Applied Surface Science 317 (2014) 125–130

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The effects of cold rolling temperature on corrosion resistance of pure iron

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ARTICLE INFO

Article history:
Received 17 June 2014
Received in revised form 12 August 2014
Accepted 12 August 2014
Available online 19 August 2014

Keywords:
Grain size
Microstructure
Corrosion resistance
Cryogenic cold rolling

ABSTRACT

The effects of cold rolling temperature on grain size and grain orientation of pure iron were investigated. Comparing with sample rolled at room temperature, the grain refinement was facilitated in sample obtained by cryogenic cold rolling at liquid-nitrogen temperature. However, the grain orientation changed little for two samples. It was shown that cathodic hydrogen evolution reaction could govern the corrosion reaction for pure iron in sulfuric acid solution. The grain refinement obtained by rolling improved the corrosion resistance of iron in sulfuric acid solution, borate buffer solution and borate buffer solution with chloride ion. However, comparing with iron rolled at room temperature, the corrosion resistance of iron obtained by cryogenic temperature rolling was lower. Comparing with iron rolled at room temperature, higher dislocation density in iron rolled at cryogenic temperature reduced its corrosion resistance.

1. Introduction

Recently, some severe plastic deformation (SPD) techniques, including high-pressure torsion (HPT) [1], equal channel-angular pressing (ECAP) [2] or accumulative roll bonding (ARB) [3], etc., have received the greatest attention for grain refinement. However, cold rolling needs specimen with a larger dimension. It was possible that more refined grains could be obtained if the total deformation level was larger than 50% in rolling processes for bcc structure materials [4].

Nanocrystallization of a coarse-grained polycrystalline material provides a new approach to improve its corrosion resistance without changing chemical composition. While the enhanced dissolution rates of nanometer grain for conventional polycrystalline materials were attributed to the high volume fraction of grain boundaries and triple junction [5,6]. The improvement of corrosion resistance in nanometer grained pure iron was attributed to the increase of the surface energy [7]. The orientation of pure iron affected its corrosion resistance [8]. It was noticed that the binding energy (or surface energy) of atoms in the (1 1 0) plane was the minimum for bcc metals, in which the activity of atoms was inhibited [9]. The severe plastic deformation resulted in the texture structure <1 1 1> (1 1 0) (preferential crystalline orientation), which could enhance corrosion resistance of ingot iron [10].

This report in the present study demonstrated that the effect of cold rolling temperature on corrosion resistance of pure iron in different corrosion environments.

2. Experimental

2.1. Preparation and characterization of samples

The as-received iron (99.95%, wt.%) was in the form of a thick sheet with 12 mm in thickness. The samples were solution annealed at 750 °C and then quenched into room-temperature water. Some samples were rolled to 95.83% thickness reduction at room temperature and cryogenic temperature (cryogenic cold rolling was carried out after the sample was immersed in liquid-nitrogen for enough long time), respectively. The grain size and grain orientation of all the samples were analyzed by X-ray diffractometry (XRD). The measurements were carried out with the Rigaku Ultima IV X-ray diffractometer and the scanning rate was 4°/min. Cu K_α (0.154056 nm) radiation at 40 kV and 40 mA was used.

2.2. Electrochemical experiments

Electrochemical tests were performed in 0.5 M H_2SO_4, borate buffer solution (0.075 M $Na_2B_4O_7{\cdot}10H_2O$ + 0.05 M H_3BO_3, pH 9.2)

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http://dx.doi.org/10.1016/j.apsusc.2014.08.065
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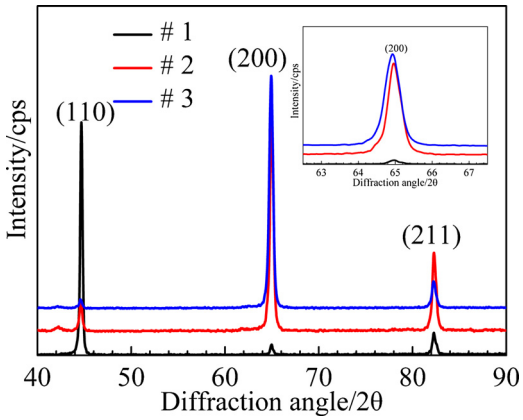

Fig. 1. The X-ray diffraction patterns of all the samples: (a) # 1: solid solution annealed (b) # 2: cold rolling at room temperature, (c) # 3: cryogenic rolling.

without and with 0.5 M NaCl at ambient temperature. The tested sample surface in experiment was the rolled surface. Electrochemical tests were performed with a CHI 660B electrochemical station (Chenhua instrument Co. Shanghai, China) controlled by a computer and software in three-electrode cell. The electrochemical cell was a classical three-electrode system. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was very high density graphite electrode. Working area of sample was 1 cm^2. The samples were mechanically polished with 3000 grit SiC paper, and then they were polished with 0.1 μm alumina polishing powder, degreased with alcohol, cleaned in water, and then dried in warm air. The electrochemical impedance spectroscopy (EIS) measurement was carried out at open circuit potential (OCP), and the amplitude of AC sine wave was 5 mV. The applied frequency ranged from 0.01 Hz to 100 kHz. The impedance data were analyzed by Zsimpwin software. Three tests were performed in each sample for reproducibility.

3. Results and discussion

3.1. XRD measurements

Fig. 1 represents XRD results for solid solution annealed and cold rolled iron. The XRD peaks of cold rolled samples are broadened, indicating a grain refinement. The full width of XRD peak in sample obtained by cryogenic cold rolling is larger than that in sample obtained by cold rolling at room temperature in the inset in Fig. 1, indicating the average grain size of the latter is bigger than that of the former. The severe plastic deformation results in preferential crystalline orientation (2 0 0) and significant decreased

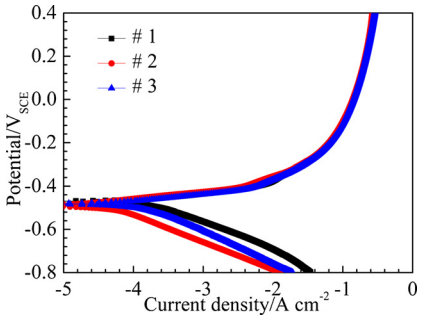

Fig. 2. Potentiodynamic polarization behavior of iron in 0.5 M H_2SO_4 solution. The scan speed was 0.00167 V/s, the same below.

orientation (1 1 0) with the highest atomic density. Moreover, textured structure difference between cold rolled samples is very small. Moreover, comparing with iron rolled at room temperature, the larger half width of XRD peak in iron rolled at cryogenic temperature also is attributable to its higher dislocation density.

3.2. Electrochemical measurements

The potentiodynamic polarization behaviors of different samples in 0.5 M H_2SO_4 are shown in Fig. 2. The values of anodic current are independent of sample, however, the behaviors of cathodic currents are different. Comparing to solid solution annealed sample, the grain refinement reduces cathodic currents. However, the cathodic current density in iron obtained by cold rolling at room temperature is slightly lower than that in iron obtained by cryogenic cold rolling. Fushimi et al. [11] found that cathodic hydrogen evolution reaction (HER) equations (1) and (2) governed the corrosion reaction on the iron in sulphuric acid, and covalent bonding of Fe and H played important roles in the HER and anisotropic corrosion behaviors of pure iron.

$$M + H_3O^+ + e = MH_{ads} + H_2O \quad (1)$$

$$MH_{ads} + H_3O^+ + e \rightarrow M + H_2O + H_2 \quad (2)$$

The result in Fig. 2 indicates that the corrosion performance on the iron is mainly governed by the cathodic reaction.

The EIS test was carried out to further investigate the electrochemical characteristics of all the samples. Nyquist plots for solid solution annealed and cold rolled iron in 0.5 M H_2SO_4 solution at the OCP for 1 h are shown in Fig. 3a. The Nyquist plots of all the samples have depressed capacitive semicircles and smaller inductance loop. The diameter of capacitive semicircle is associated with charge-transfer resistance, i.e. corrosion resistance, while inductance loop shows relaxation process of ions adsorbed on passive film on the surface of iron. An increase in the semicircle radius indicates

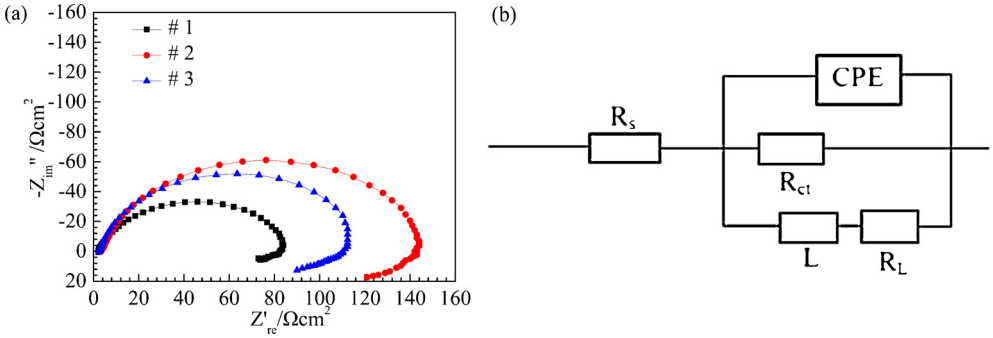

Fig. 3. (a) Nyquist plots for solid solution annealed and cold rolled iron in 0.5 M H_2SO_4 solution at the open circuit potential for 1 h, (b) the equivalent circuit of passive films for samples with capacitance loop and inductance characteristic, where R_S, the electrolyte resistance; CPE, the capacitance of passive layer; R_{ct}, the charge transfer resistance, R_L, the adsorption resistance of transition product; L, inductance.