Microstructure Development of Oxide Scale during Steam Oxidation of the Fe–20Cr–30Ni–2Nb (at%) Austenitic Steel at 1073 K

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Novel austenitic steel of which composition is Fe–20Cr–30Ni–2Nb (at%) is one of the promising material for further advanced steam power plants, which will be operated at 973 K or higher temperature such as 1073 K. This steel is strengthened by intermetallic compounds and has creep rupture strength 80 MPa at 973 K for 10⁵ h. Further investigations are needed to improve both creep rupture strength and steam oxidation resistance of the steel for application at 1073 K. This paper focuses on steam oxidation resistance of the steel at 1073 K. Steam oxidation has been conducted to clarify microstructure development of the oxide scale and to evaluate long-term steam oxidation resistance based on the kinetic data. Microstructure observation reveals that Cr₂O₃ layer is easy to form at the scale/steel interface compared with the commercial austenitic steels, because the transition from internal to external oxidation has finished within about 20 ks. Surface oxygen potential measurement by using oxygen concentration cell is also useful technique to detect Cr₂O₃ formation in the scale. Based on the kinetics data, this steel has a good steam oxidation resistance compared with the commercial austenitic steel such as type 316 steel and is applicable to further advanced steam power plants. [doi:10.2320/matertrans.M2013258]

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1. Introduction

Austenitic steels have been widely used as materials for super-heater and re-heater tubes of fossil fuel power plants.¹,² Improvement of thermal efficiency is essential to save energy and to reduce CO₂ emission. Recently, the highest steam condition in Japan is 620°C (893 K)/25 MPa. A challenge of operation at 700°C (973 K) (A-USC) is required to develop novel piping materials. The authors are now challenging to develop new austenitic steel for realizing 800°C (1073 K) class power plants. For realizing further advanced steam power plants, heat resistant steels are needed to possess both creep rupture strength of 100 MPa and good steam oxidation resistance at operating temperatures for 10⁵ h. Commercial austenitic heat resistant steels such as SUS347HFG cannot meet these requirements, because carbides in the steels become unstable and decompose at higher temperature. On the other hand, nickel base alloys have enough creep rupture strength but the cost is too expensive. Takeyama³) has proposed a newly developed austenitic heat resistant steel of which composition is Fe–20Cr–30Ni–2Nb (at%). This steel is strengthened by intermetallic compounds and has creep rupture strength of 80 MPa at 973 K for 10⁵ h. Further investigations are needed to improve both creep rupture strength and steam oxidation resistance of the steel for application at 1073 K.

Yamashita et al.⁴) examined oxidation tests of the solution treated Fe–20Cr–30Ni–2Nb (at%) austenitic steel at 973 K in both air and steam atmospheres. The same oxidation atmospheres were also carried out by using pre-aged sample in which intermetallic compounds precipitated. Continuous Cr₂O₃ layer formed on the steel in air and oxidation behavior was independent of heat treatment before oxidation. In steam oxidation, oxidation behavior of the solution treated sample was strictly different from that of the aged sample. In the steam atmosphere, oxide scale of the pre-aged sample exhibited a duplex structure which consisted of Fe₃O₄ as the outer scale and a mixture of (Fe,Cr)₂O₃ and Ni as the inner scale. Ni particles and voids were observed at the interface of the duplex scale. The growth rate of the duplex scale was almost the same as that of type 316 steel.⁵) In the solution treated sample, there are two kinds of scale morphology depending on the grain orientation of the steel. Although thin layer of duplex scale with an inner continuous Cr₂O₃ was covered on the steel in the early stage, the thick duplex scale, which has the similar morphology as seen on the pre-aged sample, was fully covered on the steel for long-term exposure. It is clearly shown that steam oxidation resistance of the solution treated sample was much better than that of the pre-aged sample. Further investigations are needed to clarify microstructure development of the oxide scale and to evaluate long-term steam oxidation resistance at 1073 K.

Chemical potential of oxygen at the surface of the oxide scale is one of the useful thermodynamics information to estimate oxidation behavior during oxidation. Akiba et al.⁶) proposed a novel technique for measuring the chemical potential of oxygen at the surface of the growing oxide scale by using an oxygen concentration cell with CaO stabilized ZrO₂ (CSZ) solid electrolyte. This method can be applied to detect the formation of continuous layer of Cr₂O₃ in the oxide scale during steam oxidation. In the early stage of steam oxidation, the chemical potential of oxygen at the surface is much lower than that in the atmosphere, because Fe oxide forms on the steel. When the Cr₂O₃ layer forms in the oxide scale, the chemical potential of oxygen at the surface increases and is almost as same as that in the atmosphere. Continuous monitoring of the oxygen chemical potential at the surface gives us the change of oxidation behavior due to the formation of Cr₂O₃ layer.

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In this study, steam oxidation of the Fe–20Cr–30Ni–2Nb (at%) steel at 1073 K has performed to clarify microstructure development of the oxide scale and to evaluate long-term steam oxidation resistance based on the kinetic data. Moreover, the chemical potential of oxygen at the scale surface has been continuously monitored to elucidate microstructure development of the oxide scale during steam oxidation.

2. Experimental

2.1 Samples

Fe–20Cr–30Ni–2Nb (at%) austenitic steel was prepared by a vacuum induction melting. This steel was hot forged to be rod ($\varphi = 12$ mm) at 1553 K. The chemical composition of the steel is shown in Table 1. The rod was solution treated at 1523 K for 3.6 ks in air and was quenched in water. Average grain size after the solution treatment is about 150 $\mu$m. The solution treated rod was aged at 1173 K for 864 ks in air and was quenched in water. Fe$_2$Nb Laves phase was precipitated in the matrix at this temperature. The rod after aging was sliced into 1.5 mm in thickness and coupons were ground on an abrasive paper up to #2000 and polished with diamond abrasive paste. The sample was cleaned in ethanol by using an ultrasonic cleaner prior to oxidation tests.

Table 1 Chemical composition of the Fe–20Cr–30Ni–2Nb (at%) austenitic steel.

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<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
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<td>bal.</td>
<td>19.65</td>
<td>29.94</td>
<td>1.88</td>
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2.2 Steam oxidation

Steam oxidation of the steel was carried out at 1073 K in the stream of Ar–15%H$_2$O gas mixture. Purified Ar gas was humidified by passing through a distilled water which temperature was kept at 327 ± 1 K. Flow rate of the gas stream was $1.7 \times 10^{-6}$ m$^3$ s$^{-1}$ (100 mL/min) and oxygen partial pressure of the gas mixture was controlled to be $10^{-7}$Pa at 1073 K, which is in stable region of magnetite. Temperature and oxygen partial pressure in the vicinity of the sample was continuously monitored by an R-type thermocouple and CaO stabilized ZrO$_2$ (CSZ) oxygen sensor which was located 1 cm below the cell. The electrochemical cell for the oxygen sensor is described as follows.

(-) Pt|steel|oxide scale, gas($2\mu_{O,ad}$)CSZ|gas($\mu_{O,Atm}$), Pt (+) (1)

The electromotive force for the cell ($E_{cell}$) is expressed as follows.

$$E_{cell} = (\mu_{O,Atm} - 2\mu_{O,ad})/4F$$

where $F$ is the Faraday constant. $2\mu_{O,ad}$ and $\mu_{O,Atm}$ denote chemical potential of oxygen at the surface and in the atmosphere, respectively. The chemical potential of oxygen in the atmosphere was monitored by the oxygen sensor which was located 1 cm below the cell. The electrochemical cell for the oxygen sensor is described as follows.

(-) Pt, gas($\mu_{O,Atm}$)CSZ|gas($\mu_{O,Air}$), Pt (+) (3)

The electromotive force of the oxygen sensor ($E_{sensor}$) is described as follows.

$$E_{sensor} = (\mu_{O,Air} - \mu_{O,Atm})/4F$$

where $\mu_{O,Atm}$ is chemical potential of oxygen in air. Based on eqs. (2) and (4), one can calculate the chemical potential of oxygen at the surface of the oxide scale as follows.

$$2\mu_{O,ad} = \mu_{O,Atm} - 4F(E_{cell} + E_{sensor})$$

Figure 1 shows surface appearance of the electrochemical cell for measuring the chemical potential of oxygen at the scale surface. The specimen was placed on a solid electrolyte of CSZ tube. The CSZ tube was cut into the shape which has 3 legs. One leg of the CSZ was fabricated to be sharpened as small as possible to ensure that gas supply is enough at triple phase boundary. The other 2 legs were insulates with Al$_2$O$_3$ plate to assure that the electrochemical reaction at the oxide scale occurs only at one contact point between the CSZ and the specimen. The reference electrode of the cell was fixed at the position of 20 mm away from the tip. Temperature of the cell was monitored by using R-type thermocouple.

The cell and the CSZ oxygen sensor were set at the isothermal zone of the furnace tube and heated up to 1073 K with the heating rate of $8.3 \times 10^{-2}$ K s$^{-1}$ (5 K min$^{-1}$). Ar–15%H$_2$O gas mixture was flowed into the furnace tube during the heating. Flow rate of the gas stream was $1.7 \times 10^{-6}$ m$^3$ s$^{-1}$ (100 mL/min). When temperature reached at around 850 K, the electromotive force was generated on the cell. Measurement was proceeded at the time when temperature of the sample reached 850 K ($t = 0$). Electromotive forces of the cell and the oxygen sensor were continuously measured at 1073 K up to 258.8 ks. After the measurement, the cell was cooled down to room temperature with the cooling rate of $8.3 \times 10^{-2}$ K s$^{-1}$ (5 K min$^{-1}$).
2.4 Analytical methods

After steam oxidation, phase identification was carried out by X-ray Diffraction (XRD). Surface and cross-section of the oxide scale were observed by a Field Emission-Scanning Electron Microscope (FE-SEM). The cross-section of the scale was fabricated by focused ion beam method (FIB). Elemental analysis was carried out by energy dispersion spectroscopy (EDS). The thickness of the oxide scale was measured by BE images obtained from FE-SEM.

3. Results

3.1 Steam oxidation behavior of the steel in the early stage

Figure 2 shows XRD pattern of the samples after steam oxidation at 1073 K for up to 177.8 ks. Total exposure time as shown in Fig. 2 is the sum of heating time from 850 K to 1073 K and holding time at 1073 K. X-ray penetrated though the oxide scale and the peaks of Fe3O4, Ni and γ-Fe were detected in all samples. Although (Fe,Cr)3O4 forms as the inner scale or in the internal oxidation zone, it cannot be seen by XRD. In our previous studies, metallic Ni particles were observed at the interface of the duplex scale. As we will show later, Ni diffraction spectra come from metallic Ni particles which are located beneath the Fe3O4 scale. The peak shift of Ni diffraction pattern is observed around 2θ/deg. = 43.7 in the early stage (5.1 ks), whereas there is no peak shift of γ-Fe. It indicates that metallic Ni particles include Fe in the early stage and the concentration of Fe in the particles decreases with increasing oxidation time. Moreover, weak spectra of Cr2O3 were observed after 91.4 ks.

Figure 3 shows surface morphology of the oxide scale formed on the samples at 1073 K. Fe3O4 covers the surface and its grain size becomes large with oxidation time. Part of the metallic Ni–Fe particles, which size is around 1 μm, is observed between coarse Fe3O4 grains (3–5 μm) in the early stage (up to 18.4 ks).

Figure 4 shows the cross-sectional BE images of the oxide scale after steam oxidation at 1073 K up to 177.8 ks. Figures 5 and 6 show the elemental mappings of the sample after steam oxidation for 5.1 ks and 177.8 ks, respectively. The cross-section of the oxide scale was prepared by focused ion beam method (FIB). In the early stage (5.1 ks), Fe3O4 covers the surface and both internal oxidation and discontinuous Cr2O3 layer are observed beneath the Fe3O4 scale. Metallic particles are located at initial surface, especially above the internal oxidation zone. The layer of Cr2O3 is locally formed at the side of the IOZ after the oxidation for 5.1 ks and Cr depletion is observed in the substrate close to the well-developed Cr2O3 layers after 177.8 ks. When continuous layer of Cr2O3 is fully covered at the scale/steel interface (18.4 ks), internal oxidation zone (IOZ) becomes inner scale which consists of a mixture of (Fe,Cr)3O4 and Ni–Fe alloy. The origins of (Fe,Cr)3O4 and Ni–Fe alloy are precipitated oxides and matrix in the IOZ, respectively. Cr depletion zone in the substrate is observed beneath the Cr2O3 scale due to the growth of Cr2O3 layer (91.4 ks and 177.8 ks). Ni enrichment is observed and there is no Fe2Nb Laves phase in the depletion zone. Continuous layer of Nb-rich oxide is...
observed at the Cr2O3/steel interface. Figure 7 shows the elemental mappings of the oxide scale after steam oxidation for 177.8 ks. Nb-rich oxide is located beneath the Cr2O3 layer (bright phase between the Cr2O3 layer and substrate shown in SEI) and small amount of Cr is included in this oxide. As we will show later, Nb-rich oxide is identified to be NbO2 by XRD. Further analysis is needed to identify this oxide layer.

Figure 8 shows thickness of the oxide scale after short-term steam oxidation at 1073 K. In the short-term steam oxidation, oxide scale mainly consists of magnetite as the outer scale, the mixture of Fe–Cr spinel and Ni–Fe alloy as the inner scale and Cr2O3 layer. The growth of Cr2O3 layer obeys parabolic rate law. Whereas the growth rates of both inner scale and outer scale obeys parabolic rate law in the early stage, the growth rates of the outer and inner scale are decreased due to the growth of the Cr2O3 layer.

Figure 9 shows XRD pattern of the samples after the long-term steam oxidation at 1073 K. X-ray penetrated though oxide scales, because the peaks of the substrate are detected in all samples. The peaks of Fe3O4 and Ni are mainly detected. There is no peak shift of Ni after 43.7 ks. The diffraction pattern of Cr2O3 is observed after 86.4 ks and its
Fig. 5  Elemental mappings of the sample after steam oxidation for 5.1 ks at 1073 K.

Fig. 6  Elemental mappings of the sample after steam oxidation for 177.8 ks at 1073 K.

Fig. 7  Elemental mappings of the oxide scale after steam oxidation for 177.8 ks.
intensity becomes larger with increasing oxidation time. NbO₂ is detected together with Cr₂O₃ after 1209.6 ks.

Figure 10 shows the elemental mappings of the sample after the long-term steam oxidation at 1073 K for 1209.6 ks. Oxide scale exhibits a duplex scale, which consists of Fe₃O₄ as the outer scale and Cr₂O₃ as the inner scale. A continuous layer of Nb-rich oxide is also observed at the Cr₂O₃/steel interface.

The thickness of inner scale in Fig. 10 is very thin, indicating the formation of Cr₂O₃ layer in the early stage. Ni enrichment is observed and Fe₂Nb Laves phase is dissolved into the substrate in the Cr depletion zone. It is clearly observed that the morphology of the oxide scale in the long-term exposure is almost the same as that formed in the early stage.

3.2 Surface oxygen potential measurement

Figure 11 shows temperatures and electromotive forces generated in both the cell and the oxygen sensor during surface oxygen potential measurement at 1073 K. The temperature difference between the sample and the Pt electrode in the cell (fixed at 20 mm below the specimen) is around 5 K, while the temperature difference between the sample and the oxygen sensor is around 20 K. Although the difference about 20 K in temperature gives the difference about 12 mV in EMF, this is still in the range of EMF fluctuation in this measurement. When temperature of the
sample reaches to around 850 K, the cell is working. In this study, measurements are proceeded at the time when temperature of the sample reaches 850 K (t = 0). In the early stage up to about 20 ks, electromotive force of the cell (E\text{cell}) exhibits a positive value and increases to about 180 mV. EMF gradually decreases to about 70 mV after 100 ks and reaches to 50 mV at the end of the measurement. On the other hand, electromotive force of the oxygen sensor (E\text{sensor}) is almost constant values of around 630 mV, which corresponds to the chemical potential of oxygen in the atmosphere.

4. Discussion

4.1 Microstructure development of the oxide scale formed on the Fe–20Cr–30Ni–2Nb steel during steam oxidation at 1073 K

Microstructure development of the oxide scale formed on the steel at 1073 K is discussed based on microstructure observation. Figure 12 shows a schematic illustration of microstructure development of the oxide scale during the early stage of steam oxidation. Fe3O4 covers the surface as the outer scale and both internal oxidation and discontinuous Cr2O3 layer forms in the early stage of steam oxidation (Fig. 12(a)). Ueda et al.7 investigated the effect of water vapor on the transition from internal to external oxidation of the Fe–xCr–30Ni (at%) alloy (x = 5, 20 and 30) at 1073 K under the Fe/FeO equilibrium. Oxide map obtained in the paper7 indicated that the Fe–20Cr–30Ni (at%) alloy is in the transition region and oxide scale consists of both internal and external oxidations. When internal oxidation occurs in the early stage, Fe–Cr spinel is precipitated as internal oxides and the nodules of Ni–Fe alloy forms on the IOZ due to the precipitation of oxides in the matrix. The metallic nodule starts to oxidize to form magnetite as the outer scale and remaining nodules are located at the interface of the duplex scale. Based on the Fe–Ni–O ternary phase diagram at 1065 K,9 Ni–Fe alloy is equilibrated with (Fe,Ni)3O4 in the low P\text{O}_2 region.

When the transition from internal to external oxidation has finished and the continuous layer of Cr2O3 has fully covered the oxide scale/steel interface, the IOZ formed in the early stage becomes inner scale (Fig. 12(b)). The inner scale consists of (Fe,Cr)3O4 and Fe–Ni metallic alloy. In this steel, the transition from internal to external oxidation has finished within 18.4 ks at 1073 K (Fig. 4). Nb addition to the steel enhances Cr2O3 formation, because Nb may react with dissolved oxygen in the steel. Nb concentration in the substrate is about 0.8 at% and the small amount of Nb acts as an oxygen getter.

After formation of the continuous Cr2O3 layer, the growth rate of the oxide scale is decreased by the Cr2O3 layer. Moreover, the chemical potential of oxygen at the Cr2O3/inner scale interface increases, resulting in the oxidation of metallic phases in the duplex scale. Oxidation of metallic phases gives many voids in the oxide scale (Fig. 12(c)). On the other hand, Cr depletion zone starts to form in the substrate, because of the growth of Cr2O3 layer. Precipitated free zone of Fe2Nb Laves phase is also observed in this zone. When Fe and Cr in the substrate is consumed by the formations of Cr2O3 and other Fe base oxides, enrichment of Ni occurs. Based on the quaternary phase diagram of Fe–Cr–Ni–Nb at 1073 K, enrichment of Ni in the matrix changes thermodynamic stability of Fe2Nb Laves phase. Fe2Nb Laves phase becomes unstable in this bulk composition and may dissolve into the substrate. Dissolved Nb is oxidized to form Nb oxide at the Cr2O3/steel interface.

4.2 Relation between scale formation and oxygen chemical potential at the scale surface in the early stage of steam oxidation

Figure 13 shows the chemical potential of oxygen at the scale surface (2\mu\text{O}_{ad}) during steam oxidation of the steel at 1073 K. The chemical potential of oxygen at the scale surface is calculate based on eq. (5). The oxygen chemical potential in the atmosphere (\mu\text{O}_{2,Atm}) is also plotted in Fig. 13. Measurement was proceeded at the time when temperature of the sample reaches 850 K (t = 0). In the early stage up to
around 20 ks, the chemical potential of oxygen at the surface drops 60 kJ mol$^{-1}$ lower than that in the atmosphere and it gradually increases up to around 100 ks and becomes constant value, which is 20 kJ mol$^{-1}$ lower than that in the atmosphere. In the early stage, magnetite covers the surface and growth rate of the oxide scale obeys parabolic rate law. The chemical potential of oxygen at the surface decreases due to the consumption of oxygen. After continuous Cr$_2$O$_3$ layer forms at the scale/steel interface (after 20 ks), outward diffusion of cation though the Cr$_2$O$_3$ scale is limited and the growth rate of the oxide scale is suppressed by the Cr$_2$O$_3$ layer (Fig. 8). Decrease of oxygen consumption at the surface leads to the increase of the surface oxygen chemical potential. Figure 14 shows elemental mappings and scale morphology beneath the tip of the solid electrolyte after the measurements. Although the tip of CSZ is embedded in the outer scale, the electrochemical reaction occurs at the triple phase boundary of CSZ, magnetite and gas phase. The Cr$_2$O$_3$ layer continuously forms beneath the oxide scale near the triple phase boundary. Mass transport though the oxide scale is suppressed by the Cr$_2$O$_3$ layer, resulting in the increase of the oxygen chemical potential at the scale surface. Continuous monitoring of the oxygen chemical potential at the surface gives us the change of oxidation behavior due to the formation of Cr$_2$O$_3$ layer.

4.3 Evaluation of steam oxidation resistance at 1073 K for the application to further advanced steam power plants

Figure 15 shows the prediction of total oxide thickness after long-term exposure in steam condition at 1073 K. In the early stage up to around 24 h, the total thickness of the oxide scale formed on this steel obeys parabolic rate law. Continuous Cr$_2$O$_3$ layer does not form at the scale/steel interface in this stage and the growth rate of the oxide scale is almost the same as that of the commercial austenitic steel such as type 316 steel. The growth rate of the scale decreases after 24 h, because continuous layer of Cr$_2$O$_3$ at the scale/steel interface acts as barrier for scale formation. Although the thickness is scattering, the growth rate of the oxide scale becomes extremely small. These data points are located between type 316 steel and Fe–25Cr ferritic alloy. Around 10$^3$h, the estimated thickness in this steel is the same as that formed on Cr$_2$O$_3$ forming alloy. If the same oxide structure observed in this study is maintained and growth rate of the oxide scale is governed by mass transport through the oxide scale, this steel has a high steam oxidation resistance in the long-term exposure. After steam oxidation at 1073 K for 10$^5$h, this steel is expected to have oxide scale less than around 100 µm, which is the empirically-defined criterion of spallation. (Probability of spallation reaches 0.5, when the thickness of the inner scale becomes around 100 µm.) Based on the results, this steel is applicable as piping materials in further advanced fossil fuel power plants.

5. Conclusion

Steam oxidation of the Fe–20Cr–30Ni–2Nb (at%) austenitic steel has conducted at 1073 K to clarify microstructure development of the oxide scale and to evaluate long-term steam oxidation resistance based on the kinetic data. In the early stage, oxide scale mainly consists of outer magnetite.
and the mixture of internal oxidation zone and continuous layer of Cr$_2$O$_3$ as the inner scale. The growth rate of the scale is almost the same as that of commercial type 316 steel. After the formation of continuous Cr$_2$O$_3$ layer, internal oxidation zone becomes inner scale and the growth rate is suppressed by the Cr$_2$O$_3$ layer. In this steel, Cr$_2$O$_3$ layer is easy to form at the scale/steel interface compared to the commercial austenitic steels, because the transition from internal to external oxidation has finished within about 20 ks. The oxygen chemical potential at the scale surface decreased in the early stage compared to that in the atmosphere and recovered after the formation of continuous Cr$_2$O$_3$ layer. Based on the kinetics data, this steel has a good steam oxidation resistance compared with the commercial austenitic steels and is applicable as piping materials in further advanced fossil fuel power plants.

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REFERENCES