oxide layer, respectively. The values were almost constant independent of passivation time, film formation potential and additive element. Positive photocurrents generated from the outer part hydroxide and the inner oxide in the passive film increased as applied potential increased, which indicates that the passive films behaved as an *n*-type semiconductor. Mott-Schottky plot of capacitance showed positive slope. This means that the passive films behaved as an *n*-type semiconductor. Donor densities of the passive films estimated by the Mott-Schottky plots depended on passivation time, film formation potential and additives. Corrosion resistance of Fe-18Cr alloy was discussed in terms of the semiconductive properties.

Keywords Passive film; Stainless steel; Semiconductive property; Photoelectrochemical response; Electrochemical impedance; Corrosion

1. Introduction

Thin oxide films formed on metal and alloy surface in an electrolyte, so-called “passive film”, play an important role in preventing material degradation due to corrosion. Structure, chemical composition and electronic property of the passive films are correlated with corrosion behavior. In order to reveal the structure and chemical composition passive films have been subjected to ultra high vacuum (UHV) surface analyses such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) [1–3]. Semiconductive properties, that is, electronic properties of the passive films are investigated using photoelectrochemical response and electrochemical impedance spectroscopy. For the photoelectrochemical response, photo effect is applied into characterization of the passive films. Semiconductive properties such as band gap energy, flat band potential, type of conduction and band bending are analyzed from a current or potential change by photo irradiation. For the electrochemical impedance spectroscopy, the capacitance of space charge region is measured and analyzed to estimate donor density, flat band potential and type of conduction. Semiconductive properties of passive films on metals and alloys have been investigated using these techniques [4–8]. Schmuki [9] and other authors [6, 10, 11] described the electronic structure of passive films on Fe, Cr and stainless steels. According to their papers, passive films on Fe exhibit *n*-type semiconductive behavior, whereas *n*- and *p*-type semiconductive properties were observed for passive films on Cr depending on experimental conditions such as

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potential and pH. We also have examined semiconductive properties of the passive films formed on Fe-Cr and Ni-Cr alloys and proposed bi-layer electronic energy band structure models to explain the complicated results [12].

In this paper, we report semiconductive properties of passive films on stainless steels in a borate buffer solution and correlation between the semiconductive properties and corrosion behavior.

2. Experimental

Specimens were vacuum melted Fe-18Cr alloy and also sputter-deposited Fe-18Cr with some additives. Procedure to fabricate sputter-deposited alloys was described elsewhere [13]. A platinum and a Ag/AgCl electrode were used as a counter and a reference electrode, respectively.

It is very difficult to remove air-formed film formed on the surface in a neutral solution. In the present work, the specimen was activated in a dilute sulfuric acid solution and then passivated at various potentials in a borate buffer solution. The specimen was polarized at $-1000 \text{ mV}_{\text{Ag/AgCl}}$ in $0.01 \text{ kmol m}^{-3} \text{ H}_2\text{SO}_4$ for 10 min. Finally, $0.6 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3 + 0.15 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ were added to the solution. During the process, both the specimen and the solution were not exposed to air. The specimen was polarized at various potentials to form a passive film. All the experiments were conducted at room temperature under continuous deaeration with high purity N_2 gas.

A 500 W Xenon arc lamp with a grating monochromator was employed to generate monochromatic light for the photoelectrochemical response measurements. The specimen electrode was illuminated in an electrochemical cell through a quartz window. The intensity of the irradiated light was calibrated using a photodiode optical power meter. The specimen was polarized at a fixed potential for a desired period to form a passive film. Photocurrent response was occasionally measured during passivation. Subsequently, the applied potential was changed stepwise with interval of 100 or 200 mV in the less noble direction. The photocurrent was measured at each

applied potential. The photocurrent response was measured as a transient of current after the specimen was exposed to the light and then interrupted typically for 10 s. The wavelength of the irradiated light was changed from 250 to 500 nm at each cycle of light exposure. No lock-in technique was adopted.

A frequency response analyzer (FRA, NF Co., Model 5050A) equipped to the potentiostat was used for electrochemical impedance measurements. A personal computer controlled the FRA, acquired and analyzed data. Imaginary part of the impedance (Z'') was measured as a function of the applied potential and corresponding capacitance of space charge layer (C) was obtained from $C = -1/\omega Z''$. The capacitance of passive film was calculated from the impedance obtained at 1 Hz where Bode plot of the impedance spectra exhibits a capacitive region. The electrochemical impedance was intermittently measured during the course of passivation at a constant potential. Then the applied potential was changed, stepwise, in the less noble direction and the impedance was measured at each potential.

3. Results

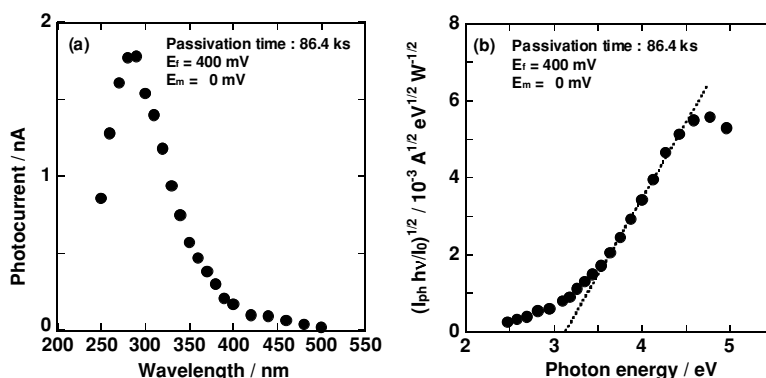
3.1. Photoelectrochemical response

Photocurrent was measured at various applied potentials between 0 and $500 \text{ mV}_{\text{Ag/AgCl}}$ for up to 24 hours. Photocurrent is not constant during photoirradiation and exhibits transient [14]. Therefore difference between the current just before irradiation and after 10 s is defined as a photocurrent. Example of photocurrent spectrum is shown in Fig. 1(a) as a function of irradiated light wavelength. Since the intensity of the irradiated light is not constant for each wavelength, the photocurrent spectrum should be normalized into a photoelectrochemical action spectrum as described in the following.

Absorption coefficient, α , of a crystalline semiconductor depends on the photon energy according to Eq. (1):

$$\alpha \propto (h\nu - E_g)^n / h\nu, \quad (1)$$

Fig. 1 (a) Example of photocurrent spectrum for the passive film on Fe-18Cr in a borate buffer solution and (b) photoelectrochemical action spectrum of steady photocurrent shown in Fig. 1(a). E_f : Film formation potential; E_m : Photocurrent measuring potential



where E_g is band gap energy, and $h\nu$ energy of the incident photons. For a crystalline semiconductor, value of n is 0.5 or 2 depending on the electron transition process; 0.5 for a direct transition and 2 for an indirect transition. The type of transition and E_g can be determined from the photoelectrochemical spectrum, provided that the photocurrent, i_{ph} , is proportional to the absorption coefficient, α . Assuming that the photo excitation occurs as an indirect transition which is usually observed for passive film on Fe-Cr alloys, Eq. (1) can be described by

$$i_{ph} \cdot h\nu/I_0 = const.(h\nu - E_g)^2, \tag{2}$$

Therefore,

$$(i_{ph} \cdot h\nu/I_0)^{1/2} = S \cdot (h\nu - E_g), \tag{3}$$

where S is constant. E_g is determined from $(i_{ph} \cdot h\nu/I_0)^{1/2}$ vs. $h\nu$ plot as the photon energy where the $(i_{ph} \cdot h\nu/I_0)^{1/2}$ equals to 0. The slope, S , is adopted as the degree of photo response.

The photoelectrochemical spectrum plotted using Eq. (1) is shown in Fig. 1(b). This spectrum did not show one straight line, but exhibited a line with two different slopes. As usually known, passive films consist of not single, but multi layers. Therefore this spectrum was separated into two components using the procedure described elsewhere [15]. E_g s were recognized as approximately 2.4 eV and 3.4 eV, that were nearly constant independent of polarization periods, film formation potentials and additive elements. Sunseri et al. [6] and authors of the present work [12–15] reported that E_g s of 2.4 eV and 3.4 eV are derived from Cr hydroxide and Cr oxide, respectively. Angle-resolved XPS has revealed that passive films on Fe-Cr alloys are usually composed of an inner oxide layer and an outer hydroxide layer. Therefore it was found that the passive films on Fe-18Cr alloys are composed of an inner oxide layer with an E_g of 3.4 eV and a covering hydroxide layer with an E_g of 2.4 eV.

Figure 2 shows slopes of the photoelectrochemical spectrum, S , for passive films formed at various applied potentials. Positive photocurrents generated in the hydroxide and the oxide layer increased as the applied potential increased. Both hydroxide ($E_g = 2.4$ eV) and oxide layer ($E_g = 3.4$ eV) of passive films formed on Fe-18Cr alloys in a borate buffer solution exhibit typical n -type semiconductive behavior. Observed flat band potential, E_{fb} , for each layer was approximately -300 mV_{Ag/AgCl}.

3.2. Electrochemical impedance spectroscopy

Space charge region of a semiconductive passive film was characterized by evaluating the capacitance of the passive film. Using a similar procedure to that for photocurrent measurements, specimen was polarized at various potentials and

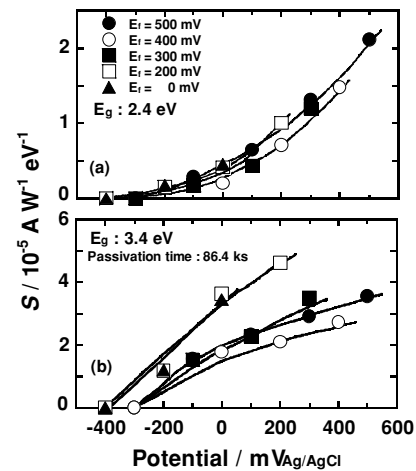


Fig. 2 Variations in slopes of photoelectrochemical spectrum, S , for (a) hydroxide layer with E_g of 2.4 eV and (b) oxide layer with E_g of 3.4 eV as a function of measuring potential

then the applied potential was sequentially shifted in the less noble direction at intervals of 100 mV. The capacitance was measured at each applied potential. According to the Mott-Schottky theory [16], the space charge capacitance of n -type semiconductor is give by Eq. (4).

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0qN} \left(E - E_{fb} - \frac{kT}{q} \right), \tag{4}$$

where N denotes donor density of a passive film, ϵ is the dielectric constant of the passive film, ϵ_0 the vacuum permittivity, q the elementary charge, k the Boltzman constant, T the absolute temperature, and E_{fb} the flat band potential. In this paper, the term kT/q was ignored as it was only around 25 mV at room temperature. This approach has been used for estimation of the carrier density of passive films [17–23].

Figure 3 exhibits the Mott-Schottky plots for the passive films formed on Fe-18Cr at various applied potentials for

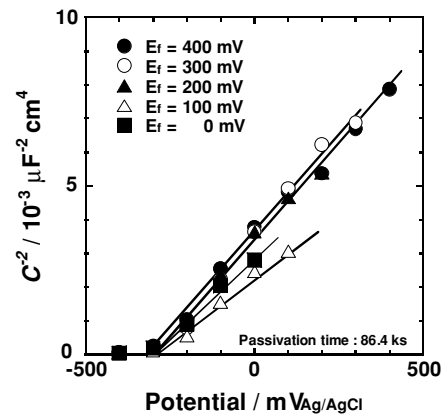


Fig. 3 Mott-Schottky plots for passive films formed on Fe-18Cr alloy at several potentials in a borate buffer solution

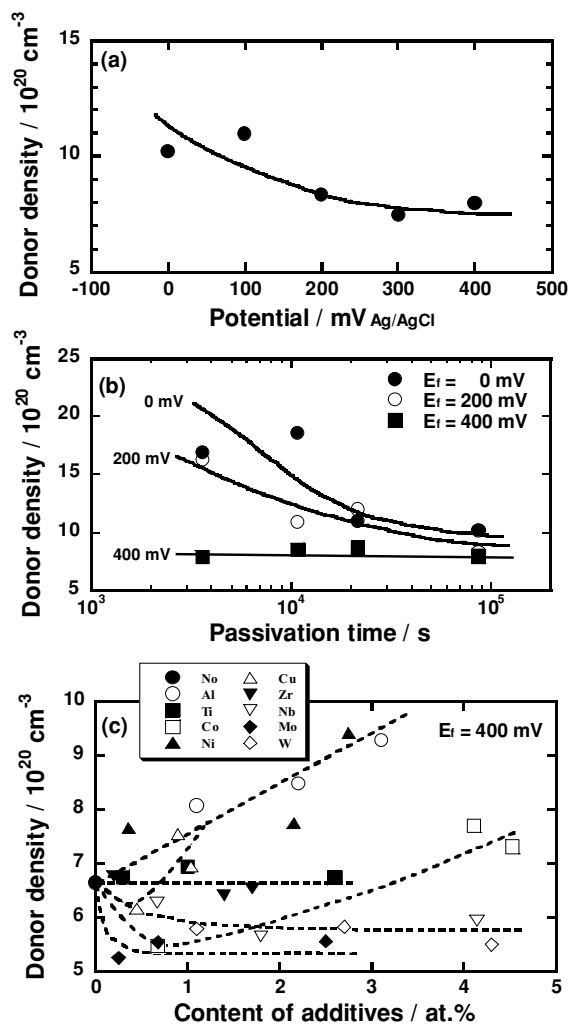


Fig. 4 Changes in donor densities of passive films on Fe-18Cr alloy (a) with film formation potential, (b) with passivation time and (c) additive elements

24 hours. Straight lines with positive slopes reveal an *n*-type semiconductive behavior. The presumed flat band potential, E_{fb} , is $-300 \text{ mV}_{\text{Ag}/\text{AgCl}}$, which is derived from the intercept of the straight lines to *x*-axis. This capacitance may arise in the space charge region developed in the outer hydroxide layer for the reasons discussed elsewhere [14].

Figure 4 shows variations in donor density obtained from the slope of the Mott-Schottky plot. As shown in Figs. 4(a) and (b), the donor densities of passive films formed on Fe-18Cr in the borate buffer solution decrease as film formation potential and passivation time increase. It is also observed that at a low film formation potential like $0 \text{ mV}_{\text{Ag}/\text{AgCl}}$ the donor density decreases abruptly with time in the early stages of passivation. Figure 4(c) shows the influence of additive elements on donor densities of passive films. Ni and Al increased the donor densities with increasing their content while Nb, Mo and W decreased the donor density. Cu and Co decreased

these densities once in a small amount and then increased them with increasing the amount. For Zr or Ti addition, donor densities were almost constant independent of their amounts.

4. Discussion

4.1. Influence of additive elements on semiconductive properties

Corrosion behavior of stainless steel highly depends on its alloying elements. Numerous works have revealed beneficial and/or harmful effect of each additive element. Semiconductive properties of passive films may be affected by additive elements. Therefore it is necessary to investigate the influence of additive elements on the semiconductive properties of passive films. However most additive elements do not dissolve homogeneously in alloys but change microstructure. In other words, additive elements modify metallurgical structure of alloys, for example, grain size, lattice structure and precipitate formation that highly influence on corrosion behavior. Therefore it is necessary to prepare materials in which the additive elements are completely dissolved as a solid solution. As reported previously, a sputter-deposited thin film produced by an ion-beam sputtering technique consists of homogeneous equiaxed nano-crystallines without any precipitates [24, 25]. Therefore only chemical effect of the additive elements on the semiconductor properties of the passive films can be discussed. In the present work, the influence of additive elements on semiconductive properties was examined using the sputter-deposited Fe-18Cr alloys with various additive elements.

As mentioned above, additive elements did not change the band gap energy of passive films but changed the donor density. Fe-substituted Cr oxide and hydroxide layers in the passive film may form some sort of three-dimensional networked structure, like the percolation model proposed by Newman and Sieradzki [26–28]. Additive elements may be incorporated into the passive film and substituted for Fe and/or Cr ions. Therefore a continuously connected domain of Cr oxide and hydroxide is formed to introduce a channel for photo-excited electrons and holes, resulting in constant band gap energy independent of additive elements. However, incorporated additive elements should change an electronic state depending on their ionic valence and etc.. Additive elements with a higher valence than Cr(III) decrease defects of passive films, whereas additives with a lower valence than Cr increase the defects. As shown in Fig. 4(c), therefore, Mo(VI), Nb(VI) and W(VI) ions incorporated into the passive film decreased the donor densities and Al(III) and Ni(II) ions increased them. However Cu(I or II) and Co(II) decreased the donor densities in a small amount. Ti(IV) and Zr(IV) did not

change them. Influence of additive elements on the donor densities may depend on the amount of additives incorporated into the film. Therefore small amounts of Ni and Co decreased the donor densities. For Ti, Zr addition they were constant in the contrary.

4.2. Correlation between semiconductive properties and corrosion behavior

Potential gradient in passive film controls transportation of charged species including ions and electrons. Therefore electron energy band structure is related to corrosion behavior.

As mentioned above, the passive film on Fe-18Cr alloy formed in a borate buffer solution is composed of an inner oxide covered by a hydroxide layer. As previously reported, a passive film formed on Cr and Fe-Cr alloys in a sulfuric acid solution also has a similar duplex structure. However, there are differences in the electronic structure between these passive films. Oxide and hydroxide layer of the passive film formed in a borate buffer solution behave as *n*-type semiconductor layers and in most of passive potential region both layers are polarized to be a depleted state. Therefore the energy band slopes both in the inner oxide and outer hydroxide layer ascend towards the film/electrolyte interface as shown in Fig. 5(a) [14]. Under such energy states, both the outward migration of cations and inward migration of anions and electrons are possible. Consequently a passive film may continue to grow under high electric fields, which results in a more protective film. Localized corrosion, however, may be initiated by harmful anions, such as Cl⁻ and SO₄²⁻ that penetrate the passive film. Therefore passive films do not necessarily suppress corrosion.

On the other hand, a passive film on Cr and Fe-Cr alloys formed in a sulfuric acid solution consists of a *p*-type inner oxide layer, which is in the depleted state in the most of passive potential region, and a *n*-type (probably) outer hydroxide layer as presented in Fig. 5(b) [12]. Energy band slope in the inner oxide layer descends towards the surface. Therefore film growth is not promoted by the potential gradient. The outer hydroxide layer exhibits *n*-type semiconductor properties, but ion migration is difficult in the hydroxide layer because the electric field in the layer might be small, which is attributed to the fact that photocurrent generated in the layer was not significant [12].

As mentioned above, corrosion resistance of alloys are related to electronic structure, that is, the semiconductive properties of passive films. Figure 6 shows the relationship between pitting potential and donor density of passive films formed on Fe-18Cr. It is found from this figure that pitting potential increases with decreasing donor density of passive film. This result may suggest that donor site in the film acts as adsorbed site for harmful anions such as Cl⁻ and SO₄²⁻.

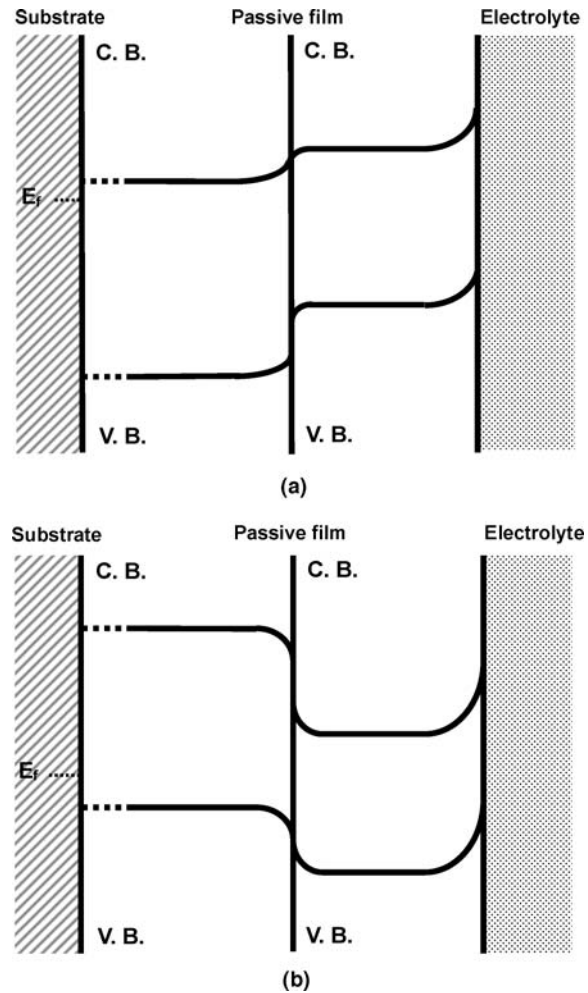


Fig. 5 Schematic illustrations of electronic band structure models of passive films on Fe-18Cr (a) in a borate buffer solution and (b) in a sulfuric acid solution

Adsorbed anions can penetrate through the film along potential gradient as presented in Fig. 5(a) and then cause localized corrosion such as pitting. This may be the reason that pitting potential increased with decreasing donor density of passive films.

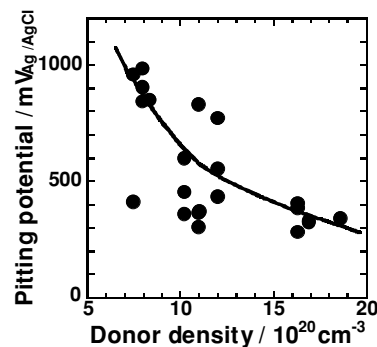


Fig. 6 Correlation between pitting potential and donor density of passive film on Fe-18Cr

It is found from the present work that electronic properties of oxide films on metals and alloys are one of important factors to characterize nature of materials. Photoelectrochemical response and electrochemical impedance spectroscopy provide information about the electronic properties of passive films. In the present work the influence of passivation time, applied potential and additive element is characterized using both techniques. Further investigation is expected to reveal the relationship between semiconductor parameters and corrosion behavior.

5. Conclusion

Semiconductive properties of passive films on Fe-18Cr were investigated using photoelectrochemical response and electrochemical impedance spectroscopy. Photoelectrochemical spectrum was separated into two components derived from Cr hydroxide ($E_g = 2.4$ eV) and Cr oxide ($E_g = 3.4$ eV). E_g s were almost constant independent of passivation time, applied potential and additive element. The photoelectrochemical response for each component showed a positive photocurrent which increased with increasing applied potential. This means that passive films on Fe-18Cr consist of isotype heterojunction of n -type semiconductors. Mott-Schottky plot exhibited a positive slope which suggests an n -type semiconductive behavior. Donor density of the passive film which can be estimated from the Mott-Schottky plot depended on passivation time, applied potential and additive element. Corrosion behavior and film growth were discussed in terms of electronic properties of the passive film.

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