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Corrosion Evolution of Low Alloy Steel in Deaerated Bicarbonate Solutions

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Corrosion evolution during immersion tests (up to 43 days) of NiCu steel in deaerated 0.1 mol/L bicarbonate solutions was investigated by electrochemical measurements, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Results show that NiCu steel transformed from the anodic dissolution in the early stage of immersion to a metastable passive state in the final stage as the open-circuit potential value shifted positively, which was aroused by the precipitation of corrosion products. This process was mainly promoted by the trace amount of oxygen. Simultaneously, dominant cathodic reaction transformed from the hydrogen evolution in early stage to reduction processes of corrosion products in later stages. Possible corrosion processes were discussed with the assistance of a corresponding Pourbaix diagram.

1. Introduction

Now and in the next decades, the management and disposal of nuclear high-level waste (HLW) is one of the largest and most costly challenges facing the world[1,2]. For isolating HLW from the biosphere for many tens of thousands of years, deep geological disposal relying on series of natural and engineered barriers is considered to be the most preferable option[3]. One important component of the engineered barriers is a metallic canister and its corrosion resistance in deep groundwater environments is a key to the effectiveness of the waste disposal[4-7]. The reason is that, once the waste package is settled, groundwater around would seep back into the host formation, albeit at a fairly slow pace, permeate through the backfill materials, arrive at the surface of the canister and then, there comes the dissolution of the canister and the following leak of radionuclides through the barriers[6,7]. While among all candidate canister materials, carbon steel is considered as a corrosion allowance material and has been adopted as the first choice in several countries because of its low cost, high strength and long industrial fabrication experience[8-12]. In this paper, carbon steel alloyed with 3.0% Ni and 0.3% Cu (mass%), also known as low alloy steel, is studied as the promising candidate canister material due to its better corrosion resistance where the amount of air-born salinity is much higher[13-16].

In oxic environments, carbon steel is usually covered by corrosion product films and the cathodic reaction is mainly dominated by reduction of oxygen:

$$\begin{aligned} &O_2+2H_2O+4e^- = 4OH^- \\ &E_e(\text{vs SCE}) = 1.47-0.0591\text{pH}+0.0147\lg p_{O_2} \end{aligned} \tag{1}$$

where E_e represents the equilibrium potential of Eq. (1) and p_{O_2} the partial pressure of O_2. Under these circumstances, the corrosion potential (E_{corr}) is always high, even for a bare metal[17]. However, for the actual redox condition in the repository, the situation becomes much more sophisticated. On the one hand, the deep groundwater environment will evolve from an initial aerobic phase to the final stable anaerobic condition (extremely low oxygen concentration actually) due to the continuous consumption of oxygen[8]. On the other hand, water radiolysis[18] or sustained permeation of groundwater (although in a very low pace) may also produce certain amounts of oxygen. These two competitive processes together will build a mildly oxidizing environment. The duration of this transition phase is assumed to be up to decades or even hundreds of years[8,18], which will directly decide the service stability and safety of the canister materials,

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i.e., the disposal. As a consequence, it is of great necessity and importance to study the corrosion patterns of canister materials in solutions with trace amounts of oxygen.

Bicarbonate solutions are selected as the test solution in this work since carbonate/bicarbonate ions are known as the dominant ions in deep groundwater environments and the corrosion behaviour of candidate canister materials in this kind of solutions are arousing intensive attentions[19-31]. Besides, the buffer capacity of bicarbonate solutions is also helpful in maintaining the solution pH value in the immersion test.

In the experiment, immersions (up to 43 days) were carried out to evaluate the evolution of E_{corr} in test solutions with different oxygen contents. The information of both dominant redox processes and corrosion patterns were provided by studying electrochemical results, X-ray diffraction (XRD) measurements and a corresponding Pourbaix diagram. The work here mainly focuses on the influence of trace amounts of oxygen and is a precursor of our other relevant studies.

2. Experimental

2.1. Materials and solutions

Low alloy steel containing Ni and Cu, with the chemical composition (in wt%) of 0.21 C, 0.21 Si, 0.58 Mn, 0.017 P, 0.0036 S, 3 Ni, 0.3 Cu and Fe (balance), was used. The samples, with dimension of 10 mm × 10 mm × 3 mm, were cut from the hot rolled ingot, which is a typical ferrite/pearlite steel as shown in Fig. 1. The samples were ground on SiC papers (grades 150-2000#) and polished with the diamond paste of 1.5 μm particle size. Thereafter, they were rinsed with deionized water, degreased with acetone and dried before test.

The electrolytes, 0.1 mol/L $NaHCO_3$ solutions (this concentration is measured to be the upper concentration limit[9,32]), were prepared with analytical grade reagents and deionized water. As a buffer solution, the pH can be maintained at around 8.33. The solutions prepared for the potentiodynamic polarization were deaerated by purging N_2 (99.999%) for 1 h prior to the test. While solutions for immersion tests can be categorized into three groups. No. 1 was exposed to air and the dissolved oxygen should be less than 9 ppm. No. 2 was deaerated by purging N_2 (99.999%) constantly for 1 h prior to and throughout tests, and hence the O_2 content in the electrolyte should be no more than 0.45 ppb according to Henry's law[36]. No. 3 was deaerated by purging N_2 (99.999%) for 1 h prior to the test and the electrolytic cell was properly sealed to maintain the oxygen being consumed. A sketch map of experimental apparatus is drawn in Fig. 2[11]. All experiments were performed at around 30 °C in a thermostatic water bath during the whole immersion test.

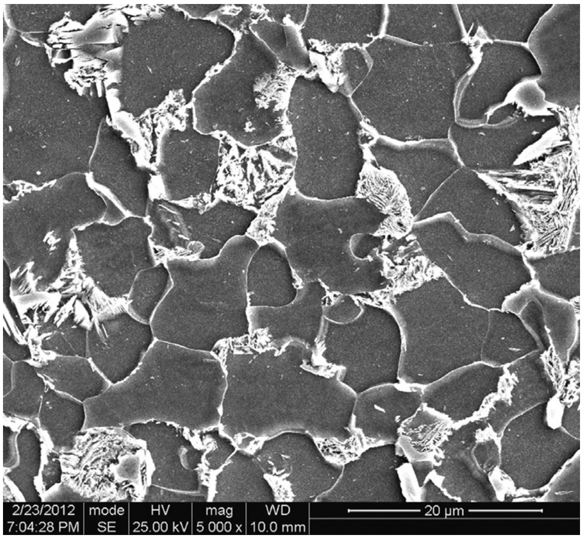

Fig. 1. SEM micrographs of the specimen.

2.2. Electrochemical measurements

The polarization measurement was carried out by using a classical three-electrode cell with platinum as the counter electrode (CE), saturated calomel electrode (SCE, +241 mV vs SHE) the reference electrode (RE), and steel sample with an exposed area of 1 cm^2 the working electrode (WE). After WE was immersed in the solution for about 30 min to earn a stable open-circuit potential, the polarization curve was obtained at a 10 mV min^{-1} constant scan rate, from −1.0 V to 0.4 V (SCE), with a PARSTAT 2273 electrochemical test system.

In order to follow the formation and growth mechanisms of corrosion products, immersion tests were performed on the three-electrode test system as mentioned above for up to 43 days, by using an HA-151A potentiostat to monitor the open-circuit E_{corr} change. When the electrodes were immersed in solutions, a low cathodic current density of 30 $\mu A/cm^2$ was applied on WE for oxides removal for 30 min, by using the HA-151A potentiostat.

During the test period, in situ electrochemical impedance spectroscopy (EIS) measurements were carried out once a week in solution No. 3 with a PARSTAT 2273 electrochemical test system. The applied alternating potential varied from ±5 mV around the open-circuit potential with a frequency ranging from 100 kHz to 10 mHz. The ZSimpWin software was used for fitting EIS data. All potential values reported were relative to SCE.

2.3. Surface analysis

After immersion, the samples in solution No. 3 were taken out, quickly dried with nitrogen gas flow and stored in grip seal bags filling with N_2 (99.999%). X-ray diffraction (XRD) was carried out on the rusted sample to determine the crystalline nature of corrosion products. The XRD measurements were performed by using a Rigaku-D/max 2500 PC diffractometer with a Cu$K\alpha$ target under 50 kV, 300 mA and 2θ ranging from 10° to 85° at a scanning speed of 0.02°/s. Thereafter, the rusted sample was immersed in a pickling solution (20 g $(CH_2)_6N_4$ + 500 mL HCl + 500 mL H_2O) to remove corrosion products and then scanning electron microscopy (SEM, Inspect™ F, produced by FEI Company) was used to observe its surface morphology.

Besides, SEM was also used to observe the cross-section morphology on immersed sample. The rusted sample was fixed by epoxy resin at room temperature, ground on SiC papers (grades 400–2000) and polished with the diamond paste of 1.5 μm particle size at slow speed.

3. Results and Discussion

3.1. Potentiodynamic polarization curve

Fig. 3 shows the potentiodynamic polarization curve of a bare NiCu low alloying steel substrate in N_2 (99.999%) purged solution. It can be seen that the corrosion potential is about −0.78 V. Either in the low anodic or cathodic polarization potential range (below −0.7 V), the logarithm of the current density can be explained approximately by a linear dependence to the electrode potential. They obey the Butler-Volmer equation and can be