

Proceedings from the Fourth International Conference on Advances in Materials Technology
for Fossil Power Plants, October 25–28, 2004, Hilton Head Island, South Carolina.
Copyright© 2005

APPLICATION OF THE PRE-OXIDATION TREATMENT IN AR GAS TO THE NIMS HIGH-STRENGTH STEELS

H. Kutsumi
H. Haruyama
F. Abe

National Institute for Materials Science, Japan
1-2-1, Sengen, Tsukuba, Ibaraki 305-0047, JAPAN

Abstract

In National Institute for Materials Science (NIMS), a dispersion of nano-size MX nitride particles along boundaries as well as in the matrix is achieved by reducing carbon concentration below 0.02%. This gives rise to excellent creep strength at 923K, as shown by approximately two orders of magnitude longer time to rupture than P92. The addition of large amount of boron exceeding 0.01% in combination with minimized nitrogen is also very effective to improve creep rupture strength by the stabilization of martensitic microstructure during creep. We have been trying to improve the steam oxidation resistance for these steels. A combination of high Si of 0.7%, high S of 40–60ppm and pre-oxidation treatment was applied to the present 9Cr steels strengthened by boron and by fine MX nitrides. Steam oxidation tests were carried out in steam at 923 K for up to 4000h. Pre-oxidation treatment in Ar gas at 973 K for 50h significantly improved to oxidation resistance in steam at 923 K by formation of protective Cr-rich oxide layer during pre-oxidation. The present steels subjected to pre-oxidation exhibited much lower mass gain in steam at 923 K than Mod.9Cr-1Mo steel at 873 K. The mass gains of the steels oxidized for over 1000h were lower than that of T91 at 873K. After pre-oxidation treatment, the mass gains of the present steels (oxidized in steam at 923K for over 4000h) were about zero, much lower than those of P91 at 873K and 923K. SEM/EDS analysis and the very low level of mass gain for the present steels after the pre-oxidation treatment suggests that protective Cr-rich oxide scale forms on the specimen surface. The Protective Cr-rich oxide scale was formed by pre-oxidation treatment and the modified steels exhibit excellent oxidation resistance in steam at 923K.

1. Introduction

For construction of high efficiency ultra-supercritical (USC) power plant, large diameter and thick section boiler components, such as main steam pipe and header, are required to withstand high temperatures of more than 873K over long periods. It is necessary to develop

new steels whose creep strength and steam oxidation resistance will be superior to those of conventional high Cr ferritic steels.

In National Institute for Materials Science (NIMS), a dispersion of nano-size MX nitride particles along boundaries as well as in the matrix is achieved by reducing carbon concentration below 0.02%¹⁾. This gives to excellent creep strength at 923K. On the other hand, the addition of large amount of boron exceeding 0.01% in combination with minimized nitrogen is very effective to stabilize the martensitic microstructure during creep through the stabilization of M₂₃C₆ carbides by an enrichment of boron²⁾. So, we have been trying to improve the steam oxidation resistance for these steels.

Authors have revealed that small amounts of sulfur as low as 40ppm improves the oxidation resistance of Mod.9Cr-1Mo steel³⁾. The present authors have revealed that the formation of protective Cr-rich oxide scale is archived by pre-oxidation treatment in argon gas containing small amounts of oxygen of 0.3ppm⁴⁾, really in excellent oxidation resistance for a 9Cr steel. The effect of pre-oxidation treatment on oxidation resistance in steam becomes more significant with increasing Si content. Based on those results, a combination of high Si of 0.7 %, high S of 40-60 ppm and pre-oxidation treatment was applied to the present 9Cr steels strengthened by boron and by fine MX nitrides for the improvement of oxidation resistance.

2. Experimental

Three 9Cr steels strengthened by 100 ppm boron (MARB1), by 200 ppm boron (MARB2) and by fine MX nitrides (MARN), were used for steam oxidation test. The chemical compositions of the steels used for steam oxidation test are shown in **Table 1** and heat treatment conditions are shown in **Table 2**. Steam oxidation test were carried out in a steam atmosphere at 923 K for up to 4000h.

Table 1 Chemical composition of three kinds of steels

| Steels | C | Si | Mn | P | S | Cr | W | Mo | Co | V | Nb | sol.Al | B | N | O |
|--------|--------|------|------|-------|-------|------|------|-------|------|-----|-------|--------|--------|-------|-------|
| MARB1 | 0.082 | 0.74 | 0.50 | 0.001 | 0.006 | 9.23 | 2.50 | <0.01 | 3.30 | 0.2 | 0.049 | 0.001 | 0.0097 | 0.001 | 0.003 |
| MARB2 | 0.082 | 0.73 | 0.49 | 0.001 | 0.005 | 9.16 | 2.47 | <0.01 | 3.30 | 0.2 | 0.048 | 0.002 | 0.0190 | 0.002 | 0.002 |
| MARN | 0.0049 | 0.78 | 0.49 | 0.001 | 0.004 | 8.95 | 2.50 | 0.01 | 3.33 | 0.2 | 0.048 | 0.001 | 0.0071 | 0.05 | 0.003 |
| T91 | 0.1 | 0.24 | 0.44 | 0.005 | 0.001 | 8.74 | - | 0.94 | - | 0.2 | 0.08 | 0.014 | - | 0.058 | - |

The specimens for oxidation tests were cut into a coupon shape of 10 x 20 x 2 mm by electrical-discharge machining from the bulk material. Finally the specimens were finished up with SiC abrasive papers of 320 grit.

Schematic illustration of steam oxidation test apparatus is shown in **Fig. 1**. Steam was generated from pure water, whose dissolved oxygen was less than 10 ppb and whose electric conductivity was under 8.0 mS/m, and then introduced into a test reactor. The flow rate of steam was kept to 0.21 l by the water supply to the steam generator. After rinsed in an ultrasonic bath with methanol and acetone, specimens were set in ceramic crucibles, which were placed in the test furnace. We discharged air from the test furnace with a vacuum pump and filled it with argon gas with dew point of 208 K and oxygen content of

Table 2 Heat treatment conditions

| Steels | Normalizing | Tempering |
|--------|------------------|----------------|
| MARB1 | 1423K x 0.5h, AC | 1073K x 1h, AC |
| MARB2 | 1423K x 0.5h, AC | 1073K x 1h, AC |
| MARN | 1373K x 0.5h, AC | 1073K x 1h, AC |
| T91 | 1333K x 1.5h, AC | 1033K x 1h, AC |

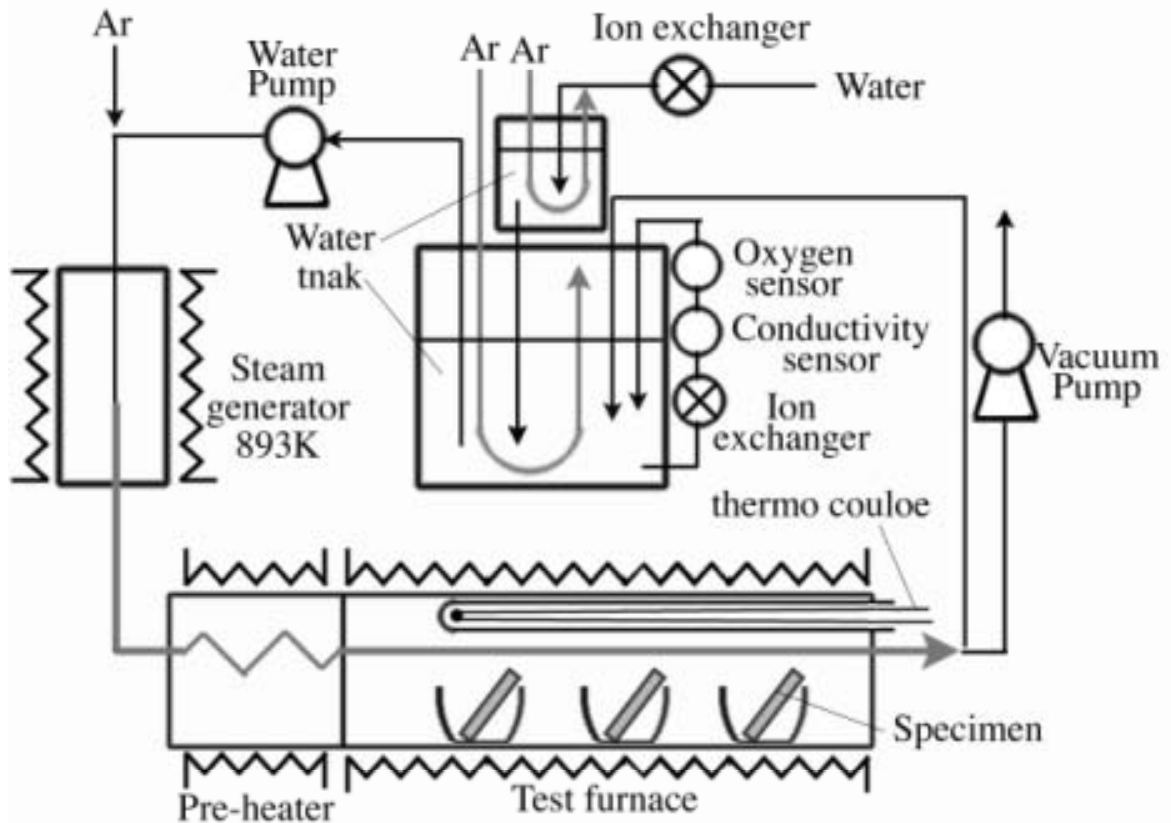


Fig.1 Steam oxidation test apparatus.

0.3 ppm and heated the test furnace up to 473K. The gas in the furnace was then exchanged with steam and then continued to be heated at 923K. The total heating operation took about 3 hours. The time for oxidation was defined as the time period from reaching oxidation temperature to shutting down the power.

On the other hand, after Ar was filled into the test furnace at 473K with above procedure, the temperature of the test furnace was heated to 973K, and pre-oxidation treatment was carried out for 50h. Then, Ar gas in the furnace was changed to steam and the steam oxidation test was carried out.

The cross section of the oxidized specimens was observed by optical microscope and scanning electron microscope (SEM). Element analysis near the specimen surface was carried out by EDX and WDX. The oxide layer was identified by thin film X-ray diffraction (XRD), XPS, and TEM.

3. Results and discussion

3.1 Effect of pre-oxidation treatment on oxidation behavior in steam at 923K

Fig.2 shows the optical micrographs of the cross section of oxide scale formed on surface of MARB1, MARB2 and MARN steels oxidized in steam at 923K for 100h and for 500h.

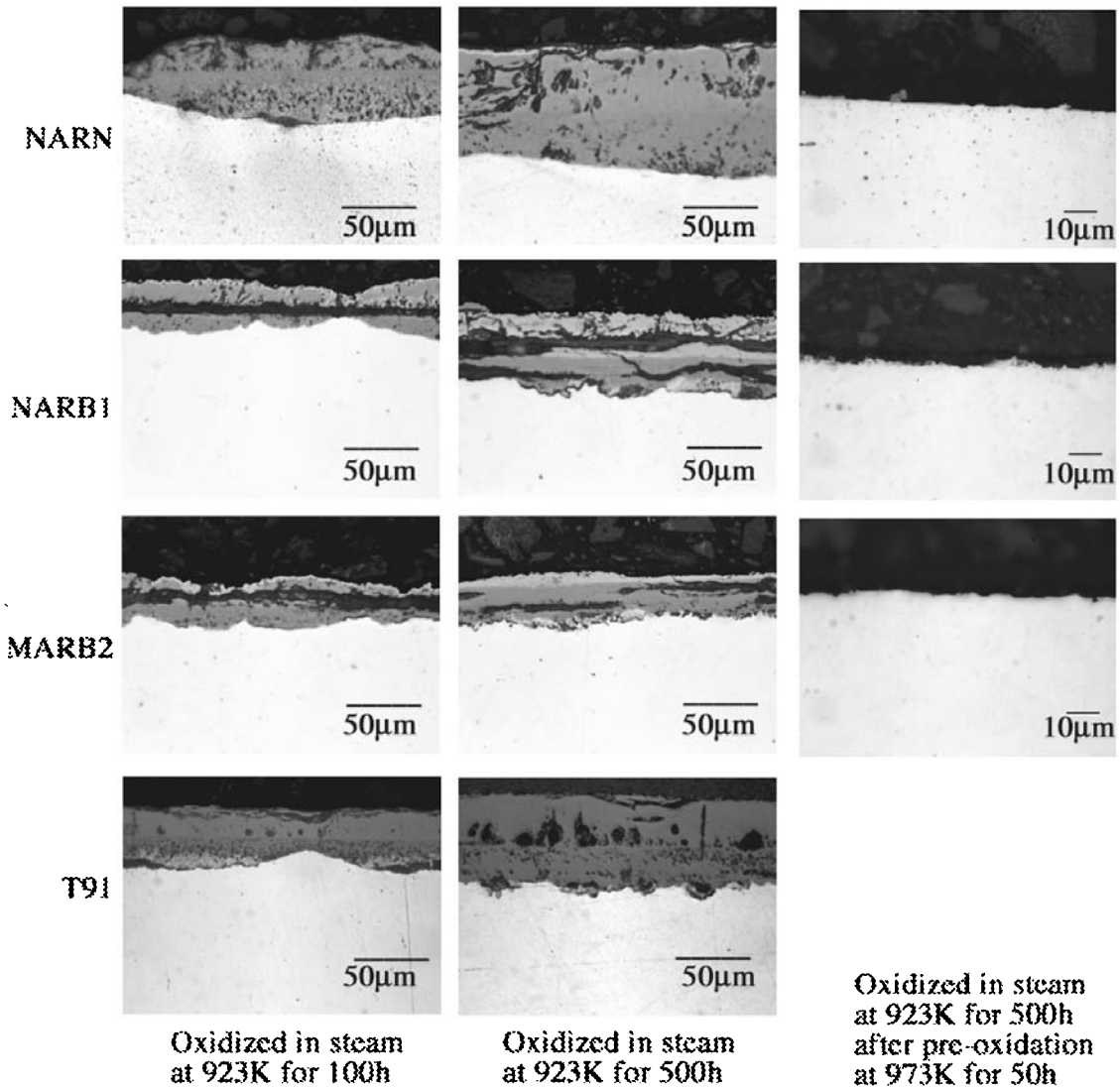


Fig.2 Oxide scales formed in steam at 923K for 100h and for 500h with and without pre-oxidation treatment

The thickness of surface oxide scales of MARB1 and MARB2 oxidized in steam at 923K for 100h and for 500h were about 30 µm and 50 µm respectively. These were thinner than that of T91, and seldom grew. The scale thickness of MARN oxidized for 500h was about 100 µm, and was somewhat thicker than that of T91. Oxide scales of all steels were two layers, composed of magnetite (Fe_3O_4) and Fe/Cr spinel oxide ($(\text{Fe,Cr})_3\text{O}_4$), but the scales of all NIMS steels were very uneven. The internal oxidized layer, which was generally seen in the base metal near the inner scale for conventional 9Cr ferritic steels, was not observed for NIMS steels. It is considered that sulfur contained in NIMS steels (40-60ppm) helped for Cr and Si to enrich near

the interface between the inner layer and base metal in the earlier stages of oxidation, and oxide layer of Si and Cr as the obstacle to oxygen's inner diffusion was formed.

On the other hand, scale thickness of NIMS steels were significantly reduced by pre-oxidation treatment. Thicknesses of the protective oxide scales were about 0.2 μ m and have not changed for 4000h. Details of the oxidization behavior for the present steels are further given in the following paragraph.

3.2 Change of the mass gains by steam oxidation

Fig.2 shows the mass gain of the present steels with and without pre-oxidation treatment, comparing with that of T91. The mass gains of MARB1 and MARB2 without pre-oxidation treatment are lower than that of T91 at 923K but higher than that at 873K for 100h. But those of MARB1 and MARB2 oxidized for 500h are lower than that of T91 at 873K.

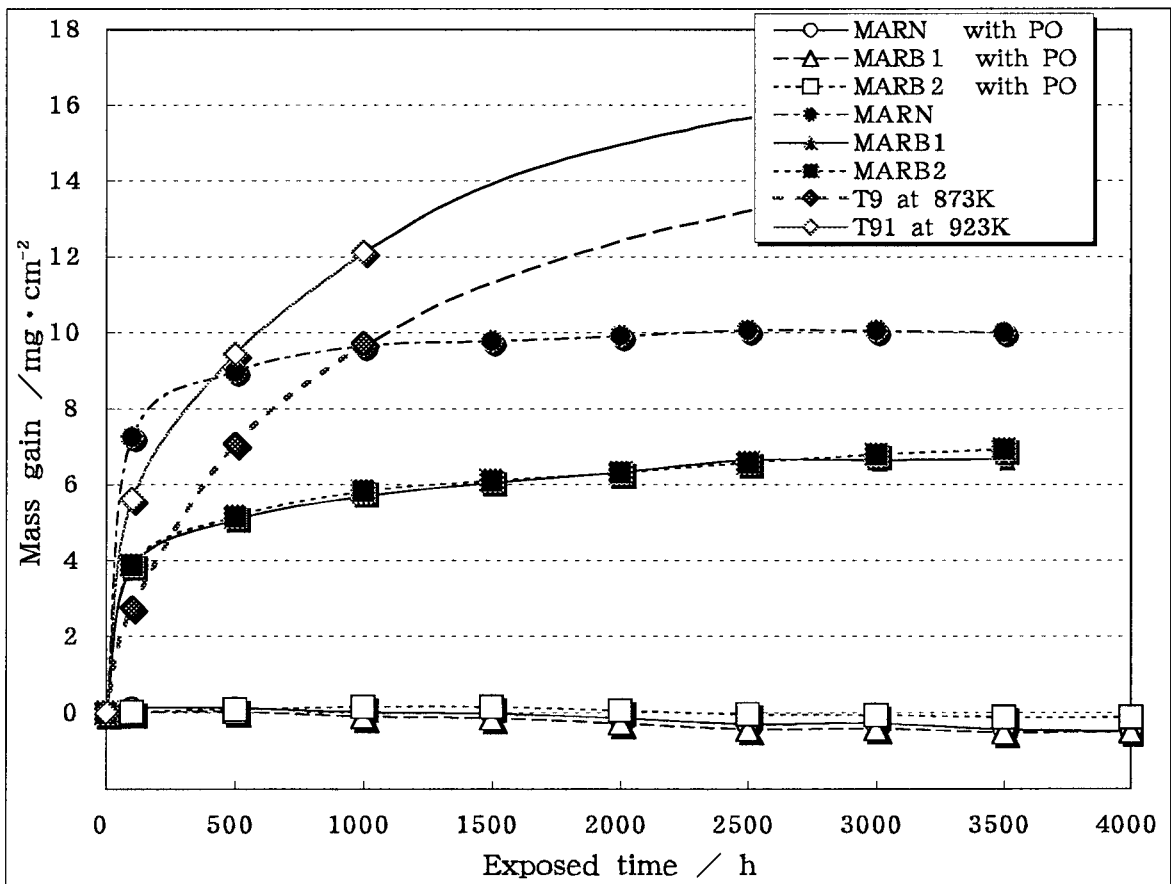


Fig.3 Mass gains of NIMS 9Cr Steels and T91 exposed in steam at 923K (and at 873K).

After pre-oxidation treatment, the mass gain of the MARB1, MARB2 and MARN steels are much lower than that of P91 at 873K and 923K. This suggests excellent oxidation resistance of the present steels. The pre-oxidation treatment significantly decreases the mass gain of MARB1, MARB2 and MARN steels in steam at 923K, although the mass gain of these steels at 923K is

lower even in no pre-oxidation condition than that of T91 at 873K and 923K. Recently, in the framework of Task3 in DOE vision 21 Project, Sarver and Tanzosh carried out oxidation test for ferritic and austenitic steels and Ni base superalloys in steam at 923K⁵. Their results demonstrated that the oxidation rate significantly decreased with Cr content in a range less than about 18% Cr. They also showed that the one exception to the Cr content effect was MARB2 steels, which displayed oxidation behavior equal to materials containing 18% Cr or more.

The oxidation rate is described by

$$\Delta W = (kt)^n$$

Where k is the rate constant and n is the exponent. The exponent n is evaluated to be 0.17, 0.16, 0.10 and 0.33 for MARB1, MARB2, MARN and T91 at 923K, while that for T91 at 873K is about 0.5, the same as reported by Komai⁶.

3.3 Structure of that oxide scale

Fig.4 and **Fig.5** shows the X-ray diffraction pattern and the SEM/EDS analysis respectively of the thin oxide layer formed on MARN steel exposed in steam at 923K for 100h after pre-oxidation treatment. X-ray diffraction peaks corresponding the Cr₂O₃, Magnetite (Fe₃O₄) and substrate (α -Fe) were detected. The phase noted as “☆:Cr₂O₃” in **Fig. 4** is similar as Eskolaite (Cr₂O₃) with rhombohedral structure. **Fig.5** shows that the thin oxide layer included Cr, Fe, Si and O.

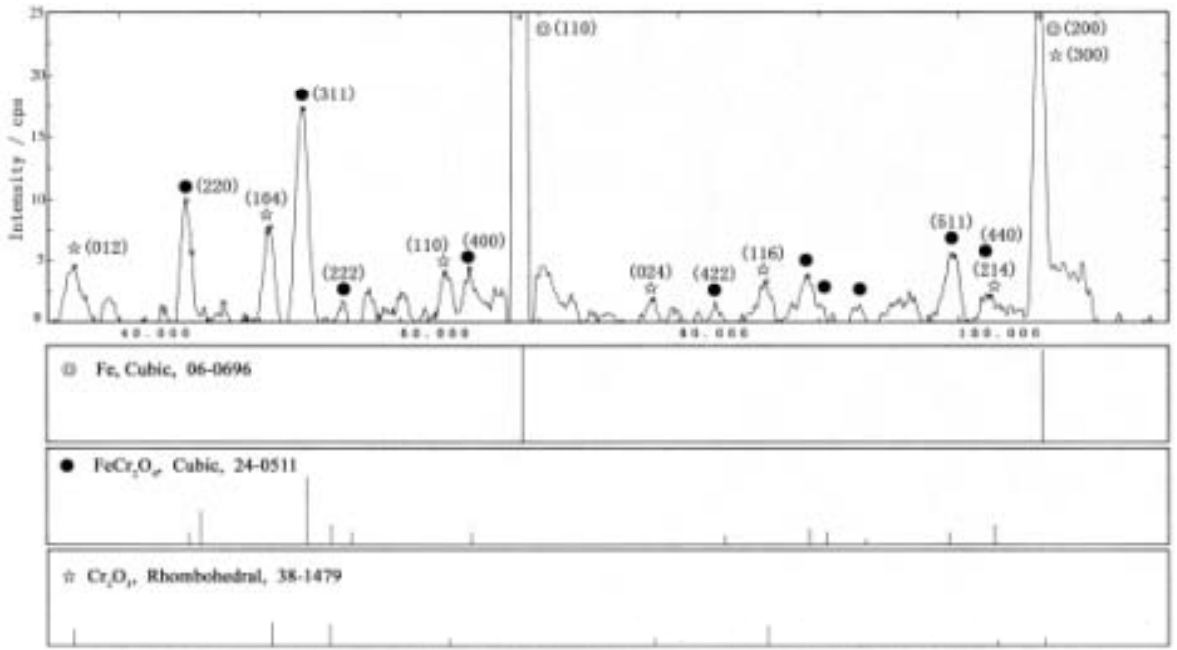


Fig.4 X-ray diffraction pattern of the thin oxide layer formed on MARN steel exposed in steam at 923K for 100h after pre-oxidation treatment.

Since the results of SEM/EDS analysis indicate that there is a high concentration of Cr in the surface layer, this phase may have the same structure as Cr_2O_3 but have a slightly different element composition. As the (110) peak of metal matrix ($\alpha\text{-Fe}$) is detected, the oxide layer seems to be very thin.

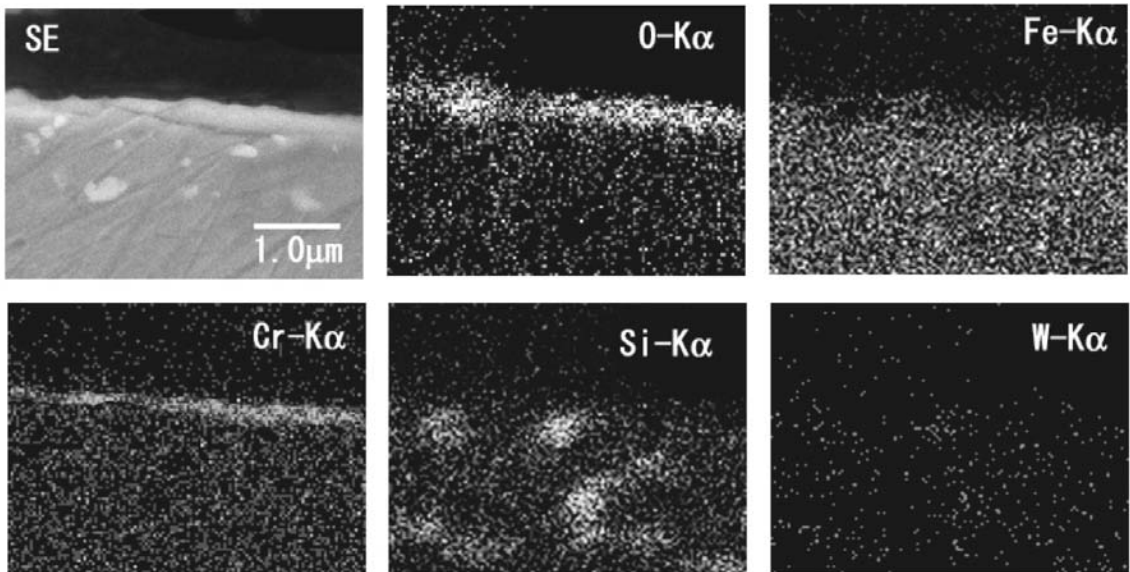


Fig.5 SEM/EDS analysis of cross section of the thin oxide layer formed on MARN steel exposed in steam at 923K for 100h after pre-oxidation treatment.

Fig.6 and **Fig.7** shows the TEM / EDS analysis and the electron diffraction pattern of the oxide

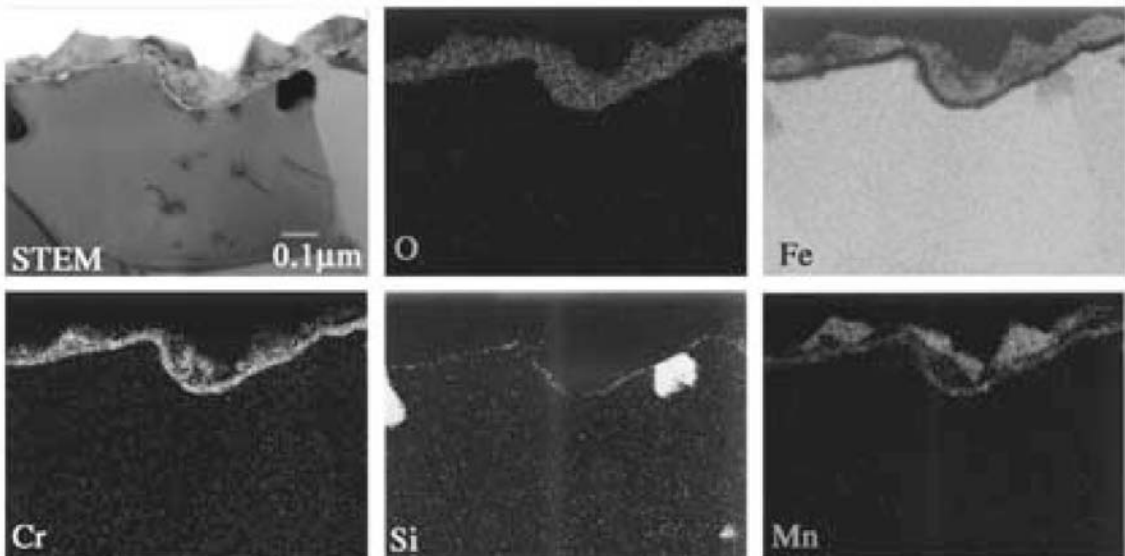


Fig.6 TEM / EDS of the oxide thin scale formed on the 9Cr-3W-NbV steel containing 0.8mass% Si by pre-oxidation treatment.

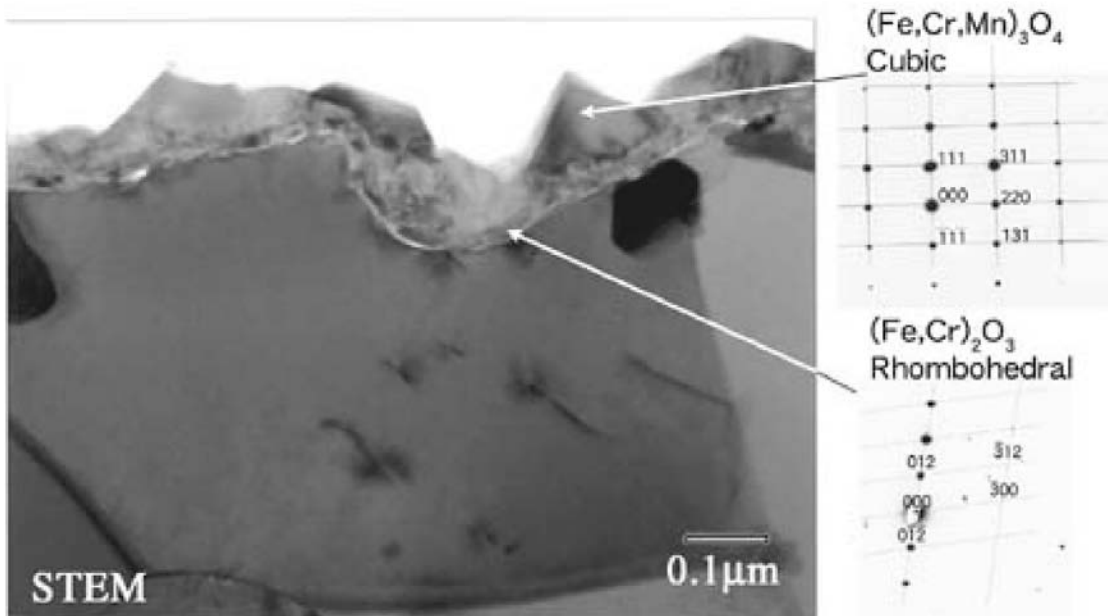


Fig.7 TEM image and electron diffraction patterns of the oxide thin scale formed on the 9Cr-3W-NbV steel containing 0.8 mass% Si by pre-oxidation treatment.

thin scale formed on the 9Cr-3W-NbV steel containing 0.8 mass% Si by pre-oxidation treatment in argon flow at 973K for 50h. Thickness of this thin oxide layer was about 0.1 μm, and it didn't change by steam oxidation. These figures show that the protective oxide layer on the surface of specimen formed by pre-oxidation in Ar is considered to be $(\text{Fe,Cr})_2\text{O}_3$ and $(\text{Fe,Cr,Mn})_3\text{O}_4$. The decrease of mass gain by the pre-oxidation treatment results from the formation of Cr-rich oxide scale during pre-oxidation.

4. Conclusion

The improvement of oxidation resistance in steam has been investigated for NIMS high-strength 9Cr steels and the following conclusions were obtained.

- (1) A combination of high Si of 0.7%, high S of 40-60ppm and pre-oxidation treatment was applied to the present 9Cr steels strengthened by boron and by fine MX nitrides.
- (2) After pre-oxidation treatment, the mass gain of the MARB1, MARB2 and MARN steels are much lower than that of P91 at 873K and 923K. This suggests excellent oxidation resistance of the present steels.
- (3) The pre-oxidation treatment significantly decreases the mass gain of MARB1, MARB2 and MARN steels in steam at 923K, although the mass gain of these steels at 923K is lower even in no pre-oxidation condition than that of T91 at 873K and 923K.
- (4) The protective oxide layer on the surface of specimen formed by pre-oxidation in Ar is considered to be $(\text{Fe,Cr})_2\text{O}_3$ and $(\text{Fe,Cr,Mn})_3\text{O}_4$. The decrease of mass gain by the pre-oxidation treatment results from the formation of Cr-rich oxide scale during pre-oxidation.

References:

- 1) M.Taneike, F. Abe and S.Sawada: Nature, 424(2003), 294.
- 2) T.Horiuchi, M.Igarashi and F. Abe: ISIJ International, 42(2002), S67.
- 3) H.Kutsumi, T.Itagaki and F.Abe: TETSU-TO-HAGANE, 88(2002), 520.
- 4) H.Kutsumi, T.Itagaki and F.Abe: CAMP-ISIJ, 15(2002),1319.
- 5) J.M.Sarver and J.M.Tanzosh: EPRI International Conference on Materials and Corrosion Experience, For Fossil Power Plants, November 18-21, USA (2003) in press.
- 6) N.Komai, F.Masuyama, Y.Sawaragi and A.Iseda:Rep. 123rd Committee on Heat-Registing Metals and alloys, Jpn. Soc., 41(2001), 239.