Corrosion Characteristics of FeCrW Model Alloys at 360 °C Pressurized Water

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1. Introduction

Extensive research has been performed for designing the future nuclear reactors including generation IV reactor (Gen IV) and nuclear fusion power reactors. However, one technical challenge is developing structural materials under the harsh operation conditions. The operational environment for these reactors is expected to be far more challenging than that of conventional commercial light-water reactors (LWRs) such as higher operating temperature, substantially increased neutron irradiation damage level, and more corrosive coolant, which could accelerate material degradation.

For example, to address the demands of such conditions in fast reactor designs and fusion reactors, ferritic martensitic steel (FM steel) has emerged as a prominent candidate for future nuclear reactor structural materials [1]. These iron-based FM steels have BCC structure to mitigate irradiation-induced swelling and contain significant amount of chromium (Cr) concentrations, providing corrosion resistance in the high operating temperatures. Nonetheless, due to the impact of irradiation on mechanical properties, the Cr content is strictly limited to a range of 9 to 12 wt.% [2]. Previous studies have indicated that these controlled Cr contents could potentially sustain prolonged operation under pressurized water reactor (PWR) conditions [3]. Hence, it is reasonable to employ these materials as structural components for forthcoming nuclear reactors [4].

In this study, as an extension of our preceding study [5], we have investigated the short-term corrosion characteristics of FeCrW model alloys in a temperature of $360 \,^{\circ}$ C static water and a dissolved oxygen level of low oxygen and 1 ppm. The W was added as the variable of the alloying component to check the influence on corrosion properties, since it has been mostly investigated with effect on mechanical properties. The results from this research, coupled with the results from preceding studies, have led us to identify the most influential factor impacting corrosion properties. Finally, based on the corrosion behavior related to the effect of dissolved oxygen concentrations, we have proposed some ideas for water chemistry control strategy.

2. Experimental Methods

The chemical compositions of the three alloys Fe12Cr1W, Fe9Cr1W, and Fe9Cr employed in this investigation are provided in Table 1. To prevent chromium volatilization during sample fabrication process, the alloys underwent a two-step melting process. Initially, they were arc melted, followed by remelting within a vacuum induction melting furnace. Subsequently, a comprehensive thermomechanical heat treatment regimen, involving hot rolling, normalization, and tempering, was administered. The detailed procedures for sample preparation can be found in our previous work [5].

Table 1: Chemical composition of the alloy (Wt.%)

	Fe	Cr	W
Fe12Cr1W	Bal.	11.4	1.04
Fe9Cr1W	Bal.	9.2	1.07
Fe9Cr	Bal.	8.8	-

The aqueous corrosion test was conducted in the static autoclave, maintaining a temperature of 360 °C with saturated pressure, while the dissolved oxygen concentration in the testing environment was controlled to achieve low dissolved oxygen condition and 1 ppm. The corrosion tests spanned durations ranging from 50 to 300 hours. After each specified time interval, the specimens' weight was meticulously gauged using a precise balance to measure weight change. The corroded samples were then examined with Scanning Electron Microscopy in conjunction with Energy Dispersive Xray Spectroscopy (SEM-EDS) and X-ray Diffraction (XRD) to analyze surface morphology and the identification of oxide phase formations. Additionally, cross-sectional SEM imaging was utilized to evaluate the growth of oxide layers on the corroded surfaces.

3. Results and discussion

3.1 Weight change measurement

Figure 1 shows the weight change measurement results of the test specimens after corrosion test up to 300 hours. During the short-term corrosion test, all samples have gained weight but neither one of the alloys showed dependency of Cr, W concentrations. However, it seems that the dissolved oxygen level has an impact on the corrosion rate. Specimens exposed to lower oxygen levels exhibited a higher weight gain in comparison to those subjected to the 1 ppm dissolved oxygen condition.

By comparing the weight change rate with F82H which tested in 300 °C high purity water with dissolved oxygen level of 20 ppb and 1 ppm [3], overall weight change rate was higher for samples tested in this study. It seems it is attributed to higher test temperature but since the alloying component is not in exact same condition, caution with the application of the results is needed.



Fig.1. Weight change measurement results after corrosion test time up to 300 hours [5].

3.2 Surface oxides analysis

The surface oxides were analyzed with SEM to observe oxide morphology and the phase of the oxides were identified using XRD.

3.2.1 Surface SEM analysis

Figure 2 is the SE image of the surface oxides of 300 hours test specimens. The blocky oxides were found in all samples regardless of alloying components or dissolved oxygen level of the test condition. However, oxides from low dissolved oxygen samples showed relatively larger oxide blocks than 1 ppm samples, and some shape change was found in 1 ppm samples after 300 hours of corrosion.



Fig.2. SEM image of surface oxides of FeCrW model alloys after 300 hours corrosion test.

3.2.2 Surface XRD analysis

Figure 3 and 4 shows the XRD results of 150 and 300 hours test samples tested in low dissolved oxygen level and dissolved oxygen level of 1 ppm respectively. The main oxide was found to be Fe₃O₄ and FeCr₂O₄. Until 150 hours of corrosion, there was no significant difference of oxide phase formed on the specimen. However, after 300 hours, the new oxide Fe₂O₃ was found, which means phase change to Fe₂O₃ started after 150 hours of corrosion in 1 ppm condition. This phase change appears to be triggered by an increase in corrosion potential brought on by an increase on dissolved oxygen level.



Fig.3. XRD results after 150 and 300 hours of corrosion test at low DO [5].



Fig.4. XRD results after 150 and 300 hours of corrosion test at DO level of 1ppm [5].

The Fe_2O_3/Fe_3O_4 ratio was calculated with the XRD intensity value and listed in table 2. It appears that transformation of oxide phase from magnetite to hematite affects from Cr and W contents in the alloy.

Table 2: $Fe_2O_3(H)/Fe_3O_4(M)$ ratio from 1 ppm 300 hours specimens XRD results.

	Fe12Cr1W	Fe9Cr1W	Fe9Cr
H/M Ratio	2.18	1.96	1.35

3.3 Oxide cross-sectional analysis



Fig.5. Cross-sectional EDS element map (Fe, Cr, O, W) of FeCrW model alloys test time up to 300 hours.

Figure 5 presents the cross-sectional SEM Energy Dispersive X-ray Spectroscopy (EDS) image subsequent to a 300-hour corrosion test. The observed oxide structures exhibited a double-layered composition, characterized by an inner layer predominantly composed of chromium-rich oxide, and an outer layer primarily comprised of iron oxide. Findings from XRD analysis confirmed the inner layer's identity as $FeCr_2O_4$ oxide, while the outer layer was identified as either Fe_3O_4 or Fe_2O_3 . The growth of oxide thickness displayed a direct correlation with the duration of the test; however, the correlation of chromium or tungsten concentrations to oxide growth were not discernibly evident and still being investigated.

4. Conclusion

The influences of alloying components, temperature, and dissolved oxygen levels on aqueous corrosion properties of FM steel were investigated. Elevating the temperature of the test environment correspondingly increased the overall corrosion rate. However, distinct correlations between alloying concentrations and corrosion rates were not conclusively established within the scope of this study.

The presence of dissolved oxygen in the water exhibited a tendency to elevate the corrosion potential,

triggering a phase transition in Fe oxide from Fe₃O₄ to Fe₂O₃. Notably, this phase transition appeared to be influenced by the Cr and W contents. As the concentrations of Cr and W increased, the relative proportion of hematite (Fe_2O_3) to magnetite (Fe_3O_4) also rose. Additionally, Fe₂O₃ oxide was exclusively identified in specimens subjected to 300-hour tests, suggesting that the shift in oxide phases likely initiated between the 150-hour and 300-hour marks. Future endeavors should focus on comprehensively investigating this phase transition delay with considering its kinetic aspects.

The findings may introduce the potential for manipulating oxide phase through precise control of the water chemistry in the aqueous environment. The subsequent phase's impact on material integrity performance demands further clarification. Importantly, gradual phase transition necessitates the application of pre-oxidation processes into water chemistry strategies.

In conclusion, this study paves the way for understanding the interplay between various factors and the corrosion behavior of FeCrW model alloy. Overall, the corrosion properties appear to be more significantly influenced by environmental components than by alloying components. Therefore, by optimizing water chemistry, oxide phase transitions can be managed, opening avenues to explore how these transitions influence material performance. Also, the consideration of the kinetics of phase changes will be pivotal to the establishment of the water chemistry strategies.

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