

Microstructure Evolution and Chemical Analysis on Carbon Steels and Fe-Cr-Mo Alloys after FAC Simulation Tests

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1. Introduction

Flow-accelerated corrosion (FAC) is an environment assisted degradation of structural materials, which usually occurs in pipelines of power plants [1]. In nuclear power plants, FAC usually breaks out in secondary pipelines where carbon steels are used as a structural material. Unlike to the general corrosion, flow of coolant induces severe concentration gradient at a structure/coolant interface thus mass transport of soluble species such as iron hydroxide is accelerated. There have been many studies to investigate the fundamental mechanism and corresponding countermeasures against FAC[2], and recently the carbon steels have been replaced by ASTM A 335 P22, which contains approximately 2.2 wt.% of Cr and 1 wt.% of Mo. By enhancing passivity of P22 by Cr, it is reported that FAC rate has been greatly reduced.

However, while corrosion behavior of Fe-based alloys is relatively well known, their behavior under high-temperature flowing water is not well investigated. In other words, effects of Cr and its corrosion and oxidation behavior is not clearly revealed. Furthermore, it is known that Mo enhances the pitting corrosion resistance of alloys however its mechanism is not clearly investigated [3-5]. Recently, replacement of Mo in alloy contents has been widely studied because of the cost of Mo. Thus, the purpose of this study is the investigation of the corrosion behavior of traditional carbon steels and Fe-Cr-Mo alloys under high-temperature flowing water by employing high resolution transmission electron microscopy(HRTEM) and synchrotron X-ray absorption spectroscopy(XAS).

2. Materials and Methods

2.1 Materials Preparation

SA516 Gr.60 and ASTM A335 P22 plates were cut into 20 x 20 x 5 mm³ sized samples and installed in the rotating cage. Prior to FAC-simulation experiments, samples were mechanically polished with #320, #400, #600, and #800 grit SiC papers, sequentially. Chemical composition of each alloys are enlisted in **Table I**.

Table I: Chemical composition of the alloys, SA516 Gr.60 and ASTM A335 P22

wt.%	C	Mn	P	S	Si	Cr	Mo
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A516	0.18	0.95	0.015	0.008	0.4	0.3	0.08
P22	0.05-0.15	0.30-0.60	0.025	0.025	0.20-0.50	1.90-2.60	0.87-1.13

2.2 FAC Simulation Experiments

Details of the FAC simulation instrument (Figure 1) is described in the authors' previous work [6]. To sum up, the samples were installed at the sample cage and co-axially fixed to the shaft of the magnedrive. For the 1 month of immersion, the RPM of the magnedrive was set to 1200 RPM equal to approximately 5 m/s as the diameter of the cage equaled 90 mm. As solution, 15 ppm ETA solution was prepared to simulate power plant water chemistries. The temperature was set to 150 °C for each test. After the FAC experiments the samples were ultrasonically cleaned in deionized water.

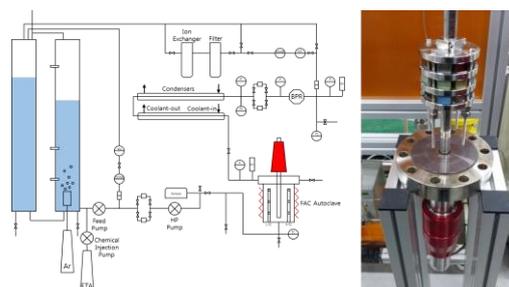


Figure 1. FAC simulation instrument and the installed samples

2.3 Microstructure and Chemical Analysis

Prior to the HRTEM (JEM-2100F, JEOL Ltd., Japan) and synchrotron XAS analysis, the samples were processed using focused ion beam in size of 6 μm * 6 μm. The diffraction patterns from HRTEM images were examined by GATAN Microscopy Suite® 3 (GATAN, Japan), and those results were compared to the JCPDS diffraction database. The XAS measurements were performed at 10A Scanning Transmission X-ray Microscopy beamline of Pohang Light Source at Pohang Accelerator Laboratory. For the XAS measurements, samples were installed in ultra-high vacuum chambers as shown in **Figure 2**.

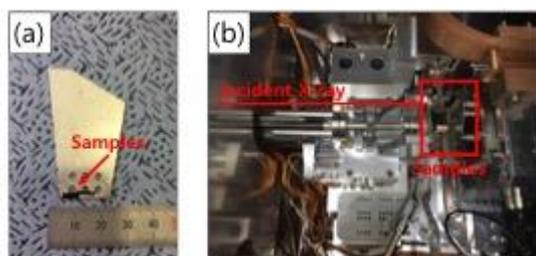


Figure 2. Installed samples and XAS measurement configurations

3. Results and Discussion

3.1 HR-TEM Analysis

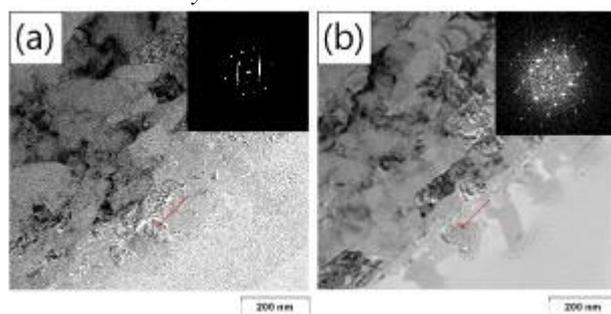


Figure 3. HRTEM images and electron diffraction patterns of the (a) SA 516 Gr.60 and (b) P22 after the 1 month of FAC simulation experiment

Figure 3 illustrated the HRTEM images and electron diffraction patterns of the carbon steel and the Fe-Cr-Mo alloys after the FAC simulation tests. At the topmost oxide layers, spinel formed and the diffraction patterns reveals that the both spinel is Fe_3O_4 .

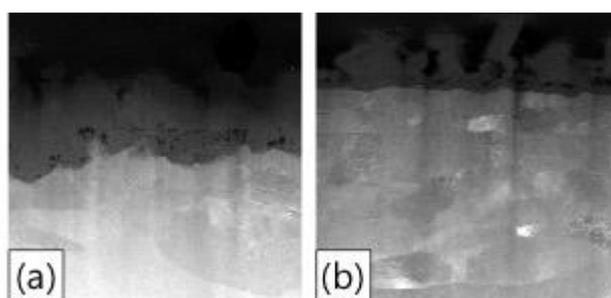


Figure 4. Oxide layer structures of (a) SA 516 Gr.60 and (b) P22 after the 1 month of FAC simulation experiment

Scanning tunneling electron microscopy (STEM) images clearly reveals the differences in morphology of the carbon steel and the Fe-Cr-Mo alloys as shown in **Figure 4**. While the carbon steel reveals porosity and exhibit relatively thick oxide, P22 reveals uniform and thin oxide layer with spinel. From the previous analysis, the spinel is found to be Fe_3O_4 for both alloys. That is, carbon steel undergoes severe FAC due to the formation of porous oxide, P22 might not undergo since it has relatively uniform and protective oxide.

3.3 XAS Analysis

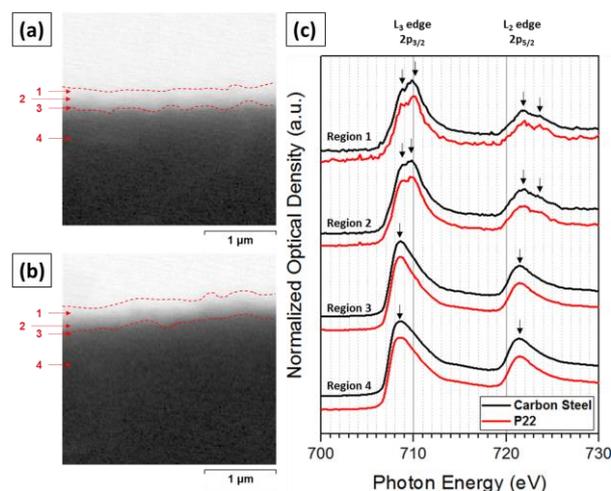


Figure 4. Fe L-edge scan (a, b) images and (c) spectra of (a) carbon steels and (b) P22.

Figure 4 displays the soft X-ray scanning images and Fe L-edge spectra. Region 1 – 4 indicates top oxide, bulk oxide, metal/oxide interface, and bulk metal, respectively. In region 1, both oxides reveals split peaks with e_g and t_{2g} . The intensity ratio of two peaks for the carbon steel is 0.892 while that of P22 is 0.905. This indicates that oxidation state of the top most oxide (i.e. spinel) is Fe^{3+} [7]. However, the intensity ratio at the region 2 is similar for two alloys (0.949 for carbon steels and 0.950 for P22). Therefore, it is expected that the chemical state of the spinel is differ for both but that of bulk oxide is in similar. Further investigation on Cr L-edge spectra will be carried out as future works.

3. Conclusions

Carbon steels undergo severe environmental-assisted degradation behavior so called FAC, and as its countermeasure the carbon steel has been replaced by P22 which contains Cr and Mo. It is generally known that Cr and Mo enhances passivity of Fe-based alloys however their corrosion and oxidation behavior has not been fully investigated especially in high-temperature flowing water environments. In this study, we employed HRTEM and synchrotron XAS techniques in order to investigate detailed microstructure evolution and chemical bonding of the commercialized carbon steel and the Fe-Cr-Mo alloys. From the analysis, it is found that while carbon steels exhibit porous oxide P22 exhibit oxide structures with thin Cr-rich oxide and spinel. Therefore, carbon steel undergoes severe FAC compared to P22 however effects of Cr and Mo and their behavior in high-temperature flowing water will be investigated.

ACKNOWLEDGEMENTS

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