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Effect of cumulative gamma irradiation on microstructure and corrosion behaviour of X65 low carbon steel

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ABSTRACT

X65 low carbon steel was exposed to Co-60 radiation source with 1.25 MeV gamma rays, and cumulatively absorbed gamma irradiation doses (1, 2, and 3 MGy) were obtained after different exposure time (333, 667, and 1000 h). The effect of cumulative gamma irradiation on microstructure and corrosion behaviour of the carbon steel in unirradiated aerobic Beishan groundwater at 25 °C was investigated by using positron annihilation, scanning vibrating electrode, and electrochemical techniques. Cumulative gamma irradiation increases vacancy intensity and decreases open circuit potential (OCP) of carbon steel. They indicate that the irradiated carbon steel is activated. Measured current density distribution above the irradiated carbon steel shows that cumulative gamma irradiation accelerates localized corrosion after 0.5 h of immersion. In contrast, the analysis of electrochemical impedance spectroscopy of the irradiated carbon steel indicates that localized corrosion is transformed into general corrosion after 12 h of immersion, which is also accelerated by cumulative gamma irradiation.

1. Introduction

Carbon steel has been selected as one of the candidate container materials in long term high level nuclear waste (HLW) disposal in China [1–3]. Researches in various disposal environments show that the corrosion rate of carbon steel is closely relevant to gamma irradiation [4–14]. In anaerobic allard and granitic groundwater, 0.01-1 kGy/h gamma irradiation accelerates the corrosion rate of carbon steel by 6–30 times [5–7]. In aerobic salt brine, 0.01-1 kGy/h gamma irradiation accelerates the corrosion rate of unalloyed fine-grained steel by 1.3-10 times [8–12]. In aerobic basalt groundwater, 3 kGy/h gamma irradiation accelerates the corrosion rate of iron-based alloy by 2–3 times [13], while 13 kGy/h gamma irradiation decelerates the corrosion rate of low carbon steel by 80 percent [14]. In general, gamma irradiation accelerates the corrosion rate of carbon steel or iron-based alloy at a dose rate of 3 kGy/h or lower, but decelerates the corrosion rate at higher dose rate such as 13 kGy/h.

Most work about the effect of gamma irradiation on metallic corrosion has been focused on the groundwater radiolysis [15–20] induced by irradiation, the interaction between gamma rays and passive film [4], and the inhibitory effect of gamma irradiation on microbially influenced corrosion (MIC) [21,22]. Daub et al. [15,16,18] indicated that gamma irradiation induced radiolysis of groundwater. The oxidizing and reducing products, such as H_2O_2, $^{\bullet}OH$, O_2, and $^{\bullet}O_2^-$, affected the corrosion rates of carbon steel by changing aqueous redox conditions of the groundwater. Shoesmith et al. [4] pointed out that the interaction between gamma irradiation and semiconducting passive film was possible to induce electro-photon effect, which was related to localized corrosion initiation or repassivation. Stroes-Gascoyne et al. [21,22] announced that 0.1-10 kGy/h gamma irradiation retarded MIC by sterilization. However, some uncertainties still exist in the mechanism by which gamma irradiation influences the corrosion reactivity of carbon steel matrix, in particular, the cumulative effect of gamma irradiation over more than 1000 years [23].

This work aims to study the effect of cumulative gamma irradiation on metal itself and subsequent corrosion behaviour in unirradiated aerobic Beishan groundwater. Firstly, X65 low carbon steel was exposed to 3 kGy/h gamma irradiation for different time

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Table 1
Composition of Beishan groundwater (mg/L).

Elements	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	pH
Contents	1696.0	60.6	281.7	211.6	141.5	1869.4	13.9	2836.5	8.35

to accumulate irradiation damage. Defect types and concentrations in the microstructure of irradiated carbon steel were detected by using positron annihilation lifetime spectroscopy (PALS) and Doppler broadening spectroscopy (DBS), and micro-hardness was investigated by using micro-Vickers' hardness (HV) tester. Secondly, the corrosion behaviour characterization of the cumulatively irradiated carbon steel was conducted in unirradiated aerobic Beishan groundwater. Open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) were examined by using Gamry Reference 600 potentiostat and the current density distribution above the irradiated carbon steel was observed by using scanning vibrating electrode technique (SVET).

2. Experimental

2.1. Materials

X65 low carbon steel controlled by thermos-mechanical control process (TMCP) was used in this study and its chemical composition (wt.%) was: 0.065% C, 0.14% Si, 1.58% Mn, 0.008% P, 0.0016S, 0.042% Al, 0.22% Cr, 0.01% Ni, 0.02% Cu, 0.05% V, 0.015% Ti, 0.063% Nb, 0.00025% Mo, 0.0002% B, 0.0025% Ca, and Fe bal. Beishan groundwater provided by one of the candidate repository in China was used as experimental medium in this study and its chemical composition was listed in Table 1.

2.2. Metallographic observation

Optical microscopy (OM) and transmission electron microscopy (TEM) were used to observe the metallography of X65 low carbon steel. The OM sample with a size of 10 mm × 10 mm × 1 mm was mechanically ground with silicon carbide paper up to 2000 grit, polished with diamond spray with a final 2.5 μm grading, and then etched by 4% nital. The TEM sample was prepared by ion milling. Scanning transmission electron microscopy (STEM) observation was performed by using a JEOL 2100 TEM/STEM instrument operating at 200 kV.

2.3. Gamma irradiation tests

Polished carbon steel plates with a size of 100 mm × 100 mm × 1 mm were irradiated by Co-60 source with 1.25 MeV gamma rays at 25 °C to simulate radionuclide decay in HLW. The thickness direction of the plates is was parallel to the propagation direction of gamma rays and 3 kGy/h absorbed dose rate was obtained. After 0, 336, 671, and 1007 h irradiation, 0, 1, 2, and 3 MGy cumulative irradiation doses were obtained in the steel plates. The following measurements used to characterize corrosion behaviour of irradiated carbon steel samples were conducted in unirradiated solutions, and the characterizations of microstructure and mechanical properties would be also conducted in a condition prevented from gamma irradiation.

2.4. Positron annihilation analysis

The type and density of defects in irradiated carbon steel were detected by PALS and DBS at 25 °C, and a ^{22}Na positron source with the radioactivity of ~13 μCi was used. The time resolution of PALS was about 195 ps (FWHM) in a conventional slow–fast coincidence system, and the total coincidence events were cumulated to over 1.5×10^6 for each spectrum. The energy resolution of DBS was 1.3 keV at 511.0 keV by using a single HPGe detector, and the total counts were cumulated to over 2.0×10^6 for each spectrum.

2.5. SVET measurements

SVET measurements were conducted on the surface of galvanic carbon steel couples composed of samples with different cumulative irradiation doses of 0&1 MGy, 1&2 MGy, and 2&3 MGy respectively. Each sample in the couples is 1.5 mm × 3 mm × 10 mm. All the measurements were conducted in unirradiated aerobic Beishan groundwater open to air at 25 °C after 0.5 h immersion. At first, the samples were mounted in insulating epoxy resin with an exposed surface of 3 mm × 3 mm, and then the surfaces were mechanically ground with silicon carbide paper up to 2000 grits, polished by diamond spray with a final 2.5 μm size, rinsed with ethanol and then dried in cold air. A Pt-Ir micro-electrode was used as vibrating electrode with an isolated platinum black electrode deposited on the tip (diameter 20 μm). The probe vibrated perpendicularly to the surface of the sample with the vibrating frequency of 330 Hz. The current density was mapped over a 40 × 40 grid generating 1600 data and the acquiring time of each data was 1 s. The probe was positioned 100 μm above the sample surface with a scanning area of approximately 9 mm^2. Prior to each SVET measurement, the resistance of the testing solution was measured by a conductivity meter as 1 Ω m, which was inputted into the software to calculate the current density. The pH values were monitored before and after each SVET test.

2.6. OCP and EIS measurements

OCP and EIS measurements of the irradiated carbon steel were conducted in unirradiated aerobic Beishan groundwater open to air by using a three-electrode electrochemical cell. The cell contained an X65 low carbon steel working electrode, a glass capillary probe connected to a saturated calomel reference electrode (SCE), and a Pt counter electrode. To prepare working electrode, carbon steel sample was sealed with epoxy resin to expose an area of 10 mm × 10 mm. The exposed surface was mechanically ground and polished as mentioned above. OCP of samples with 0, 1, 2, and 3 MGy cumulative gamma irradiation was continuously measured for 12 h at 25 °C. All the potentials in this paper are given vs. SCE as relative potentials. After 12 h of immersion, EIS measurements were taken with an amplitude of ±10 mV around the corrosion potential over the frequency range from 2.5×10^4 Hz to 3×10^{-2} Hz. Each OCP and EIS measurement was repeated at least three times to get average value with error bars.

3. Results

3.1. Metallographic structure

Fig. 1a shows metallographic structure of X65 low carbon steel, a mixture of ferrite and pearlite with a grain size of ~5 μm. Fig. 1b shows STEM bright field image observed at the interface of ferrite and pearlite. It is composed of polygonal ferrite, acicular ferrite, and pearlite.

3.2. Positron annihilation lifetime

Positron annihilation lifetime spectrum of irradiated carbon steel is analyzed as the sum of exponential decay components convoluted with Gaussian resolution function, $n(t) = \sum_i I_i e^{(-t/\tau i)}$. After subtracting source and background, the spectrum is decomposed into three components (τ_1, τ_2, and τ_3) with a variance of 1.0-1.1.

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