Journal of Alloys and Compounds 711 (2017) 155–161

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Corrosion behavior of the oxide films modified with zincizing treatment on AISI 1020 steel

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ARTICLE INFO

Article history:
Received 6 December 2016
Received in revised form
23 March 2017
Accepted 28 March 2017
Available online 29 March 2017

Keywords:
Carbon steel
Zincizing treatment
Oxide films
Electrochemical polarization
SEM
Mott-Schottky response

ABSTRACT

Oxide films were formed on AISI 1020 steel in air at 260 °C with/without zincizing treatment. Corrosion behaviors of the oxide films were investigated by electrochemical potentiodynamic polarization, scanning electron microscope (SEM), photocurrent measurement and Mott-Schottky response analysis. Compared with that without zincizing treatment, the polarization curve of the oxide films with zincizing treatment showed a higher breakdown potential, lower corrosion current density and lower passive current density. Meanwhile, the SEM images suggested that the oxide films with zincizing treatment were more compact than that without zincizing treatment. Furthermore, the photoelectrochemical response results indicated that the composition of the oxide films with zincizing treatment was $ZnFe_2O_4$, FeOOH and ZnO while the composition of that without zincizing treatment was Fe_2O_3. By zincizing treatment, the photocurrent response value and the concentration of the carriers was decreased, the flat band potential of the oxide films was moved in the negative direction.

1. Introduction

Carbon steels are widely used for construction materials of coolant feeder pipes in the primary circuit of CANDU heavy water reactors. Carbon steel pipes make up about 27% of the surface area in the coolant loop system [1]. Corrosion of the carbon steel pipes has become major problems for the operational efficiency and safety in nuclear generating stations [2,3]. Chemical control of the coolants is the key measure during operation, which involves mainly operating under alkaline conditions and mitigating the radiolytic production of oxidizing species. The alkalinity is controlled through periodic additions of LiOH, and the reducing conditions are maintained by the regular addition of hydrogen gas [4].

On the other hand, it has been considered that the stability of the oxide film formed on carbon steel is important for its corrosion behavior [5,6]. Therefore, various methods to inhibit corrosion of feeder pipes have been proposed for improving the stability of the oxide film.

Zinc injection technique is used in lots of light water reactors (LWR) to reduce LWRs radiation fields and to reduce the degradation of coolant system materials. It is considered that Zn^{2+} can be incorporated into the oxide films formed on the structure materials of coolant loop of LWRs to replace radionuclides, such as Co-58, Co-60 and so on. It is also considered that zinc injection changes the composition and structure of the oxide films, and then retards the corrosion of nickel alloys and stainless steel [7–10].

The retarding effects and mechanism of zinc injection on the corrosion of stainless steels and nickel-based alloys are investigated by many researchers. Ziemniak et al. [9] indicated that zinc ion was injected into the coolant to reduce the degradation of coolant system materials. It was considered that the retarding effects of zinc injection on the corrosion of nickel alloys and stainless steel resulted from the formation of some spinel phases, such as $ZnCr_2O_4$, in the oxide films. Hanzawa et al. [10] pointed out that the effects of zinc injected into reactor water were not only decreasing the radioactivity accumulation, but also on the oxide deposition on the fuel surface. When injecting zinc into reactor water, zinc ferrite may be formed on the surface of the fuel and circuit materials as a portion of crud or deposits. And zinc ferrite played an important role on the stability of the oxide layers on the surface. The dissolution and precipitation mechanism of the corrosion products was also influenced by the formed zinc ferrite. Liu et al. [11] evaluated the oxide film structure and the inhibition mechanism with Zn injection by calculating the potential-pH diagrams, solubilities and

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http://dx.doi.org/10.1016/j.jallcom.2017.03.327
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crystallographic features of spinels. It was suggested that the spinel oxides $ZnCr_2O_4$ and $ZnFe_2O_4$ formed on oxide film with Zn injection were more stable in comparison with other possible spinels.

The feasibility of zinc injection technique in the primary loop of CANDU was also investigated by several researchers. Walker et al. investigated the effects of zinc addition on carbon steel under CANDU pressurized heavy water reactor conditions [12]. They found that the addition of 15 ppb zinc into the primary coolant of CANDU reduced the corrosion of carbon steel. Sawicki et al. confirmed that the zinc ferrite was formed in the oxide films on carbon steel in simulated CANDU reactor coolant containing 15–60 ppb soluble zinc [13], and that zinc ferrite is electrically nonconductive, reduced electronic and ionic mobility in the corrosion film.

In this paper we modified the oxide film on carbon steel by oxidizing the steel specimen, which was wetted with zinc sulfate solution, in air at 260 °C. The electrochemical polarization behaviors and semiconductor properties of the oxide films on carbon steel were investigated by electrochemical polarization, photocurrent analysis and Mott-Schottky techniques.

2. Experimental

2.1. Coupon preparation

The chemical compositions of AISI 1020 steel used in this work are listed as below (mass, %): 0.19 C, 0.28 Si, 0.52 Mn, 0.03 P, 0.03 S and balance Fe. Coupons (14 mm × 12 mm × 3 mm) were mechanically polished through 400, 600, 800, 1000, 1200, 1500 and 2000-grit silicon carbide metallurgical papers. In order to keep the $ZnSO_4$ solution from spreading over the whole surface, a line was curved along the mid perpendicular of the sample surface, thus the $ZnSO_4$ solution could only stayed on one side. The surface of the sample was divided into two areas, i.e., the left part and the right part. The left part was for the zincizing treatment experiment and the right part was for the non-zincizing baseline test. Then samples were rinsed with ultrapure water, then with ethanol and finally with ultrapure water again, dried with cold wind and kept in a dry box.

2.2. Zincizing treatment

The cleaned sample was put in a small crucible and then a few drops of 0.24 mol/L $ZnSO_4$ solution were added on the left part of the sample until most area of the left side was covered with $ZnSO_4$ solution. The right part was for the non-zincizing baseline test. The treated sample was then put in a muffle, kept for 40 min at 260 °C, and then cooled naturally.

2.3. Surface analysis

After oxidation in high temperature air, the samples were subjected to ex-situ analyses to characterize the morphologies of their oxide films by scanning electronic microscopy (SEM).

2.4. Electrochemical measurements

The electrochemical measurements were carried out in a standard three electrodes cell of 450 mL with a quartz window as a photon inlet. The sample was encapsulated by PTFE tape with 0.28 cm^2 area exposed, and then fixed to the cell with a specimen holder, thus used as working electrode. A saturated Hg/Hg_2SO_4 reference electrode was used as reference electrode and a platinum foil as counter electrode. The electrolyte was 0.15 mol/L boric acid and 0.0375 mol/L sodium borate buffered solution ($pH = 8.4$). Before test, high purified N_2 gas was bubbled for 60 min to ensure the dissolved O_2 concentration to a low level.

The electrochemical potentiodynamic polarization was performed by scanning the polarization potential from −1.50 V to 1.00 V with the scan rate of 0.001 V/s. The electrolyte for the electrochemical potentiodynamic polarization was a buffer solution with different chloride contents. The chloride contents were chosen as 0, 0.001, 0.01 and 0.1 M, respectively. The capacitance measurements (Mott-Schottky plot) were carried out by stepping the polarization potential from 1.00 V to −1.00 V with a potential step of 0.01 V. The amplitude and the frequency of the sinusoidal perturbing signal were 0.01 V and 1 kHz, respectively.

The photocurrent was generated by focusing a monochromatic light via a quartz window onto the surface of the sample. The monochromatic light was obtained by a xenon lamp (350W, Crowntech), associated to a monochromator (1/8 m, CT110, Crowntech). The wavelength of the light was changed from 250 nm to 800 nm with a step of 10 nm. A bias of 0.60 V was applied on the specimens and the photocurrent measurement began when the current was below a certain value. The lock-in technique was applied to separate the photocurrent from the total current of the cell. The trigger signal of the light modulator was fed to the reference input of the lock-in amplifier and the current output of the potentiostat was connected to the signal input of the lock-in amplifier. The raw photocurrent was recorded by a home-made software as a function of the incident wavelength. A Si-photodiode connected to a digital ammeter positioned in the same place of the sample was used to record the light intensity in function of the incident wavelength. A mathematical transform from photocurrent in function of photon energy was applied to the photocurrent results.

3. Results

3.1. Potentiodynamic polarization

The specimens oxidized at 260 °C with/without zincizing treatment were tested in the buffer solution with different chloride contents of 0, 0.001, 0.01 and 0.1 M. The potentiodynamic polarization plots are shown in Fig. 1. It's evident that the transition region is affected from zincizing treatment. The corrosion current density (I_{corr}), the passive current density (I_p) and the breakdown potential (E_b) of each specimen are listed in Table 1. It can be seen that, compared with the specimens without zincizing treatment, the potentiodynamic polarization plots of the specimens with zincizing treatment showed a higher breakdown potential, lower corrosion current density and lower passive current density. These results indicate that zincizing treatment can obviously improve the corrosion resistance of the oxide films formed on AISI 1020 steel. These findings agree well with the other published results [14,15] that the corrosion rate of the samples generally decreases after alloying of the steel.

3.2. Morphology of the oxide film on carbon steel with zincizing treatment

Fig. 2 presents the SEM images of the oxide films of carbon steel after oxidizing at 260 °C with/without zincizing treatment. It was obvious from Fig. 2a that the oxide films formed on carbon steel without zincizing treatment were loose and porous. As for Fig. 2b, the surfaces of oxide films formed on carbon steel with zincizing treatment were densely covered by many fine particles. It was significantly more substantial than those formed without zincizing treatment.