



# Electrochemical analysis on the potential decay behavior of Fe-20Cr stainless steels in sulfuric acid solution

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## ABSTRACT

Potential decay behavior of Fe-20Cr alloy was examined by potential decay test, X-ray photoelectron spectroscopy, and Mott-Schottky analysis. The potential decay behaviors characterized by a short plateau followed by 1st decay and a long plateau followed by 2nd decay to an active state were closely associated with the duplex layer structure of passive film. We demonstrate that the short plateau followed by 1st decay is due to rapid dissolution of outer non protective Fe(III) enriched (Fe, Cr) oxide/Cr(III) hydroxide layer, whereas the long plateau followed by 2nd decay is attributed to slow dissolution of inner protective Cr(III) enriched (Fe, Cr) oxide layer.

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## 1. Introduction

Stainless steels (SSs) have been widely used as structural materials in various corrosive environments due to their excellent corrosion resistance [1]. The excellent corrosion resistance of SSs is originated from the protective nanoscale oxide layer, called passive film, formed on their surface [2,3]. However, a local breakdown of the passive film either by chemical attack of chloride ion or by mechanical means often causes a localized corrosion such as pitting corrosion. The localized corrosion of SSs have extensively been studied [4–7]. In contrast, dissolution of passive film on SSs by chemical attack of hydrogen ion in acidic environments, leading to general corrosion, has rarely been studied. The resistance to uniform dissolution of passive film or oxide layer by a chemical attack of hydrogen ion is very important in determining etching or pickling conditions of SSs [8,9].

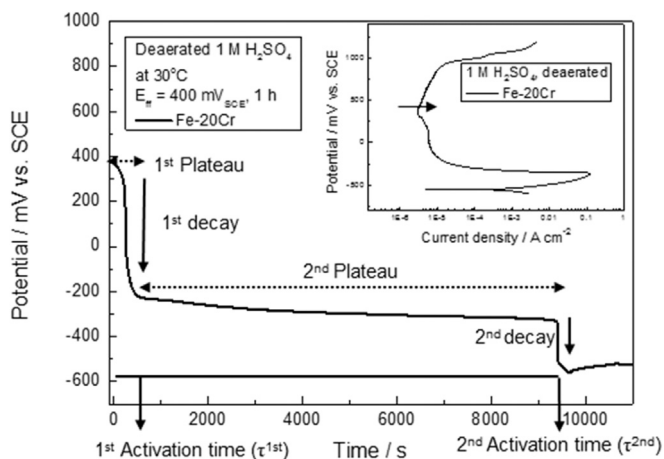
The potential decay test [10,11] or measuring corrosion potential transient of a passive metal when switched to open circuit from its passivation potential, has often been used to analyze the resistance to uniform dissolution of passive film formed on iron base alloys.

Flade [12] demonstrated that the potential decay behavior of pure iron passivated in concentrated HNO<sub>3</sub> was divided into 3 steps in an acidic solution: an abrupt decay of potential at the first step, then a gradual decay of potential for a few min at the second step, and a steep decay of potential to the corrosion potential of bare metal at the third step. After that, Lizov et al. [11] adopted the potential decay test to measure the resistance to uniform dissolution of passive film formed on SSs in an acidic solution, and pointed out that the resistance to uniform dissolution of passive film of the SSs increased with Mo content and also with passivation time. Seo et al. [13] demonstrated that the resistance to uniform dissolution of passive film formed on Fe-26Cr based ferritic SSs in an acidic solution was significantly enhanced by a small alloying addition of Nb, Ti and Mo. Oh et al. [14] measured the effects of Cu on the resistance to uniform dissolution of passive film formed on the Fe-20Cr-xCu (x = 0, 2, 4 wt%) by the potential decay test, and showed that the addition of Cu increased the resistance to uniform dissolution of passive film due to the enrichment of Cu in the passive film.

It was found from the previous studies [15–17] that SSs demonstrate a typical potential decay behavior with the two abrupt potential decay marked by the 1st decay and the 2nd decay, respectively, and the two potential plateau described by the 1st plateau and the 2nd plateau, as shown in Fig. 1. The 1st plateau is much shorter than the 2nd plateau called the 2nd activation time

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**Fig. 1.** Potential decay behavior of Fe-20Cr SS or the potential transient response measured when switched to open circuit potential from passivation at 400 mV<sub>SCE</sub> for 1 h in deaerated 1 M H<sub>2</sub>SO<sub>4</sub> solution at 30 °C. The potentiodynamic curve of Fe-20Cr SS measured in the same solution is presented in the inset.

( $\tau^{2nd}$ ), and hence the resistance to uniform dissolution of passive film has often been determined by the  $\tau^{2nd}$  that is dependent on type of alloying element, passivation potential, passivation time, pH and solution temperature, etc.

As mentioned above, the potential decay behaviors of SS have been studied on the influences of alloying elements such as Cu, Nb, Ti and Mo by a few researchers [11–14]. However, it has not yet been studied to solve the fundamental issues on the potential decay behaviors of SS such as why the 1st potential decay occurs and what happened in the composition and structure of passive film during the 2nd plateau ( $\tau^{2nd}$ ) period. The present work is to elucidate the reason why the 1st potential decay occurs after the 1st plateau and what happened in the chemical composition and defect structure of passive film during the 2nd plateau by electrochemical tests combined with analysis of passive film by X-ray photoelectron spectroscopy (XPS) and Mott-Schottky methods.

## 2. Experimental

Fe-20Cr SSs were prepared by vacuum arc melting, and then cast in the form of bar with diameter of 1 cm and length of 5 cm. The cast was homogenized for 120 min at 1200 °C, and then hot rolled into 3 mm thick plate. The hot rolled plate was cold rolled to sheet 1.5 mm thick, and then solution annealed for 20 min at 1050 °C followed by quenching in water. The chemical composition of the SS analyzed by XRF (X-ray fluorescence) is shown in Table 1.

The sheet specimen was mounted in an epoxy resin, grounded to 1500 grit SiC, polished to 3  $\mu$ m alumina paste, ultrasonically cleaned with ethanol, and then used as a working electrode for electrochemical tests such as potential decay tests and potentiodynamic tests. A conventional three electrode cell of 1 L five-neck flask was used for the electrochemical tests. The cell for the tests was equipped with the sheet specimen for working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The potential decay tests were conducted in a deaerated 1 M H<sub>2</sub>SO<sub>4</sub>, at 30 °C. The solution was deaerated by

purging with N<sub>2</sub> gas throughout the test.

The working electrode for the potential decay test was cathodically cleaned for 100 s at  $-1.0 V_{SCE}$  in order to remove an air-formed oxide on its surface, and then passivated for 1 h at 400 mV<sub>SCE</sub>. After the passivation, the change in open circuit corrosion potential was recorded with time throughout the test. The potential decay test was also conducted on the SS passivated for 1 h at 700 mV<sub>SCE</sub>, and passivated for 20 min, 3 h at 400 mV<sub>SCE</sub> in order to observe the effects of passivation potential and passivation time on the potential decay behavior of Fe-20Cr SS.

Depth concentration profile of alloying elements in the passive film was analyzed by XPS. The XPS depth concentration profiles of the passivated Fe-20Cr SS were measured using a K-alpha model (Thermo VG Scientific). For the XPS analysis, Fe-20Cr SSs were cathodically cleaned for 100 s at  $-1.0 V_{SCE}$ , and potentiostatically passivated for 1 h at 400 mV<sub>SCE</sub> in deaerated 1 M H<sub>2</sub>SO<sub>4</sub> solution. To investigate the change in the passive film during the 1st decay, XPS measurements were performed on the passive film before the 1st decay, and also on the passive film after the 1st decay, using Al K-alpha X-ray source (12 kV, 3 mA) with a pass energy of 80 eV.

Mott-Schottky type impedance tests were conducted to explore the change in electronic properties of passive film during the film dissolution process described by the 2nd plateau in Fig. 1. For the Mott-Schottky analysis, passive film was formed similarly as that for the XPS test. The capacitance of the passive film was measured by sweeping the applied potential at a scan rate of 25 mV/s from 400 mV<sub>SCE</sub> to  $-400 mV_{SCE}$ . The excitation voltage was 10 mV (peak-to-peak) at a frequency of 1 kHz [18].

## 3. Results and discussion

### 3.1. Potential decay behavior of Fe-20Cr SSs

Fig. 1 presents a typical potential decay of Fe-20Cr SS when switched to an open circuit from 1 h-passivation at 400 mV<sub>SCE</sub> in deaerated 1 M H<sub>2</sub>SO<sub>4</sub> solution at 30 °C. It is evident from the potentiodynamic curve shown in the inset of Fig. 1 that the formation of passive film at 400 mV<sub>SCE</sub> produces a very stable and protective film [14]. The potential decay curve of Fe-20Cr showed a short 1st plateau of 335 s at approximately 300 mV<sub>SCE</sub>, and rapidly decayed to a potential of approximately  $-230 mV_{SCE}$  (the 1st decay). After the 1st decay, the potential decay curve or the corrosion potential decreases very slowly to the value of  $-380 mV_{SCE}$  for 9430 s (the 2nd plateau) followed by the abrupt drop to  $-520 mV_{SCE}$  (the 2nd decay) that is corresponding to the corrosion potential to the value of  $-520 mV_{SCE}$  by the 2nd decay would cause the passive film on Fe-20Cr SS sample to be completely dissolved, and hence the SS sample is in an active state. Time to complete dissolution of passive film or the 2nd activation time exhibits the resistance of the passive film to dissolution [11,13,14]. However, the reason why the 1st decay occurred and what happened in the passive film before and after the 1st decay has not yet been investigated. Thus, we examined the change in the passive film during potential decay process by XPS depth concentration profile and Mott-Schottky analysis.

### 3.2. XPS depth concentration profile

The corrosion potential is a mixed potential at which both anodic reaction and cathodic reaction occur at an equal rate. Hence the corrosion potential would be sensitive to the chemical composition of surface oxide/hydroxide formed on SS on which the anodic and cathodic reaction would occur. The drastic change in corrosion potential in the 1st potential decay would be associated

**Table 1**  
Chemical compositions (wt.%) of Fe-20Cr alloy. Analyzed by XRF.

	Fe	Cr
Fe-20Cr	79.1	20.9

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