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Development of a Mo-free Low Alloy Steel for Flow Accelerated Corrosion Resistance in Secondary Pipeline of PWRs

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1. Introduction

Flow accelerated corrosion (FAC) is one of the most severe corrosion phenomenon, which eventually leads to wall-thinning and eventually failure of pipeline and main components of secondary system of nuclear power plants. In the equilibrium between the mass transport and the formation of Fe_3O_4, FAC continuously occurs [1, 2].

To mitigate FAC, much solution has been suggested through the history of NPPs operation such as modification of water chemistry, however, due to compatibility with other components, the solution is still in debate [3]. Recently, many parts of the pipeline in secondary system have been substituted by a low alloy steel, so called A335 P22 (P22, hereafter) [4]. Chemical composition of P22 is 2.25Cr-1Mo with small amount of Si, Mn, and C. It is known that Cr and Mo is the most effective alloy element to resist FAC. A represent mechanistic model which defines the correlation between Cr and Mo contents and relative FAC rate is Decreux's model as shown in Equation 1 [5].

$$\text{FAC Rate} = 1/(83[Cr]^{0.89}[Cu]^{0.25}[Mo]^{0.2}) \quad (1)$$

According to the model, it is certain that Mo is able to be substituted by equivalent portion of Cr. Moreover, the total length of the pipeline in secondary system is over 100 km. Mo is the most expensive alloy element and generally known as to be effective against localized corrosion. Since FAC has been known as a type of general corrosion, here we propose a Mo-free low alloy steel. From the model, we calculated equivalent chemical composition of 2.25Cr-1Mo that equals 4.2Cr. Plus, to evaluate the effects of Cr and Mo contents on the relative FAC rate, we also manufactured 3.2Cr-0.5Mo low alloy steel. In summary, FAC behavior of commercial P22, and 3 model alloys (2.25Cr-1Mo, 3.2Cr-0.5Mo, and 4.2Cr) has been tested in a FAC simulation instrument. And, their performance was evaluated in both quantitative and qualitative methods.

2. Experimental

7.1. Preparation of the Alloys

The commercial alloys, A516 Gr.60 and P22, and three model alloys were prepared for FAC simulation experiments. For P22, a seamless pipe was purchased and manufactured in 20 * 20 * 3 mm^3 size.

The model alloys were manufactured by vacuum arc remelting method. In vacuum environments, feedstock materials (>99.9 % Fe, Cr, Mo, and C) were prepared, and plasma arc melted the feedstock materials. After furnace cooling, the manufactured ingots had a size of 100 mm in diameter and 15 mm in thickness. Then the ingots were hot rolled until the thickness reaches less than 3 mm and air cooled. The hot rolled ingots finally normalized and tempered in 970 ^oC for 30 min and 675 ^oC for 10 min, respectively. After the normalizing and the tempering, the ingots were air cooled. The chemical composition and the relative FAC rate is given in Table 1. The manufactured alloys cut in 25 * 20 * 3 mm^3 size.

Table 1. Chemical composition and Decreux's FAC rate of the manufactured alloys

	[Cr] (wt.%)	[Mo] (wt.%)	[C] (wt.%)	Decreux's FAC Rate (vs. P22)
A516 Gr.60[1]	0.3	0.08	0.18	7.567
P22[2]	2.25	1	0.1	1.000
Sample 1	2.25	1	0.1	1.000
Sample 2	3.2	0.5	0.1	0.840
Sample 3	4.2	0	0.1	1.045

[1] The other elements of the alloy are 0.4Si, 0.95Mn, 0.015P, 0.008S, 0.02Al, 0.3Cu, 0.3Ni, 0.01Nb, 0.03Ti, 0.02V
[2] The other elements of the alloy are 0.30Mn, 0.025P, 0.025S, 0.5Si

7.2. FAC Simulation Experiments

To experimentally demonstrate the performance of the alloys in simulated secondary water chemistry, a loop system and an autoclave system were prepared. The loop system is composed of a high-pressure pump, water chemistry sensors (dissolved oxygen (DO) concentration, in-let and out-let conductivity, and pH), and deionizer. In the autoclave system, a magne-drive rotating cage and a heater were installed. Installed samples were rotated in 5 m/sec velocity. The test condition is enlisted in Table 2. The photography of the instrument is displayed in Figure 1.

Table 2. Chemical composition and Decreux's FAC rate of the manufactured alloys

Temperature	150 °C
Pressure	8 MPa
DO Concentration	< 1 ppb (Ar purged)
pH (Control Agent)	9.3 (Monoethanol amine, ETA)
Rotating Speed	1500 RPM = 5 m/sec
Immersion Time	14 days

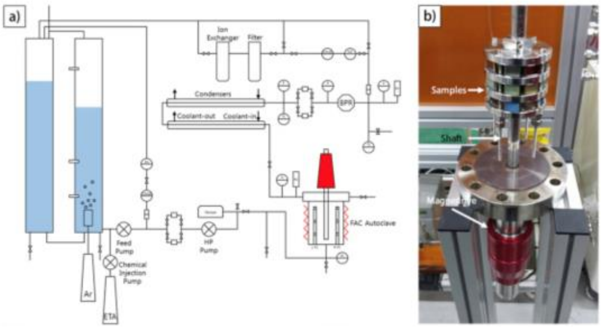

Figure 1. (a) Schematic of the loop and the autoclave system for FAC simulation tests. (b) The head of the autoclave system with the rotating cage and samples.

3. Results and Discussion

7.1. FAC Rate of the Alloys

After the tests, the immersed samples were sequentially cleaned in acetone, ethanol, and deionized water to remove non-adherent corrosion products from the surface and their weight was measured in a balance. The weight loss was divided by surface area and immersion time to calculate corrosion rate in mg/cm^2/yr as shown in Figure 2. Here, the new alloys follow Decreux's model but P22 shows different trend. This might be originated from the alloy elements effects such as Si rather than Cr or Mo. Thus further investigation on this trend will be carried out.

7.2. Microstructure

The surface morphologies of the samples are characterized by scanning electron microscopy (SEM) as shown in Figure 3. The morphology of P22, 2.25Cr-1Mo, 3.2Cr-0.5Mo, and 4.2Cr is sequentially given in (a), (b), (c), and (d). In Figure 3a, the surface of P22 is covered by oxide scales, which are estimated as iron oxides such as Fe_3O_4. Similar tendency is observable for 2.25Cr-1Mo, as shown in Figure 3b. However in case of 3.2Cr-0.5Mo and 4.2Cr in Figure 3c and 3d, small oxide scales are not observable. Since chemical analysis and cross section analysis have not been carried out, the early conjecture is that reducing Mo contents may make effects on surface morphology.

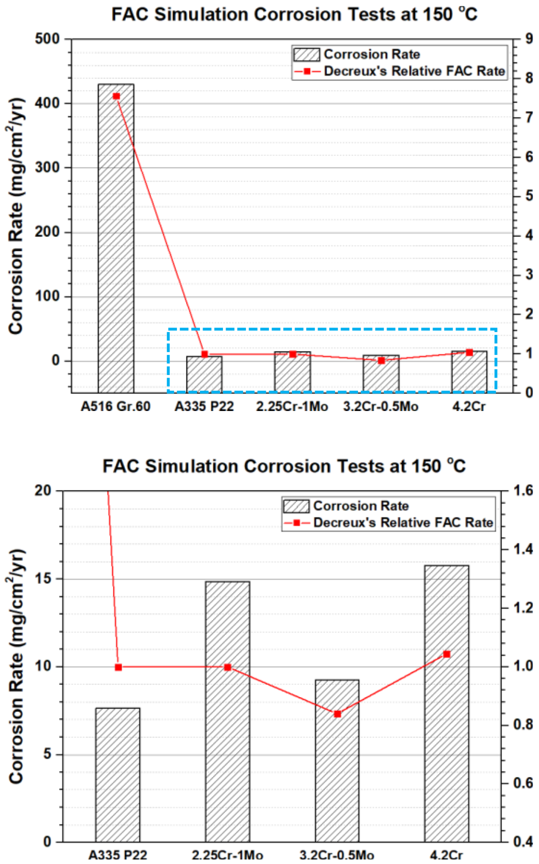

Figure 2. The corrosion rate of the alloys after the test. The corrosion rate is calculated from the weight loss of the samples. The red graph is relative FAC rate, calculated by Decreux's model in Equation 1.

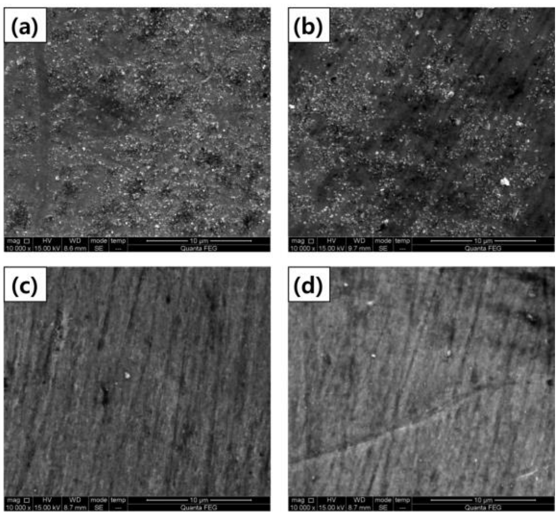

Figure 3. SEM images on the surface morphology of (a) P22, (b) 2.25Cr-1Mo, (c) 3.2Cr-0.5Mo, and (4) 4.2Cr

4. Conclusion

To develop a Mo-free low alloy steel for secondary pipeline application, vacuum arc remelting is employed. Three model alloys, with chemical composition 2.25Cr-1Mo, 3.2Cr-0.5Mo, and 4.2Cr. In simulated secondary water chemistry environments, FAC behavior of the commercial alloys and the model alloys is investigated. Even 2.25Cr-1Mo has same chemical composition in Cr and Mo, however, the corrosion rate of P22 is smaller than the model alloy. And, the corrosion rate of the model alloys follow Decreux's model. Thus, further investigation on cross section morphologies and chemical anylsis will be carried out by transmission electron microscopy (TEM).

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