PROPERTIES OF THE OXIDE FILMS ON Ni-Cr-xFe ALLOYS IN SIMULATED PWR WATER ENVIRONMENT

Xiangkun Ru1, Zhanpeng Lu1,2*, Junjie Chen1, Guangdong Han1, Jinlong Zhang1, Bangxin Zhou1,2
1 Institute of Materials Science, School of Materials Science and Engineering, Shanghai University, Shanghai 200072, P.R. China
2 State Key Laboratory of Advanced Special Steels, Shanghai University, Shanghai 200072, P.R. China
*zplu@shu.edu.cn

ABSTRACT

The oxide films formed on Ni-Cr-xFe alloys in simulated PWR primary water environments simulating normal operating conditions and abnormal conditions were characterized by scanning electron microscope, focused ion beam, transmission electron microscope, X-ray diffraction and laser Raman spectroscopy. Iron in Ni-base alloys has a strong effect on the surface morphologies of the oxides formed in the oxygenated PWR primary water, which does not significantly affect the surface morphologies of the oxides formed in the hydrogenated PWR primary water. Ni was concentrated in the oxide films formed in the oxygenated PWR primary water, but depleted in the oxide films formed in the hydrogenated PWR primary water. Cr-depletion was significant in the oxide films formed on Ni-base alloys in the oxygenated PWR primary water, which was not significant in the oxide film formed in the hydrogenated PWR primary water. Increasing the Fe content in the alloy, more and more needle-like oxides appeared in the outer layer of oxide films formed in the oxygenated PWR primary water. The needle-like oxides consisted of a lot of nano-sized iron oxides. The inner layer of oxide films formed in the oxygenated PWR primary water mainly consisted of cellular oxides. The center of cellular oxides was Ni rich whereas Cr was concentrated at the boundaries.

Keywords: Nickel alloys, Ni-Cr-xFe alloys, oxide films, simulated PWR water environment, dissolved oxygen, dissolved hydrogen, effect of Fe element.

1. INTRODUCTION

Nickel base alloys have been widely used in Pressurized Water Reactor (PWR) nuclear power plants.[1] The thermal stability[2-4], corrosion resistance in high temperature water[5-8] and environmentally assisted cracking[9,10] of nickel base alloys have been the concerns for the long-term performance of PWRs. The compositions of materials played important roles in these properties. The oxidation behaviour of nickel base alloys has been one of the hot topics for their service performance. There have been many studies related to the effects of water chemistry parameters such as dissolved oxygen (DO) [6], dissolved hydrogen (DH) [11, 12], temperature [13, 14], pH [15, 16], Zn injection [17, 18], and Li concentration [19] on oxidation behaviour in PWR primary water. The compositions of materials played important roles in oxidation behaviour. The compositions of the surfaces of alloys exposed to water environment may change during the long-term performance [20]. It is necessary to investigate the influence of the contents of alloying elements in nickel base alloys on the oxide films formed in simulated PWR water environments. The present work investigated the morphologies, phase compositions and chemical compositions of the oxide films formed on Ni-Cr-xFe alloys (x=1, 3 and 10 at%) in 310 simulated PWR water under different DO and DH conditions using scanning electron microscopy (SEM), focused ion beam (FIB) transmission electron microscopy (TEM), X-ray diffraction (XRD) and laser Raman spectroscopy (LRS).
2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The nominal contents of Ni, Cr and Fe of nickel-base alloys used in the present experiment were shown in Table 1. The binary stoichiometric Ni₂Cr and Ni₃Cr alloys and the ternary Ni₂Cr-1at.% Fe and Ni₂Cr-3at.% Fe alloys were prepared in an arc melting furnace in an argon atmosphere using a non-consumable tungsten electrode and a water cooled hearth. All ingots were forged and rolled at 1200°C, followed by a solution treatment at 1100°C for 20 min and water quenching. The final heat treatment for TT690 alloy was 715 °C for 10 h. All samples were processed into 8×5×3 mm³ plates with an electric-spark line-cutting equipment. The surfaces of samples were mechanically polished with waterproof abrasive paper from 400 grit to 1500 grit. All samples were washed with deionized water, ethanol and acetone in turn. In order to keep all the samples hanging in the autoclave, a small piece of stainless steel wire covered with Teflon tube was welded on the side of each sample.

2.2 Immersion Test

A dynamic 5L (net volume) stainless steel autoclave with a re-circulating loop was used for immersion tests in high temperature water environments under controlled water chemistries. The specimens were immersed in 310  1200 ppm B (wt.) as H₃BO₃ + 2.0 ppm Li (wt.) as LiOH solution as a simulating PWR primary water. Two kinds of high temperature water environments representing were used for immersion tests, one was named as the hydrogenated PWR primary water with DO < 5 ppb (wt.) and DH~2.5 ppm (wt.) representing the normal operating condition, and the other one was named as the oxygenated PWR primary water with DO of about 8 ppm (wt.) and DH < 5 ppb (wt.) representing abnormal operating conditions. The test duration in the oxygenated PWR primary water was 1012 h, which was 500 h in the hydrogenated PWR primary water.

3. RESULTS AND DISCUSSIONS

3.1 Immersion Tests in the Oxygenated PWR Primary Water

3.1.1 SEM Analysis

Fig. 1 showed the SEM morphologies of the oxide films on Ni-base alloys after 1012 h immersion in the oxygenated PWR primary water. The morphologies of the oxides on Fe-free Ni-base alloys were similar, which were different from those on Fe-bearing Ni-base alloys. Ni₂Cr and Ni₃Cr specimens were mainly covered with atactic oxide particles and some scattered needle-like oxide crossing the particles, as shown in Figs. 1(a) and 1(b). There were more needle-like oxides appeared in the oxide films on Ni-base alloys with higher Fe contents. The TT690 surface was mainly covered with loose needle-like oxide films and very few scattered big polyhedral oxide particles on the top, as shown in Fig. 1(e)-(f). With the increasing of Fe content, the morphologies of the oxide turned from particles to needles, even to lines and sheets. As shown in Table 2, even the atomic ratios of Ni:Cr of Ni₂Cr and Ni₃Cr were different, the Ni, Cr and Fe contents of the oxide films formed on Ni₂Cr and Ni₃Cr specimens were similar, which corresponded to the morphological result showed by the SEM photographs. The Fe content of the oxide films formed on Ni₂Cr and Ni₃Cr specimens might come from the 316L stainless steel autoclave body. During the test, the water chemistry of re-circulating loop was difficult to detect because of the leakproofness of the testing system. This should be noted when analyzing the oxidation mechanism. On the TT690 surface, the oxides showed different morphologies and different contents of Ni and Fe. The element Ni was enriched in the line-like and sheet-like oxides, while the element Fe was enriched in the particle oxides. The Cr contents of all the surface oxide films were very low, compared with that of the alloy matrix.

3.1.2 TEM Analysis

Fig. 2 showed the preparation of TEM samples with FIB. During the preparation process of TEM samples, the looseness of outer oxide films resulted in the amount of oxides taken away by FIB. The
morphologies of the oxide cross-section showed that more needle-like oxides in the outer oxide film corresponded to a looser oxide film. The morphologies of the cross-section also demonstrated the result that there were much more needle-like oxides on Ni$_2$Cr-3at.%Fe than on Ni$_2$Cr. The cross-sectional morphologies of the oxide films on the surface of Ni$_2$Cr are shown in Fig. 3. Fig. 4 showed that the oxide film formed on Ni$_2$Cr-3at.%Fe had a two-layered structure. The outer layer consisted of large atactic oxide particles and a few scattered needle-like oxides. The irregular cellular oxides of about 100 nm to several hundred nanometers in size located at the inner layer. It should be noticed that there was a very clear interface between the outer layer and the inner layer, as shown in Figs. 3(a) and 4(a), which might be the metal surface where the needle-like oxides and the irregular cellular oxides started to grow. The total thickness of the observed oxide films were about 2-3 μm. The thicknesses of the inner layers were about 700-800 nm. The EDS area mapping of the oxide films on Ni$_2$Cr and Ni$_2$Cr-3at.%Fe showed the elements distribution, as shown in Figs. 5 and 6, respectively. The mapping areas were shown in Fig. 5(a)-(b) and Fig. 6(a)-(b) by large rectangles. The outer layer with large oxide particles was Ni-enriched. For the inner layer, Fig. 5(b) and Fig. 6(b) indicated the contrast between the center part and the boundary of the irregular cellular oxides was different. The center of cellular oxides was Ni-rich whereas Cr was concentrated at the boundaries of cellular oxides. The diffraction patterns shown in Figs. 7, 8 and 9 indicated that both the large oxide particles and the inner irregular cellular oxides had NiO crystal structure. The high-resolution images of needle-like oxides in Fig. 10 showed that the needle-like oxides consisted of a lot of small oxide particles with different orientation. The composition of these small oxide particles should be spinel oxides with more Fe content. Table 3 provided the Ni, Cr, Fe and O contents of different oxides formed on Ni$_2$Cr-3at.%Fe after 1012 h immersion in the hydrogenated PWR primary water with 8 ppm DO. The statistic data indicated that the Fe content of needle-like oxides were higher than the large oxide particles and irregular cellular oxides. It was in accordance with the result that the increasing of Fe content introduced more needle-like oxides.

3.1.3 XRD Analysis and LRS Analysis

The XRD results were shown in Fig. 11. Because of the oxide films were very thin, the intensity of the peaks of alloy matrix were so high that other peaks were not detected, except the peaks of NiO. Some other oxides, such as spinel oxides, Ni(OH)$_2$ and Cr$_2$O$_3$, might exist in the oxide films.

The Raman analysis didn’t clearly show the phase compositions in Fig. 12, but oxides’ peaks such as NiO (570, 756, 872, 1108 cm$^{-1}$), spinel oxides (480, 570, 687 cm$^{-1}$), Ni(OH)$_2$ (628 cm$^{-1}$) and Cr$_2$O$_3$ (331, 426, 646 cm$^{-1}$) were observed.

3.2 Immersion Tests in the hydrogenated PWR Primary Water

3.2.1 SEM Analysis

As shown in Fig. 13, the morphologies of oxide films formed on all Ni-base alloys are similar. Specimens were mainly covered with compact atactic polyhedral oxide particles. The change of Fe content had no significant effect on the morphologies of the oxide films on these samples. As shown in Table 4, the Ni, Cr and Fe contents of the surface oxide films nearly corresponded to the alloy matrix. The Cr contents of the oxide films formed on all Ni-base alloys were much higher than that in the oxygenated PWR primary water.

3.2.2 TEM Analysis

The TEM cross-sectional morphologies of the oxide films on the Ni$_2$Cr, Ni$_2$Cr-3at.%Fe, and TT690 specimens are shown in Fig. 14. There was almost no difference except the thickness of oxide films. But the difference in thickness was not quite as obvious. The thickness of all oxide films was close to 100 nm. The diffraction patterns of the oxide particles formed on different samples are shown in Fig. 15. The Ni, Cr and Fe contents of oxide particles grown of different samples were shown in Table 5. The results indicated that the compositions of the oxide particles were typical spinel oxides (i.e., NiFe$_2$O$_4$, NiCr$_2$O$_4$.
and FeCr$_2$O$_4$). Fig. 16 showed the elements distribution in the oxide films. Ni contents of all oxide films were very low, and Cr content reduced from the interface between oxide film and matrix to the oxide film surface. Fe was concentrated at the oxide films. At the interface of the oxide films and matrix, Cr was rich and Fe was depleted. The effect of Fe content in matrix was not obvious, except the Fe contents of oxide particles on different samples (Table 5).

3.2.3 XRD and LRS Analysis

Both XRD and LRS testing results did not reflect any difference of the peaks positions. In the X-ray diffraction profiles of the oxide films, Because of the very low thin thickness, the XRD patterns showed almost no peaks of oxides can be found except the peaks of matrix. The Raman spectrum showed peaks at 530, 570, 650, 695 cm$^{-1}$. Peaks 570, 695 cm$^{-1}$ indicated spinel oxides were detected.

4. CONCLUSIONS

The present work investigated the morphologies, phase compositions and chemical compositions of the oxide films grown on Ni-Cr-xFe alloys in 310 °C in the oxygenated PWR water and the hydrogenated PWR primary water with SEM, FIB, TEM, XRD, LRS. The following conclusions can be drawn.

In the oxygenated PWR primary water, iron in Ni-base alloys has a strong effect on the surface morphologies of the oxides. The oxide films consisted of two layers. A clear interface between the inner layer and the outer layer can be found. Cr-depletion was significant in the oxide films. Increasing the Fe content in the alloy, more and more needle-like oxides, which consisted of a lot of nano-sized iron oxides, appeared in the outer layer of oxide films. The inner layer of oxide films mainly consisted of cellular oxides. The center of cellular oxides was Ni rich whereas Cr was concentrated at the boundaries.

In the hydrogenated PWR primary water, the effect of iron in Ni-base alloys was not obvious. The oxide films were observed to be only one layer, which mainly consisted of nano-sized spinel oxides. Cr-depletion was not significant in the oxide films, while Ni-depletion was obvious. Fe was concentrated in the oxide film but depleted at the interface between the oxide film and the alloy matrix.

Acknowledgements

This work was supported by the International Cooperative Project sponsored by Science and Technology Commission of Shanghai Municipality No. 13520721200, the Ph.D. Programs Foundation of Ministry of Education of China No.20123108110021, and Shanghai Pujiang Project No. 12PJ1403600.

REFERENCES


Table 1 Compositions of the investigated materials (wt.%).

<table>
<thead>
<tr>
<th>materials</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr</td>
<td>69.3</td>
<td>30.7</td>
<td>-</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-1at.% Fe</td>
<td>68.6</td>
<td>30.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-3at.% Fe</td>
<td>67.2</td>
<td>29.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Cr</td>
<td>77.2</td>
<td>22.8</td>
<td>-</td>
</tr>
<tr>
<td>TT690</td>
<td>59.4</td>
<td>29.4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Table 2 The Ni, Cr and Fe contents of the oxide films formed on Ni-base alloys after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO, taken by EDS attached to SEM (wt.%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr</td>
<td>69.45</td>
<td>4.81</td>
<td>1.22</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Cr</td>
<td>71.35</td>
<td>4.62</td>
<td>0.79</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-1at.% Fe</td>
<td>70.00</td>
<td>4.27</td>
<td>1.96</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-3at.% Fe</td>
<td>68.62</td>
<td>3.19</td>
<td>3.66</td>
</tr>
<tr>
<td>TT690 (lines and sheets)</td>
<td>51.39</td>
<td>3.30</td>
<td>10.78</td>
</tr>
<tr>
<td>TT690 (particles)</td>
<td>28.72</td>
<td>3.53</td>
<td>40.81</td>
</tr>
</tbody>
</table>

Table 3 The Ni, Cr, Fe and O contents of oxides formed on sample Ni<sub>2</sub>Cr-3at.%Fe after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO, taken by EDS attached to TEM (wt.%).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big oxide particles</td>
<td>74.86</td>
<td>1.97</td>
<td>16.06</td>
<td>7.10</td>
</tr>
<tr>
<td>Needle-like oxides</td>
<td>54.76</td>
<td>8.87</td>
<td>26.74</td>
<td>9.62</td>
</tr>
<tr>
<td>Irregular cellular oxides</td>
<td>67.51</td>
<td>8.61</td>
<td>15.25</td>
<td>8.63</td>
</tr>
</tbody>
</table>

Table 4 The Ni, Cr and Fe contents of the oxide films formed on Ni-base alloys after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH, taken by EDS attached to SEM (wt.%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr</td>
<td>64.88</td>
<td>29.41</td>
<td>0.87</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;3&lt;/sub&gt;Cr</td>
<td>71.84</td>
<td>21.80</td>
<td>0.95</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-1at.% Fe</td>
<td>64.32</td>
<td>29.14</td>
<td>1.86</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-3at.% Fe</td>
<td>62.99</td>
<td>28.38</td>
<td>3.72</td>
</tr>
<tr>
<td>TT690</td>
<td>56.63</td>
<td>28.24</td>
<td>10.58</td>
</tr>
</tbody>
</table>

Table 5 The Ni, Cr and Fe contents of the oxide particles formed on Ni-base alloys after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH, taken by EDS attached to TEM (wt.%).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr</td>
<td>11.23</td>
<td>52.27</td>
<td>36.50</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;Cr-3at.%Fe</td>
<td>11.03</td>
<td>47.31</td>
<td>41.66</td>
</tr>
<tr>
<td>TT690</td>
<td>9.09</td>
<td>37.77</td>
<td>53.14</td>
</tr>
</tbody>
</table>
Fig. 1 SEM photographs of the oxide films on samples immersed in the oxygenated PWR primary water with 8 ppm DO and DH< 5ppb for 1012 h: (a) Ni2Cr; (b) Ni3Cr; (c) Ni2Cr-1at.%Fe; (d) Ni2Cr-3at.%Fe; (e)(f) TT690.
Fig. 2 SEM morphologies of the cross-section of the oxide films formed on Ni-base alloys after immersed in the oxygenated PWR primary water with 8 ppm DO and DH< 5ppb for 1012 h. (a), and (b) Ni_2Cr; (c) and (d) Ni_2Cr-3at.%Fe.

Fig. 3 The TEM morphologies of the cross-section of the oxide film formed on Ni_2Cr specimen after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 4 The TEM morphologies of the cross-section of the oxide film grown on sample Ni2Cr-3at.%Fe after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 5 STEM image of the oxide film and EDS mapping of the oxide film grown on sample Ni$_2$Cr after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO: (a) area covered the interface; (b) irregular cellular oxide.
Fig. 6 STEM image of the oxide film and EDS mapping of the oxide film grown on sample Ni$_2$Cr-3at.%Fe after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO: (a) area covered the interface; (b) irregular cellular oxide.

Fig. 7 Diffraction pattern of the large oxide particles grown on sample Ni$_2$Cr after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO: (a) bright field image; (b) dark field image; (c) diffraction pattern.
Fig. 8 Diffraction pattern of the big oxide particles grown on sample Ni$_2$Cr-3at.%Fe after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO: (a) bright field image; (b) diffraction pattern; (c)(d) dark field image.

Fig. 9 Diffraction pattern of inner irregular cellular oxide areas on sample Ni$_2$Cr (a) and sample Ni$_2$Cr-3at.%Fe (b) after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 10 The TEM images and high-resolution images of needle-like oxides on sample Ni$_2$Cr (a)(b) and sample Ni$_2$Cr-3at.%Fe (c)(d) after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 11 X-ray diffraction profiles of the oxide films formed on samples after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 12 The Raman spectra of the oxide films formed on Ni-base alloys after 1012 h immersion in the oxygenated PWR primary water with 8 ppm DO.
Fig. 13 SEM photographs of the oxide films on Ni-base alloys after 500h immersion in the hydrogenated PWR primary water environment with 2.5 ppm DH and DO< 5 ppb: (a) Ni2Cr; (b) Ni3Cr; (c) Ni2Cr-1at.%Fe; (d) Ni2Cr-3at.%Fe; (e) TT690

Fig. 14 The TEM morphologies of cross-section of oxide films grown on sample Ni2Cr (a), Ni2Cr-3at.%Fe (b), TT690 (c) after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH and DO< 5 ppb.
Fig. 15 Diffraction pattern of the oxide particles grown on sample Ni$_2$Cr (a, b, c), Ni$_2$Cr-3at.%Fe (d, e, f) and TT690 (g, h, i) after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH and DO< 5 ppb: (a, d, g) bright field image; (b, e, h) dark field image; (c, f, i) diffraction pattern.
Fig. 16 STEM image of the oxide film and EDS lining of oxide films grown on sample Ni$_2$Cr (a), Ni$_2$Cr-3at.%Fe (b), TT690 (c) after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH and DO< 5 ppb.
Fig. 17 X-ray diffraction patterns of the oxide films formed on Ni-base alloys after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH and DO< 5 ppb.
Fig. 18 The Raman spectra of the oxide films formed on Ni-base alloys after 500 h immersion in the hydrogenated PWR primary water with 2.5 ppm DH and DO< 5 ppb.