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Influence of grain refinement on the electrochemical behavior of AISI 430 ferritic stainless steel in an alkaline solution

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ABSTRACT

In this paper, the effect of grain refinement on the electrochemical behavior of AISI 430 ferritic stainless steel in 0.1 M NaOH solution was investigated. Potentiodynamic polarization curves showed that fine-grained samples have less corrosion potential, higher corrosion current density, and less protective passive film in comparison to coarse-grained samples. Electrochemical impedance spectroscopy (EIS) analysis revealed that implementing the thermomechanical operation led to lower polarization resistance. Also, Mott–Schottky analysis revealed that the passive films on both fine-grained and coarse-grained samples behave as n-type and p-type semiconductors and the semiconductor character of the passive films did not change by grain refinement. Moreover, it was found that the calculated donor and acceptor densities increased with grain refinement. Thus, the presented results indicated that grain refinement weakens the corrosion and passivation behavior of AISI 430 stainless steel in this alkaline solution.

1. Introduction

Grain refinement is an important issue in alloys, especially stainless steels, due to improvement of both strength and toughness [1,2]. A number of studies have been done for producing fine-grained steels with various techniques. The most important methods utilized to reduce grain size are severe plastic deformation, thermomechanical processes, and various surface modification techniques [3–7]. In the case of grain refinement in stainless steels, austenitic grades have been the subject of most recent investigations in the field of microstructural studies and mechanical properties. This special attention to austenitic grades is mainly due to their high susceptibility to be grain refined by reversion annealing of the strain-induced martensite (SIM) to austenite [8–14]. Furthermore, by reviewing the scientific literature, it can be seen that most investigations have been done in the field of corrosion of fine-grained austenitic stainless steels and there are fewer studies about corrosion behavior of bulk grain refined ferritic grades [15–22].

The effect of grain refinement on corrosion is still a controversial issue among researchers and both increases and decreases of corrosion resistance have been reported after reducing grain size. Di Schino and Kenny [23], in evaluating the general corrosion behavior of low nickel-high nitrogen austenitic stainless steels in the boiling 5 wt.% H_2SO_4 solution showed the increase of corrosion rate with decreasing the grain size. Wu et al. [24], in their investigation of electrochemical corrosion behavior of Fe–Ni–Cr steel in 0.05 mol/L H_2SO_4 solution containing 0.25 mol/L Na_2SO_4 showed that grain refinement causes enhancement of active dissolution and decrease of passive capability of the alloy. Jinlong and Hongyun [25] investigated the corrosion resistance of fine-grained AISI 304 stainless steel in a borate buffer solution with and without chloride at two different temperatures. Their results showed the improvement of corrosion resistance of fine-grained steel with respect to a coarse-grained one in all cases. Zheng et al. [26], in their studies on AISI 304 stainless steel in 0.5 M H_2SO_4 solution reported the improvement of corrosion resistance after grain refinement. Comprehensive review articles on electrochemical corrosion behavior of fine-grained alloys, particularly stainless steels, were presented by Gupta and Birbilis [27], Ralston and Birbilis [28], and Liu et al. [29].

Since literature assessment indicates that the electrochemical behavior of fine-grained ferritic stainless steel has been less studied (especially in alkaline solutions) [30], the main purpose of this work is to evaluate the effect of the grain refinement (through a thermomechanical route) on the corrosion resistance and semiconducting behavior of the passive films formed on AISI 430 stainless steel in 0.1 M NaOH solution.

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Table 1
Chemical composition of AISI 430 ferritic stainless steel.

	Cr	Ni	Mo	Mn	Si	C	P	Cu	N	Co	Fe
AISI 430/wt.%	16.50	0.13	0.02	0.53	0.50	0.05	0.025	0.07	0.06	0.02	Bal

2. Experimental procedures

2.1. Thermomechanical operation

The chemical composition of the AISI 430 ferritic stainless steel used in this experiment is shown in Table 1. The samples were prepared with length of 5 cm, width of 3 cm, and thickness of 0.5 cm. As it can be seen in Fig. 1, thermomechanical treatment includes four steps [30]: (1) a solution annealing at the temperature of 1200 °C for 3600 s and then water quenching, (2) a temper annealing at 770 °C for 7200 s followed by water quenching, (3) multi-pass cross cold rolling to about 95% thickness reduction with a two-high rolling mill under oil lubrication, and (4) recrystallization annealing at 800 °C for 120 s and quenching in water.

2.2. Scanning electron microscope (SEM) observations

A JEOL JSM-840A SEM was used to examine the microstructure of coarse-grained and fine-grained specimens. For this purpose, the specimens were polished and electro-etched in an etchant solution containing 60 ml HNO_3 + 40 ml distilled water. The electrolytic etch was carried out at the voltage of 2 V DC and the current density of 0.1 A cm^{-2} for 120 s [30].

2.3. Electrochemical measurements

All samples were polished to 2000 grit and cleaned by distilled water prior to each test. The electrochemical experiments were performed in a conventional three-electrode flat cell using an μAutolab Type III/FRA2 system controlled by a personal computer. A platinum wire, an Ag/AgCl electrode (in a saturated KCl solution), and ferritic stainless steel samples were used as the counter electrode, reference electrode, and working electrodes, respectively. All experiments were performed at room temperature in a 0.1 M NaOH solution prepared from analytical grade chemicals and distilled water.

Prior to each electrochemical test, the specimens were exposed to the 0.1 M NaOH solution for 1800 s until the steady corrosion potentials were obtained. The electrochemical measurements were performed in the following sequence:

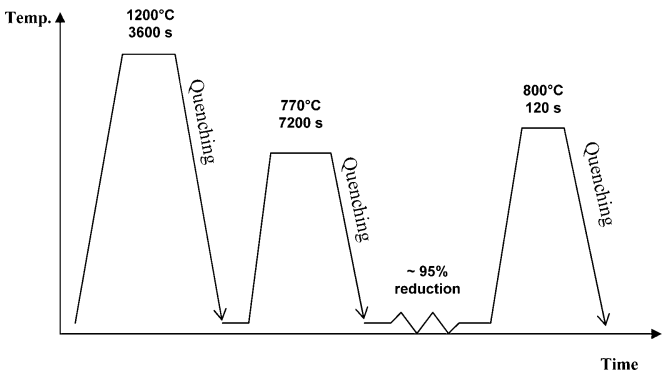

Fig. 1. Schematic illustration of the thermomechanical process for obtaining fine-grained AISI 430 ferritic stainless steel.

(a) Potentiodynamic polarization tests were measured with a scan rate of 1 mV s^{-1} starting from −0.25 V (vs. E_{corr}) and ending at 0.7 $V_{Ag/AgCl}$.
(b) EIS measurements were recorded over the frequency range of 100 kHz to 10 mHz with a 10 mV amplitude. NOVA impedance software was used for modeling the EIS data and curve-fitting method.
(c) Mott–Schottky analysis was performed on the passive films at a frequency of 1 kHz using a 10 mV ac signal and a step potential of 25 mV. After the electrode stabilization at open circuit potential (OCP), the potential was swept in the cathodic direction, from the initial potential of 0.6 $V_{Ag/AgCl}$ to the final potential of −0.6 $V_{Ag/AgCl}$.

3. Results and discussion

3.1. Microstructure observations

The microstructure of coarse-grained and fine-grained samples is shown in Fig. 2. It is obviously seen that the grain size of AISI 430 stainless steel is significantly reduced by thermomechanical operation.

As it is observed in Fig. 2a, the average grain size of coarse-grained samples is about 500 μm. After thermomechanical operation, the average size is about 5 μm (Fig. 2b). Indeed the applied thermomechanical operation reduced the grain size 100 times.

3.2. OCP measurements

OCP curves of fine-grained and coarse-grained specimens in 0.1 M NaOH solution are presented in Fig. 3. As it can be seen, both curves show similar trend of rising potential toward positive values during the test period. Such behavior can be attributed to the continuous formation of the passive film on the surface [31].

As it is observed, although the free potentials of both coarse-grained and fine-grained specimens are increasing over time to higher values, the free potential of fine-grained specimens has a less positive shift in comparison to coarse-grained ones. It can be said that the surface of coarse-grained specimens has a faster passivation tendency than fine-grained specimens in the same period of the exposure in the solution. In other words, a more protective and stable passive film is formed on the surface of coarse-grained specimens than fine-grained ones.

3.3. Potentiodynamic polarization measurements

Potentiodynamic polarization curves of coarse-grained and fine-grained samples in 0.1 M NaOH solution are depicted in Fig. 4. As it is seen, the same curve shape is obtained for both fine-grained samples and coarse-grained ones, but there are obvious differences between the two curves. In comparison with coarse-grained samples, the corrosion potential of fine-grained samples decreased, while their corrosion current density and passive current density increased. These results confirm that grain refinement did not improve corrosion parameters in alkaline solutions, which is the result of less protective passive film formed on the fine-grained specimens.

As it is seen in Fig. 4, the corrosion potential of coarse-grained samples is more positive rather than fine-grained ones which is in agreement with the OCP plots (Fig. 3). On the other hand, the corrosion potentials, which were obtained by the potentiodynamic polarization method, are to some extent different from those obtained by open-circuit potentials. These differences are interpreted based on to the partial reduction of metal ions in the passive film and the changes occurring in the chemical composition and