Relationship between Pre-Oxidized Film Structures and Corrosion Resistance of Ferritic Stainless Steels in High Temperature Pure Water

Kazuo Yamanaka* and Yasushi Matsuda*

The effect of pre-oxidation conditions on metal release of Ti-added SUSXM8 and 410Ti ferritic stainless steels in deaerated pure water at 488 K was investigated. The pre-oxidation treatments in the atmosphere of low oxygen potential, such as high purity argon gas and high vacuum condition at 1123 K for short time, were effective in decreasing the metal dissolution. The pre-oxide films were composed of outer Ti_2O_3 and inner $MnCr_2O_4$ layers. Therefore, a small quantity of titanium addition to high purity ferritic stainless steels was effective in decreasing the metal dissolution through the formation of thin titanium oxide film, together with the suppression of the sensitization, by heat-treatment in the atmosphere of low oxygen potential. The key factors controlling the metal dissolution are thickness and denseness together with chemical composition of the oxide films.

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I. Introduction

Deposition of radioactive corrosion products on the primary water components causes radiation build-up in light water reactor (LWR) plants. Reduction of radiation exposure is one of the most important subjects of LWR plants as well as improvements of reliability and availability⁽¹⁾.

Several methods, including zinc injection into the primary water⁽²⁾, use of low cobalt materials and pre-filming of the primary water components⁽³⁾⁽⁴⁾ for suppressing corrosion and deposition of radioactive ions, have been proposed and applied to some actual plants.

The pre-filming methods of the primary water components have been carried out during the nuclear heat-up phase of the preoperation process. It is, however, difficult to apply such pre-filming methods to heater tubes of feedwater and moisture separator heater (MSH) systems because of the lack of heat source. Thus, a preliminary film treatment before construction seems to be necessary to such components. This paper describes the effect of pre-oxidized film treatments of the ferritic stainless steels on metal release in high temperature water in relation to the film structure.

II. Experimental Procedures

1. Materials

SUS410 Ti (13 %Cr-Ti) and XM8 (18 %Cr-Ti) ferritic stainless steels, containing titanium more than 20 times the sum of carbon and nitrogen to prevent the in-

Table 1 Chemical compositions of the steels (mass %).

Steels	C	Si	Mn	P	S	Ni	Cr	Ti	N
XM8	0.008	0.40	0.48	0.020	0.001	0.20	17.77	0.60	0.0087
410Ti	0.006	0.46	0.41	0.026	0.001	0.17	13.08	0.56	0.0095

tergranular stress corrosion cracking (IGSCC) in high temperature water, were used. Table 1 shows the chemical compositions of the steels. The steels were melted industrially by an electric arc furnace, and tubes of 19.05 mm in diameter and 1.90 mm in thickness were obtained by hot forging, hot rolling and cold rolling.

Test pieces of 40 mm in length were cut out from the tube, and their internal and external surfaces were polished with SiC paper up to #1000, and degreased with acetone.

Pre-filmed specimens were prepared by oxidizing in a tubular furnace heated by a nickrome wire heater under the following conditions:

- (1) Exposed in argon gas of 99.999, 99.99 and 99.9% at 1123 K for 30 ~ 1800 s (0.5 ~ 30 min).
- (2) Exposed in vacuum of 2.7×10^{-3} , 2.7×10^{-2} , and 2.7 Pa at 1123 K for 600 s (10 min).

2. Corrosion test in high temperature water

Corrosion tests were undertaken in a stand-still autoclave made of SUS316L at 488 K for 1.8 Ms (500 h) and 7.2 Ms (2000 h) in deaerated pure water (electrical conductivity: $< 20 \mu S/m$). DO (Dissolved oxygen) concentration in the test solution was as low as 5-10 ppb. Some tests were carried out by using a platinum container put in the autoclave as shown in Fig. 1 to avoid the contamination by dissolved metal ions from the autoclave.

The amount of the dissolved metal (W_s) was calculated

* Iron and Steel Research Laboratories, Sumitomo Metal Industries, Ltd., Amagasaki 660, Japan.

Fig. 1 Autoclave test equipment.

using the following equation⁽⁵⁾:

$$W_s = W_2 - W_3 + \alpha \{ (W_3 - W_4) - (W_2 - W_1) \} \quad (1)$$

where

W_1 is the initial mass of specimen

W_2 is the mass after oxidation treatment

W_3 is the mass after the corrosion test

W_4 is the de-scaled mass after the corrosion test

α is the index referring to the mass ratio of oxygen to the oxide (e.g. $\alpha = O_3/M_2O_3 \approx 0.33$)

De-scaling was done by immersing the specimen in boiling 10% NaOH + 30 g/L $KMnO_4$ solution for 300 s (5 min), in boiling 10% ammonium citrate for 300 s (5 min), and the specimen was washed with pure water.

3. Surface film analysis

Surface film analysis was done using a Laser Raman spectroscope (LRS; Nippon Spectroscopy Co., Type NR-1100), an ion micro mass analyser (IMMA; ARL Co.) and an analytical electron microscope (AEM; Hitachi, Type HU-700H). The specimens for AEM were prepared as thin foils extracted in 5% bromine alcohol. The assignment of the LRS spectra was done with reference to standard LRS spectra measured for known oxide substances made by High Purity Chemical Laboratory Co., which were identified by X-ray diffraction.

III. Experimental Results

1. Analysis of the oxide films

Figure 2 shows the results of film analysis by AEM of high purity (99.999%) argon gas oxidized SUSXM8

Fig. 2 Film analysis by AEM (analytical electron microscope) of high purity (99.999%) argon gas oxidized SUSXM8 stainless steel.

stainless steel heat-treated at 1123 K for various time intervals. Titanium concentration of the film linearly increases with logarithm of oxidation time, and the film oxidized for 1800 s (30 min) at 1123 K is composed of about 90% titanium. As can be seen in Fig. 2, the film morphology oxidized at 1123 K for short time (30 s) is porous. It is, however, observed that the metal surface is covered with fine oxide particles all over by oxidizing for more than 60 s and the coarsening of oxide particles occurs by increasing the oxidation time at 1123 K. A similar compositional change in oxide films is observed for SUS410Ti as shown in Fig. 3.

Figure 4 shows in-depth profiles of Ti, Cr, Mn, Fe and O elements in the oxide film of SUS410Ti steel formed in high purity (99.999%) argon gas at 1123 K for various time, analyzed by IMMA. The titanium concentration at

Fig. 3 Film analysis by AEM (analytical electron microscope) of high purity (99.999%) argon gas oxidized SUS410Ti stainless steel.

Fig. 4 In-depth profiles of Ti, Cr, Mn, Fe and O elements by IMMA of high purity (99.999%) argon gas oxidized SUS410Ti stainless steel heat-treated at 1123 K for various time.

the metal surface increases with increasing oxidation time at 1123 K for both SUS410Ti and XM8 steels, whereas the chromium and manganese concentrations are high at the inner layer beneath the metal surface and almost unchanged with oxidation time at 1123 K.

Figure 5 shows the relationship between the thickness of oxide film and oxidizing time at 1123 K for both SUS410Ti and XM8 steels in high purity argon gas atmosphere. The film thickness is expressed by sputtering time taken for the O intensity of IMMA to reach a level

Fig. 5 The relationship between the thickness of oxide film and oxidation time at 1123 K for both SUSXM8 and 410Ti stainless steels in high purity argon gas atmosphere.

comparable to that of the metal matrix. It can be seen from Fig. 5 that the thickness of the oxide film linearly increases with logarithm of oxidation time for both SUS410Ti and XM8 steels. It was estimated that the film thickness of the steels oxidized in high purity argon gas at 1123 K for 600 s (10 min) may be about 100nm under the condition of the sputtering rate (~ 0.3 nm/s) of the present work.

LRS spectra of steels oxidized in high purity argon gas indicated mainly two types of oxides, Ti_2O_3 and MnCr_2O_4 . Figure 6 shows an example of the film analysis by LRS of SUS XM8 steel oxidized in high purity argon gas at 1123 K for 600 s (10 min). Figure 7 shows LRS spectra for standard spinel type oxides and titanium oxides

Fig. 6 Film analysis by LRS of high purity (99.999%) argon gas oxidized SUSXM8 stainless steel heat-treated at 1123 K for 600 s.

Fig. 7 Laser-Raman spectra of several standard spinel oxides and titanium oxides.

used for identification of film components.

The LRS spectrum shown in Fig. 6 suggests the presence of Ti_2O_3 . Furthermore, IMMA (Fig. 4) and LRS (Fig. 6) data suggest that the oxide film formed on the steels in high purity argon gas may have a double layer structure consisting of outer Ti_2O_3 and inner MnCr_2O_4 layers.

The effect of argon gas purity on the composition of oxide film formed on the ferritic stainless steels at 1123 K was studied by AEM and LRS. Figure 8 shows film analysis by AEM of SUSXM8 stainless steel argon-oxidized at 1123 K for 600 s (10 min). Lowering argon gas purity tends to decrease titanium concentration and to increase chromium and manganese concentrations. The oxide phases in the argon gas purity range from 99.999 to 99.9% could be identified to be Ti_2O_3 and MnCr_2O_4 .

The effect of vacuum pressure on the oxide film compositions of the ferritic stainless steels vacuum-oxidized at 1123 K was also studied. Figure 9 shows the effect of vacuum pressure on the oxide film compositions of SUSXM8 stainless steel vacuum-oxidized at 1123 K for 600 s (10 min). The oxide film highly concentrated with titanium is formed in high vacuum (above about 10^{-2} Pa)

Fig. 8 Effect of argon gas purity on oxide film composition of SUSXM8 stainless steel oxidized in argon gases at 1123 K for 600 s.

conditions, whereas the film becomes enriched in chromium and manganese in low vacuum (below about 10^{-2} Pa) conditions.

Fig. 9 Effect of vacuum pressure on oxide film composition on SUSXM8 stainless steel vacuum-oxidized at 1123 K for 600 s.

2. Immersion test in high temperature water

Figure 10 shows the immersion test results of ferritic stainless steels oxidized in high purity argon at 1123 K for various time intervals in high temperature pure water at 488 K for 1.8 Ms (500 h). In this figure, the vertical axis refers to the ratio of metal release of oxidized specimen to as-polished specimen. Thus, the smaller this value, the better is the suppression of the metal dissolution. The minimum metal dissolution is obtained by argon-oxidized for 600 s at 1123 K for both SUS410Ti and XM8 steels. Prolonged oxidation over 600 s was useless for the reduction of metal dissolution.

Figure 11 shows the effect of argon gas purity on the metal dissolution of ferritic stainless steels pre-oxidized in argon gases at 1123 K for 600 s in high temperature pure water at 488 K for 1.8 Ms. The metal dissolution from both SUS410Ti and XM8 steels increases with lowering argon gas purity below about 99.99%. In vacuum-oxidized ferritic stainless steels, similar results were obtained that the metal dissolution increased with increasing pressure higher than about 10^{-2} Pa.

3. Film analysis after immersion test in high temperature water

To clarify the stability of the pre-filming in high temperature water, the corroded films after immersion test

Fig. 10 Effect of oxidation time on the corrosion resistance of ferritic stainless steels oxidized in high purity (99.999%) argon gas in high temperature deaerated pure water at 488 K for 1.8 Ms.

Fig. 11 Effect of argon gas purity on the corrosion resistance of argon-oxidized ferritic stainless steels in high temperature deaerated pure water at 488 K for 1.8 Ms.

were analysed by AEM and LRS.

Figure 12 shows analytical results of surface films by both AEM and LRS for high purity (99.999%) argon-oxidized SUSXM8 steel at 1123 K for 600 s before and after immersion in high temperature deaerated pure water at 488 K. After immersion for 864 ks (240 h) at 488 K, as shown in Fig. 12(b), the angular blackish corrosion products [B parts in Fig. 12(b)] are observed in various places on the film and seem to be mainly FeCr_2O_4 .

On the other hand, the bright fields [A parts in Fig. 12(b)] except blackish corrosion products are assumed mainly as Ti_2O_3 identical with the pre-oxidized film.

After immersion for 1.8 Ms (500 h) at 488 K, as shown in Fig. 12(c), all over the surface of the specimen is covered with the blackish corrosion products mainly composed of FeCr_2O_4 . However, the bright parts of the specimen without corrosion products [A parts in Fig. 12(c)] have almost the same composition as that of the pre-filmed specimen.

From these results, the thin titanium-rich pre-oxidized film remains stable in high temperature water and is covered with the corrosion products mainly composed of FeCr_2O_4 spinel oxide.

IV. Discussion

1. Characteristics of the oxide films of Ti-added ferritic stainless steels

A small quantity of titanium addition to high purity ferritic stainless steels led to formation of thin titanium oxide film by heating in low oxygen potential atmosphere such as high purity argon gas and high vacuum condition at 1123 K and to decrease in metal dissolution in high temperature pure water, as shown in Figs. 8, 9 and 10.

Yoshihara and Nii⁽⁶⁾ have already reported that the precipitation of titanium carbide on the surface of

Fig. 12 Surface film analysis by AEM and LRS of high purity (99.999%) argon-oxidized SUSXM8 stainless steel [1123K-600 s] before and after immersion in high temperature deaerated pure water at 488 K (Platinum vessel used).

SUS321 containing 0.037% C occurs by heating in a high vacuum condition at 1100 K. In our experiments, although the precipitation of titanium carbide may be difficult because of very low concentration of carbon dissolved in the bulk, titanium oxides are formed on the metal surface. Titanium diffused onto the surface of the stainless steels is exposed to the low oxygen potential atmosphere and combined with oxygen to form titanium oxides (mainly Ti_2O_3). Although a stable phase of titanium oxide is TiO_2 , a metastable Ti_2O_3 may remain stable because of very low concentration of oxygen in the atmosphere and possibly because of relatively short oxidation time.

With raising the oxygen potential in the atmosphere, chromium and manganese preferentially became oxidized and the chromium and manganese enriched oxide films were formed. This is consistent with the relationship between oxygen partial pressure and Gibbs free energy of the formation of several oxides⁽⁷⁾.

2. Stability of oxide film in high temperature water

The stability of the oxide film having a double layer structure of $\text{Ti}_2\text{O}_3 + \text{MnCr}_2\text{O}_4$ was discussed on the basis of the pH-potential diagrams of Ti- H_2O (a) and Ni- H_2O (b) at 523 K as shown in Fig. 13.

Fig. 13 pH-potential diagrams at 523 K.

The diagram for Ti- H_2O was obtained by following the same procedures derived by Hirano and Kurosawa⁽⁸⁾ using Gibbs' free energy equations for ion concentration of 10^{-1} mol/m^3 . The diagram for Ni- H_2O was referred by Hemmi *et al.*⁽⁹⁾ The pH value of high temperature pure water in the temperature range of 473 ~ 523 K was reported to be around 5.6⁽¹⁰⁾ and indicated by vertical broken lines in Fig. 13. The corrosion potential of SUS304 stainless steel in deaerated high temperature pure water of 473 ~ 523 K was reported to be around -600 mV (SHE)⁽¹¹⁾. The corrosion potential of SUS304

stainless steel in high temperature pure water at 505 K was reported to be -500 to -50 mV (SHE)⁽¹¹⁾ in the DO level of 20 to 200 ppb, corresponding to normal operation conditions of BWR, and indicated by the horizontal shaded bands in Fig. 13. NiFe_2O_4 spinel oxide can exist stably in a potential range of -600 to -50 mV (SHE). The spinel oxide MnCr_2O_4 may exist stably under these environments because of the same crystal structure as NiFe_2O_4 .

On the other hand, TiO_2 is stable in both deaerated high temperature pure water and BWR conditions as can be seen in Fig. 13(a). However, since almost no DO exists in deaerated water in the present experiment, the oxidation reaction of $\text{Ti}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow 2\text{TiO}_2$ seems hardly to occur and Ti_2O_3 may remain stable after immersion test in high temperature water.

Thus, it may be concluded from the above discussion that a double layer film of Ti_2O_3 and MnCr_2O_4 seems to be stable in deaerated high temperature pure water.

The corrosion products newly formed in the high temperature water were mainly FeCr_2O_4 and somewhat differed from $\text{Ni(Fe, Cr)}_2\text{O}_4$ formed in SUS304L austenitic stainless steel as already reported⁽¹²⁾, but both were in the same crystal structure of spinel oxide M_3O_4 (M: Metal).

Since the corrosion products were formed on the

pre-filmed steels as shown in Fig. 12, the metal dissolution can be effectively suppressed for a long period of time by the preliminary treatment for the formation of a thin oxide film onto the steel surface. It should be noted that the key factors controlling the metal dissolution are thickness and denseness together with chemical composition of the oxide films. Figure 14 schematically shows the key factors of the pre-oxidized film controlling the metal dissolution in high temperature water. As shown in Fig. 10, the optimum thickness exists for suppression of the metal dissolution, and film thickening by prolonged oxidation treatment lowers the suppression efficiency. Similar results were already obtained by Fujiwara *et al.*⁽⁵⁾ for SUS304L steel. This may be interpreted as follows: excessive increase in film thickness induces the stress in the oxide film and results in detachment at the oxide film/steel interface.

Concerning denseness of the film, as can be seen in Fig. 2, the oxide film formed in low oxygen potential atmosphere is composed of fine oxide particles and hence contains many defects in the film. We had already reported that the oxide film formed by the wet pre-filming methods, such as immersion treatments in high temperature water and nitric acid solutions, was dense and smooth and was effective in decreasing the metal dissolution⁽¹³⁾. The wet pre-filming methods can, therefore, form the dense oxide film in comparison with the dry methods such as this paper, although the application to the actual plant is limited.

V. Conclusions

The effect of oxidation conditions on metal release of both SUSXM8 and 410Ti ferritic stainless steels in deaerated pure water at 488 K was investigated. The behavior of metal release was also discussed in relation to the surface films which were formed by various oxidation conditions. The results obtained are as follows:

(1) The pre-oxidation treatments in the atmosphere of low oxygen potential such as high purity argon gas and high vacuum condition at 1123 K for short time were effective in decreasing the metal dissolution, and the oxide films primarily had a double oxide layer consisting of outer Ti_2O_3 and inner MnCr_2O_4 layers.

(2) Titanium concentration of surface oxide film increased in proportion to the logarithm of heating time at 1123 K.

(3) A small quantity of titanium addition to high purity ferritic stainless steels was effective in decreasing the metal dissolution through the formation of thin titanium oxide film, together with the suppression of the sensitization, by heat-treatment in the atmosphere of low oxygen potential.

(4) It may be concluded that the key factors controlling the metal dissolution are thickness and denseness together with chemical composition of the oxide films.

REFERENCES

- (1) R. A. Show, C. J. Wood, M. D. Noughton and H. Ocken: *Proc.*

Fig. 14 The key factors of the pre-oxidized film controlling the metal dissolution in high temperature water.

- Water Chemistry for Nuclear Reactor Systems III*, BNES, 1983.
- (2) W. J. Marble: EPRI Report NP-4072, June 1985.
- (3) R. H. Asay: *Power*, **131** [4] (1987), 15.
- (4) T. Honda, A. Minato, M. Izumiya, K. Ohsumi and H. Mitsubayashi: *J. Nucl. Sci. & Tech.*, **20** (1983), 871.
- (5) K. Fujiwara, H. Tomari, T. Nakayama and K. Shimogori: *Boshoku Gijutsu*, **36** (1987), 368.
- (6) K. Yoshihara and K. Nii: *J. Japan Inst. Metals*, **46** (1982), 963.
- (7) J. F. Elliott and M. Gleiser: *Thermochemistry for Steelmaking*, Vol. 1 (1960), Addison-Wesley.
- (8) H. Hirano and T. Kurosawa: *Boshoku Gijutsu*, **34** (1985), 92.
- (9) Y. Hemmi, S. Negishi, H. Yamazaki, Y. Morikawa and T. Baba: Proc. 1988 Annual Meeting of Japan Atomic Energy Soc., J-23 (1983).
- (10) J. R. Fisher and H. L. Barnes: *J. Phys. Chem.*, **76** (1972), 90.
- (11) M. E. Indig and J. E. Weber: *Corrosion*, **41** (1985), 19.
- (12) K. Yamanaka and Y. Matsuda: *Boshoku Gijutsu*, **39** (1990), 283.
- (13) K. Yamanaka and Y. Matsuda: *Proc. of 37th Joint Symposium on Corrosion Science and Technology*, D-106, August, 1990.