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# Effects of alloying elements, Cr, Mo and N on repassivation characteristics of stainless steels using the abrading electrode technique

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## Abstract

Cr, Mo and N are important alloying elements for passive film formation and repassivation but their roles in passive film still need explainable. In order to investigate effects of alloying elements on the stability of passive film and its repassivation, ferritic stainless steels such as Fe–Cr and Fe–Cr–Mo alloys and austenitic stainless steels such as type 316L, and type 316LN were examined. The electrochemical characteristics of the passive film were investigated by in situ dc and ac electrochemical methods. The resistance to localized corrosion is believed to have much to do with the repassivation of the passive film and its stability. The effects of alloying elements on the current transients were systematically examined by using the abrading electrode technique and electrochemical impedance spectroscopy (EIS). The experimental results were analyzed in order to elucidate the relationship between passive film stability, repassivation, and alloying elements.

*Keywords:* Repassivation; Passive film; Abrading electrode technique; Electrochemical impedance spectroscopy (EIS); Charge transfer resistance ($R_{ct}$)

## 1. Introduction

Stainless steels have excellent corrosion resistance, resulting from thin and protective passive films, which prevent metals from reacting with corrosive environments. The influence of alloying elements on corrosion resistance is related with the stability of the passive film and its repassivation kinetics. The breakdown of this film can occur by chemical or by mechanical attack in corrosive media resulting in the localized corrosion. Pits formed by film breakdown can be the potential initiation sites for various localized corrosion such as pitting, crevice corrosion and stress–corrosion cracking [1,2]. Thus, in order to prevent localized corrosion, it is important for stainless steels to have a stable passive film with rapid repassivation even in severe corrosive environments. It is believed that the stability of passive films and their repassivation kinetics are subject to the influence of metallurgy, applied repassivation potentials, pH and chloride ion concentration in aqueous solutions [3–9]. The present study is designed to explain the relationship between the passive film stability, repassivation kinetics and alloying elements, Cr, Mo and N. In order to understand the effect of alloying elements on the corrosion resistance to corrosion of various stainless steels, in situ dc and ac electrochemical techniques were carried out. The influence of alloying elements on repassivation was systematically investigated using the abrading electrode technique [8,9] and ac impedance spectroscopy. Furthermore, the effects of the chloride ion concentration and the applied potential were also investigated.

## 2. Experimental details

### 2.1. Materials and preparations

Fe–$x$Cr ($x = 0$, 13, 18, 25, 30, 40 and 100 wt.%) alloys and Fe–18Cr–$x$Mo ($x = 1$, 4, and 6 wt.%) alloys were prepared by melting in a vacuum arc melting furnace back-filled with argon, and subsequently remelting numerous times to ensure proper mixing. Austenitic stainless steels such as type 316L and type 316LN with the variation of N concentrations from 0 to 0.15 wt.% were prepared in the form of ingots by melting in vacuum induction melting furnace. After all samples were solution-treated at 1050–1270 °C to avoid segregation, they were hot-rolled by 50–83% reduction in thickness, annealed at 1050–1100 °C, followed by water quenching. Each specimen was wet-ground up to 2000 grit SiC paper followed by fine polishing with a suspension of 0.05 μm particles of alumina. The samples were degreased with ethyl alcohol and acetone

### 2.2. Electrochemical measurements

The 0.1N $H_2SO_4 + x$NaCl ($x = 0$, 0.1 and 0.6N) acidic solution (pH 1.6) were prepared with distilled water and reagent grade $H_2SO_4$ and NaCl. The solution was de-aerated with high purity Ar before testing and kept under Ar atmosphere

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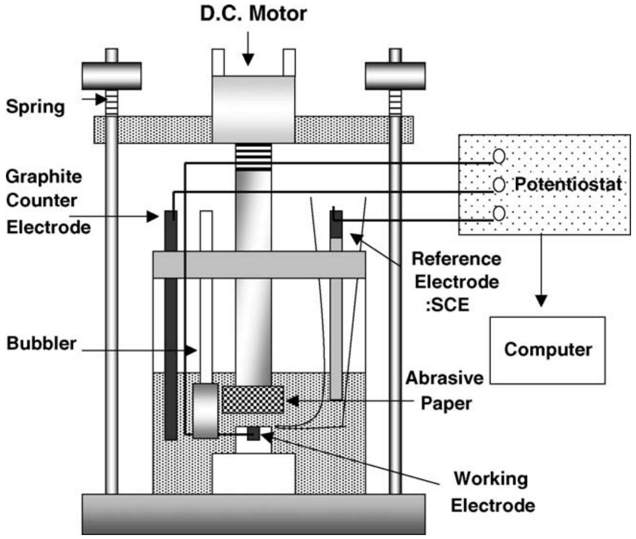

Fig. 1. Apparatus for abrading electrode used in the study of repassivation kinetics of free electrode surface.

during testing. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

Potentiodynamic polarization experiments were performed on specimens using a CMS 105B potentiostat controlled by a computer software (CMS 105). An abrading electrode technique was employed to obtain information on the repassivation kinetics of oxide films repassivated on the surface of specimens after exposure of the bare surface to the solution. The electrode was abraded with an SiC disc while immersed in the electrolyte to acquire current transients as shown in Fig. 1. The specimen was mounted in the center of a polyethylene resin (diameter = 1 cm) with a exposed area of $8 \times 10^{-2}$ cm$^2$ which was welded to a current collector of copper wire. The specimen surface was renewed by abrading with the SiC disc sintered from 1200 grit. The disc was fixed to the rotating shaft operated by dc motor. A saturated calomel electrode (SCE) was used as the reference electrode, located nearest to the working electrode. Finally a graphite was used as the counter electrode. During the abrading, the specimen was instantaneously raised by a mechanical spring. The resulting current transient was acquired at a constant applied potential from the moment just after interrupting the abrading action on the specimen.

In order to evaluate the electrochemical behavior of repassivated films, ac impedance spectroscopy measurements were performed by using a potentiostat and a lock-in amplifier (SR810) with an electrochemical impedance software (CMS300) under static conditions upon completion of the abrading tests. Measurements were taken by superimposing an ac voltage 10 mV amplitude on the measured rest potential of the abraded specimen with the frequency range from 0.01 Hz to 10 kHz.

## 3. Results and discussion

### 3.1. *Effect of Cr content on the passivity and the repassivation*

Stainless steels basically derive their passive characteristics from alloying with Cr. Alloying element, Cr is known to increase resistance to pitting by the increase of the pitting potential in the noble direction, reducing the passive current density. This is illustrated clearly by the data for a series of Fe–Cr–Ni alloys in a sulfuric acid solution [10], and for Fe–Cr alloys in a chloride solution [11], respectively. A.J. Sedriks summarized the effect of alloying elements in stainless steels on the anodic polarization curve [12]. According to his schematic summary, Cr increases the pitting potential, decreasing the passive current density and the critical anodic current density.

Fig. 2 shows potentiodynamic polarization curves for pure Fe, pure Cr, and Fe–*x*Cr (*x* = 13, 18, 25, 30, and 40 wt.%) alloys in aqueous 0.1N $H_2SO_4$ without and with $Cl^-$ ion. Fig. 2(a) shows results for anodic polarization curves for Fe–Cr alloys with varying Cr content in aqueous 0.1N $H_2SO_4$ without any $Cl^-$ ion, representing two kinds of passive potential regions which consisted of the primary low current density plateau and the secondary high current density plateau [13]. As Cr content increased, the primary passive current density decreased, exhibiting the secondary passive region disappeared. However, in the case of pure Fe, the high current density region was

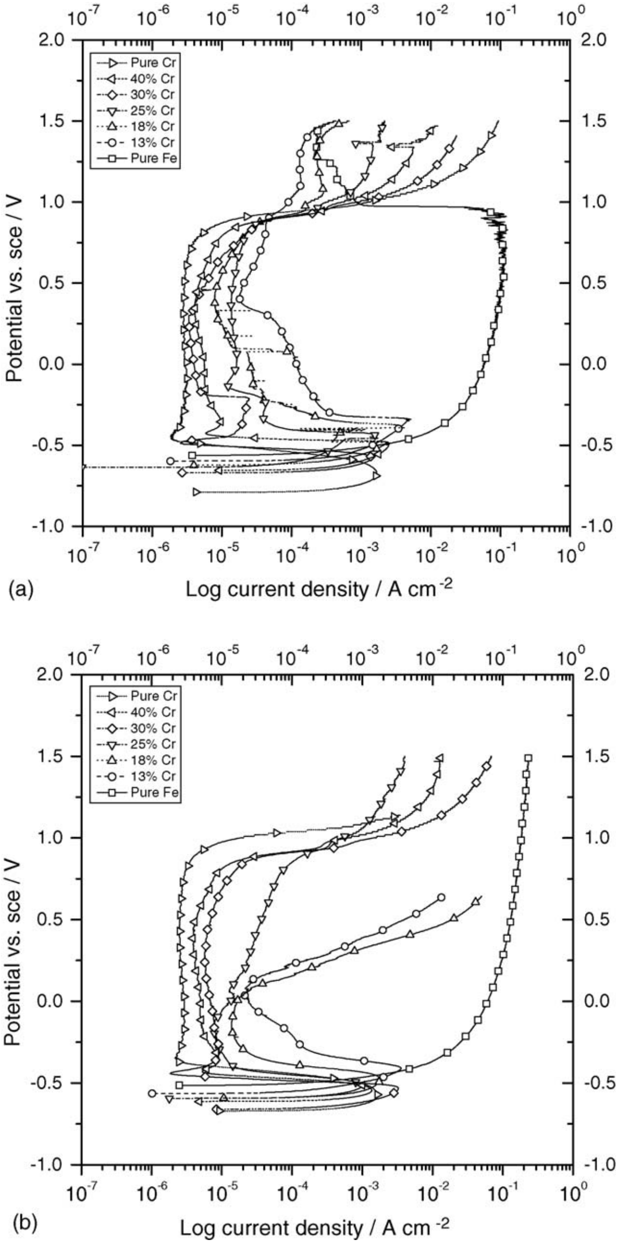

Fig. 2. Potentiodynamic polarization curves for Fe–Cr alloys in deaerated 0.1N $H_2SO_4$ without and with $Cl^-$ ion according to the variation of Cr content: (a) 0.1N $H_2SO_4$ and (b) 0.1N $H_2SO_4$ + 0.1N NaCl.