Thermodynamic Consideration of the Steam Oxidation Resistance of Austenitic Stainless Steels Forming Intermetallic Compound*1

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Steam oxidation resistance of Fe–20Cr–30Ni (at%) austenitic stainless steels with Nb, Mo, Ta, and W was investigated at 700°C. The Cr2O3 layer uniformly formed at the boundary between a spinel-type oxide scale and a metal substrate of alloys containing Nb, Mo, or W inhibits processing strain by shot-peening at the surface of the alloy. 

1. Introduction

The steels and alloys that are used to develop the heat-resistant materials in various power plants are required to ensure good high-temperature strength and hot corrosion resistance. Currently, the austenitic stainless steels whose high-temperature strength improves with increasing precipitation are applied to develop heat-resistant materials for a power plant. Takeyama et al. developed a heat resistant material based on Fe–20Cr–30Ni, containing 2.0Nb, to improve the high-temperature strength.1–3) This alloy precipitates the Laves phase (Fe2Nb) at the grain boundary and γ″ (Ni3Nb) at the inside of the grain as intermetallic compounds are maintained at 700°C to 900°C. Takeyama compared the high-temperature creep strength of the Fe–20Cr–30Ni–2.0Nb with that of standard steels,4) which clarified that this alloy is inferior to Ni-based Inconel740 but superior to TH347H (Fe–18Cr–12Ni–Nb, mass%) in terms of high-temperature creep strength. Intermetallic compounds at the grain boundary and inside the grain improve the high-temperature creep strength.

However, it is also important to improve the hot corrosion resistance caused by Cl and S from fossil or biomass fuel at the outer surface and the high-temperature steam oxidation at the inner surface of the tubes. Particularly, the oxidation in steam is observed to be more accelerated than that in air.5) To maintain a good resistance for steam oxidation, it is important to uniformly form protective Cr2O3 at the surface of the alloy during the early stage of oxidation. There are a few methods by which uniform Cr2O3 can be obtained during the early stage as follows: by increasing the Cr concentration,6) by accelerating the Cr diffusion with a fine grain of the alloy,7,8) or by accelerating the Cr diffusion with the addition of processing strain by shot-peening at the surface of the alloy.9)13) As mentioned previously, to improve the high-temperature strength of the heat resistance materials by increasing the steam temperature and pressure of power plants, additional elements are used to strengthen the precipitation. Therefore, it is critical to understand the relation between precipitation, containing additional elements and steam oxidation resistance mainly affected by the formation of Cr2O3. However, there are no considerations about such a relation between the precipitation behavior and steam oxidation resistance. In this study, the effect of additional elements, such as Nb, Mo, Ta, and W, forming intermetallic compounds on steam oxidation resistance was clarified.

2. Experimental Procedure

Table 1 lists the chemical composition of the test alloys (in at%). Fe–20Cr–30Ni test alloys, containing Nb, Mo, Ta, or W up to 2.5%, were prepared by vacuum melting. Steel plates were further obtained by hot rolling to 5-mm thickness at 900 to 1100°C. Subsequently, they were homogenized at 1080 to 1200°C for 10 to 60 min in air to obtain a 3 to 4.5 ASTM (American Society for Testing and Materials) grain size. Specimens of approximately 2t × 10w × 25L mm were cut from the ingot and ground to a 2000#grit finish using SiC paper and a 3-μm Al2O3 paste. The specimens were further polished electrochemically using mixed acid containing sulfuric acid and phosphoric acid. Before oxidation test, the polished specimens were ultrasonically degreased in acetone.

The steam oxidation tests were conducted in a horizontal vessel with a heat resistant steel tube. Steam containing 100 ppb of oxygen was used as a test gas. The specimens were exposed through the steam in the horizontal vessel to a 100% steam atmosphere. The vessel was heated at a rate of 4°C/min to 700°C and was maintained at 700°C for 2 to 200 h. After completing the oxidation tests, the specimens were cut by a cross section polisher (JEOL IB-19530CP) and polished electrochemically using mixed acid containing sulfuric acid and phosphoric acid. Before oxidation test, the polished specimens were ultrasonically degreased in acetone.

*1This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. 81 (2017) 427–434.
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Keywords: austenitic stainless steel, steam oxidation, chromium oxide, chemical potential, intermetallic compound
substrate were observed using an optical and a scanning electron microscope (SEM ELIONIX ERA-8900FE). 10 points of the inner oxide scale were randomly measured, and the average of them was evaluated as steam oxidation resistance. The oxide scales formed on the alloy substrate were identified by transmission electron microscope (TEM JEOL 200CX, JEM-2100). The element distributions were measured on the oxide scale by a field emission-electron probe micro analyzer (FE-EPMA JEOL JXA-8530F).

3. Results and Discussions

3.1 The effect of additional elements on the formation of the oxide scales

Generally, oxidation resistance is considered to be the complete thickness of the oxide scale. In a steam atmosphere, however, it is difficult to measure the entire thickness of the multi-layered oxide scale because the outermost one is possible to be partially spalled. In this study, therefore, the thickness of the inner oxide scale was measured and evaluated to be the steam oxidation resistance. To confirm the difference between the outer and inner oxide scale formation behavior, the thicknesses of the outer and the inner oxide scales at the surface of the alloy, containing 0.5% Nb, were measured. As depicted in Fig. 1, the thickness of the inner oxide scale was approximately the same as that of the outer oxide scale regardless of the heating time. This indicates that it is appropriate to evaluate the steam oxidation resistance based on the thickness of the inner oxide scale.

Figures 2 to 5 depict the relations between the thickness of the inner oxide scale and the amounts of additional elements of specimens after heating to 700°C for 200 h in a steam atmosphere, respectively. The inner oxide scale of Fe–20Cr–30Ni alloy was 16 to 20 µm thick. In the case of Nb or Mo addition, the variations in the thicknesses of the inner oxide scales were small with not more than 0.5% addition where it decreased with an addition of more than 0.5%. For 2% Nb and Mo added alloys, the inner oxide scale grows from 5 to 8 µm thick. In the case of W addition, the thickness of the inner oxide scale with 0.5% addition became half of that with no addition, and it remained with an addition of more than 0.5%. As compared with the addition of Nb or Mo, W addition exhibited a drastic retardation effect on the oxide scale. However, Ta addition exerted no effect on the formation of the oxide scale until the addition reached 2.1%.

Figures 6 to 9 depict the distributions of the alloying elements in the oxide scale on Fe–20Cr–30Ni alloys with no additional elements, 2.5Nb, 2.0Mo, and 2.0W after heating for 200 h to 700°C. Every alloy contained two phases of

| Remark | Cr  | Ni  | Nb  | Mo  | W  | Ta |
|--------|-----|-----|-----|-----|----|----|
| Base   | 20.0| 30.2| -   | -   | -  | -  |
| 0.5Nb  | 19.9| 30.1| 0.48| -   | -  | -  |
| 1.0Nb  | 20.1| 30.1| 0.98| -   | -  | -  |
| 1.5Nb  | 19.8| 29.7| 1.36| -   | -  | -  |
| 2.0Nb  | 19.9| 29.9| 2.06| -   | -  | -  |
| 2.5Nb  | 20.0| 30.0| 2.48| -   | -  | -  |
| 0.5Mo  | 20.0| 30.0| -   | 0.50| -  | -  |
| 1.0Mo  | 20.0| 30.1| -   | 1.00| -  | -  |
| 1.5Mo  | 19.9| 30.0| -   | 1.50| -  | -  |
| 2.0Mo  | 20.1| 30.1| -   | 2.01| -  | -  |
| 0.5W   | 20.0| 30.1| -   | -   | 0.50| -  |
| 1.0W   | 20.0| 30.0| -   | -   | 0.98| -  |
| 2.0W   | 20.0| 30.0| -   | -   | 1.97| -  |
| 2.0Ta  | 20.1| 30.1| -   | -   | -  | 2.07|
Fig. 4 Thickness of the inner oxide scale for the test alloys with W exposed in steam at 700°C for 200 h.

Fig. 5 Thickness of the inner oxide scale for the test alloys with Ta exposed in steam at 700°C for 200 h.

Fig. 6 Distribution of alloying elements in oxide scale on Fe–20Cr–30Ni alloy exposed in steam at 700°C for 200 h.

Fig. 7 Distribution of alloying elements in oxide scale on Fe–20Cr–30Ni–2.5Nb alloy exposed in steam at 700°C for 200 h.
oxide scales, seemed to be the outer Fe oxide and inner Fe–Cr spinel oxide. In case of an alloy with no additional elements, Ni was concentrated at the outside of the boundary between the outer and the inner oxide scales. In this case, Ni was not oxide but metal Ni because there was no distribution of O with Ni. Cr was uniformly distributed on the inner oxide scale. However, there is no concentration of Cr at the boundary between the inner oxide scale and the alloy substrate. Further, the alloys with Nb, Mo, or W addition were observed Cr concentration at the boundary between the inner oxide scale and the alloy substrate. The concentrated Nb, Mo, and W existed locally in the inner oxide scales. Ni existed in a dispersed manner in the inner oxide scale.

3.2 The time variation for the growth of the oxide scales

Figure 10 depicts the time variation for the growth of the oxide scales of solute specimens containing 0.5% or 2.5% added Nb, respectively. Until heating for 10 h, no difference was observed in the oxide scale thickness of 5 µm. After heating for 10 h, though, significant differences have happened between alloys with 0.5% and 2.5% Nb. For 0.5% Nb alloy, the oxide scale grew with the heating time, and reached 14 µm thick after heating for 50 h. In contrast, the inner oxide of the alloy with 2.5% Nb was still 5 µm. This indicated that the growth of the oxide scale was considerably inhibited.
The time variation for the relation between the formation of intermetallic compounds and the distribution of Cr concentration was indicated at the oxide scale. Figure 11 depicts the photographs, containing the grain boundaries of the alloy with 2.5% Nb after 5, 10, or 15 h, respectively, and the distributions of Cr concentration simultaneously observed at the oxide scale. At 10 h, intermetallic compound began to precipitate at the grain boundary; further, the amount of intermetallic compounds increased with the time variation. However, the Cr concentration at the boundary between the inner oxide scale and the alloy substrate did not alter after heating for 5 and 10 h. Further, Cr began to concentrate at the boundary between the inner oxide scale and the alloy substrate after heating for 15 h.

3.3 Behavior of growing the oxide scale at the surface of the aged test specimens

Steam oxidation tests were conducted for the alloy with 2.5% Nb previously precipitating the intermetallic compound by aging treatment. Figure 12 depicts the time variation of the inner oxide scale. In case of the solute specimens, the thickness of the oxide scale was increased before 10 h; subsequently, the growth of the oxide scale was inhibited. However, the oxidation of the aging specimens was immediately inhibited after initiating the steam oxidation test as compared to that of the solute specimens, and the oxide scale was only 2 µm thick after heating for 20 h, which is less than half of that of the solute specimens after heating for the same duration.

Figure 13 depicts the Cr distributions of the oxide scales of the aging specimens after heating for 5 h measured by FE-EPMA. It was observed that Cr$_2$O$_3$ was uniformly formed at the boundary between the inner oxide scale and the alloy substrate.

4. Discussions

4.1 Possibility of the inhibition of growing oxide scale by the oxide of additional elements

Cr in alloys is oxidized in the oxidizing atmosphere, uniformly forming continuous Cr$_2$O$_3$. The diffusion coefficient of oxygen in Cr$_2$O$_3$ depicts a 5-figure smaller value as compared to that observed in Fe and Ni.$^{14-16}$ This is why the formation of continuous Cr$_2$O$_3$ retards the growth of the
oxide scale. Nb, Mo, and W exhibit the possibilities of contribution improving the steam oxidation resistance with a uniform formation of continuous oxides at the surface of the alloy. Therefore, the effect of the oxides, containing these elements on the steam oxidation resistance, was indicated. Ueda et al. reported that the concentration of Nb increased as the Nb oxide at the boundary between the inner oxide scale and the alloy substrate, which is the austenitic stainless steel containing Nb.\(^{17}\) However, the diffusion coefficient of oxygen in Nb\(_2\)O\(_5\), a typical Nb oxide, is \(4.0-8.3 \times 10^{-15}\) m\(^2\)/s based on the partial pressure of oxygen.\(^{18}\) At 900°C, this value is similar to that observed in Fe and Ni. Therefore, the effect of Nb oxide on the steam oxidation resistance is observed to be smaller than that in Cr\(_2\)O\(_3\). On the other hand, the diffusion coefficient of oxygen in Mo and W oxide is not measured. The existence of the oxides, containing these elements, was initially observed by TEM. Figure 14 shows the EDX (Energy Dispersive X-ray analysis) quantitative and structural analysis near the boundary between the inner oxide scale and the alloy substrate containing 2\% Mo and 2\% W, respectively, after heating to 700°C for 200 h. Cr\(_2\)O\(_3\) was formed at the innermost oxide scale layer; however, Mo or

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**Fig. 13** Distribution of alloying elements in oxide scale on Fe-20Cr-30Ni-2.5Nb alloy exposed in steam at 700°C for 5 h.

**Fig. 14** TEM images and quantitative analyses by EDX of oxide scale at scale/alloy interface of Fe-20Cr-30Ni alloys with (a) 2Mo and (b) 2W.
intermetallic compounds of both Fe₂Nb and Ni₃Nb, while the volume in the alloy structure. The alloy with Nb precipitates Mo, and W, where the mole fraction indicates the rate of mole addition of 0.5% W accelerates the precipitation of intermetallic compounds, containing Fe, Al₂Cr₃, and Nb precipitates intermetallic compounds containing Fe (see Figs. 2 to 5) and uniformly form Cr₂O₃ (see Figs. 7 to 9) at scale/alloy interface. Thus, it is indicated that the precipitation of intermetallic compounds containing Fe affects the formation of oxide scale, and the mechanism was discussed in terms of thermodynamics of diffusion.

4.3 Thermodynamic factor of diffusion for Cr₂O₃ formation affected by the precipitation of intermetallic compounds containing Fe

An outward flux of Cr, affecting the formation of Cr₂O₃, is expressed by Fick’s laws of diffusion, eq. (1). This can be transformed into eq. (2) by rewriting the chemical potential to depict the Cr activity as follows:

\[
J_{Cr} = -D_{Cr}^{eff} \frac{\partial \mu_{Cr}}{\partial z} \quad (1)
\]

\[
J_{Cr} = -D_{Cr}^{eff} \frac{\partial \ln a_{Cr}}{\partial z} \quad (2)
\]

where, \(D_{Cr}^{eff}\) is the diffusion coefficient of Cr, \(\mu_{Cr}\) is the chemical potential of Cr, \(a_{Cr}\) is the Cr activity, and \(z\) is the distance from the boundary between the inner oxide scale and the alloy substrate. The change of \(a_{Cr}\) due to the precipitation of intermetallic compounds can be explained using Fig. 17 as follows.

At the early stage of steam oxidation, Fe and Fe–Cr oxide scales are formed at the surface of the alloy, decreasing the concentrations of Fe and Cr beneath the oxide scale (II) as compared with the alloy substrate (I). This indicates that the Cr activity beneath the oxide scale (II) becomes smaller than that in the alloy substrate (\(a_{Cr}^{I}\)) and that the gradient of Cr activity exists between these two regions. Further, the precipitation of intermetallic compounds containing Fe reduces the concentration of Fe at the areas of I and II, and the concentration of Ni increases relatively; therefore, the composition of I and II change to I’ and II’, respectively. Thus, we can hypothetically state that the amounts of Ni variations are the same and that the reduction of Cr activity beneath the oxide scale (\(a_{Cr}^{I} - a_{Cr}^{I}\)) is bigger than that in the alloy substrate (\(a_{Cr}^{I} - a_{Cr}^{II}\)) on a logarithmic axis. Thus,
increasing the gradient of Cr activity increases $J_{Cr}$, which accelerates the formation of a protective uniform Cr$_2$O$_3$ scale at the surface of the alloy. This aforementioned hypothesis is typically depicted in Fig. 18(a) and (b). In the case of intermetallic compounds containing Ni, the Ni concentration decreases at the alloy substrate and beneath the oxide scale from the chemical component at I and II in Fig. 17. The decrease of Ni concentration undergoes very little change of Cr activity. Therefore, the gradient of Cr activity does not change, and it could not improve the formation of Cr$_2$O$_3$. This hypothesis can be summarized as follows: the formations of uniform Cr$_2$O$_3$ at the surface of the alloys with Nb, Mo, or W addition are improved because of the increment in the gradient of Cr activity with the increase in the precipitation of intermetallic compounds containing Fe.

5. Conclusions

Alloys of Fe–20Cr–30Ni with Nb, Mo, Ta, or W addition were oxidized in steam at 700°C. The results can be summarized as follows.

1) The thickness of the inner oxide scales of the alloy with Nb, Mo, or W, which accelerates the precipitations of intermetallic compounds containing Fe, decreased with an increase in the amount of additional elements after heating for 200 h. However, that of the alloy with Ta, which does not form an intermetallic compound containing Fe, was not observed the effect on the thickness of the inner oxide scales of the alloy.

2) After heating for 10 h, the difference of the oxidation behavior between 0.5Nb and 2.5Nb alloys was observed when the intermetallic compound containing Fe began to precipitate in the alloy with 2.5Nb; further, the growth on the oxide scale was inhibited by uniformly forming Cr$_2$O$_3$.

3) The growth of the oxide scale of the alloy with 2.5Nb containing the already precipitated intermetallic compounds by aging treatment was inhibited by uniformly forming Cr$_2$O$_3$ during the early stage of the oxidation test.

4) The Nb can react with oxygen as Nb$_2$O$_5$ where the Mo and W oxides were not formed at the surface of the alloys. However, the diffusion coefficient of oxygen in Nb$_2$O$_5$ exhibits a similar value to that in Fe and Ni, suggesting that the effect of the oxide formation on the steam oxidation resistance should be small.

5) The Fe concentration in the alloy substrate decreases with the precipitation of intermetallic compounds containing Fe, which relatively increases the Ni concentration. Therefore, the gradient of Cr activity between the alloy substrate and beneath the oxide scale in the Cr depletion zone, increasing the outward flux of Cr, accelerates the formation of uniform Cr$_2$O$_3$.

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