Characterization of Hot-Steam Oxidation Tested Chromosiliconized Heat-Resistant Austenitic Stainless Steel

Yasuhiro Hoshiyama1,*, Xiaoying Li2, Hanshan Dong2 and Akio Nishimoto1

1Department of Chemistry and Materials Engineering, Kansai University, Suita 564-8680, Japan
2School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

In this study, a duplex chromising-siliconizing coating was produced on heat-resistant austenitic stainless steel by pack cementation. The chromising-siliconizing of the duplex chromosiliconized coating was evaluated in 873 K hot steam for $3.6 \times 10^3$ ks, and the oxidized as well as the coated samples were characterized. A duplex chromosiliconizing coating has been successfully applied to heat-resistant austenitic stainless steel by pack cementation. This coating containing Cr and Si can effectively improve the oxidation resistance of heat-resistant austenitic stainless steel in 873 K hot steam for $3.6 \times 10^3$ ks. [doi:10.2320/matertrans.M2011396]

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1. Introduction

Austenitic stainless steels have long been used in power generation because of their good corrosion resistance, adequate mechanical properties, good formability, and cost-effectiveness. Demand for high energy efficiency and low CO$_2$ emission has led to the ever-increasing service temperatures of power generation equipment. However, the oxidation resistance of austenitic stainless steels is not adequate in high-temperature environments.

Therefore, various attempts have been made to modify the structures and compositions of austenitic stainless steel surface to combat high-temperature oxidation.1–7) Although an increase in the amount of chromium in steels can improve their corrosion resistance, it also increases the brittle transition temperature. It has been reported that the addition of silicon to stainless steels could improve their high temperature oxidation resistance.8–11) Halide-activated pack cementation has been proved to be an effective method to produce oxidation-resistant coatings by co-depositing chromium with silicon or aluminum on steels.12–14) However, simultaneous deposition of chromium and silicon by pack cementation could be effective in protecting austenitic stainless steels from hot corrosion and oxidizing environments at high temperature.

In this study, a duplex chromising-siliconizing coating was produced on heat-resistant austenitic stainless steel by pack cementation. The oxidation resistance of the duplex chromosiliconized coating was evaluated in 873 K hot steam for $3.6 \times 10^3$ ks, and the oxidized as well as the coated samples were characterized.

2. Experimental Procedure

The substrate material used in the present work was heat-resistant austenitic stainless steel with the following nominal composition (mass%): 15–18Cr, 13–16Ni, 0.08–0.18C, 2.5–4.0W and balanced Fe. Samples of 25 mm $\times$ 15 mm $\times$ 4 mm were cut from a 4 mm thick sheet material, ground up to 1200 grit SiC. Prior to pack cementation treatment, the surfaces were ultrasonically cleaned in acetone and dried using hot air.

The pack powders used for the diffusion treatment were Cr and Si as master alloys, Al$_2$O$_3$ as filler, and NaF, NH$_4$Cl and AlF$_3$ as halide activator salts. Al$_2$O$_3$ crucible containing the substrates and pack powders was placed in an electric tube furnace in an Ar atmosphere (Fig. 1). The simultaneous chromium and silicon diffusion treatment was conducted using a two-step process: 1073 K for 7.2 ks followed by 1323 K for 10.8 ks (Fig. 2). The composition of pack powders and details of the treatment are given by Nishimoto et al.11)

After the diffusion treatment, the surface coating on one side of the samples was removed by grinding to serve as the benchmark of the substrate. The polished side and non-polished side of the sample will hereafter be referred to as
side A and side B, respectively. Oxidation tests of the samples were carried out in EMPA (Swiss Federal Laboratories for Materials Science and Technology) in 873 K hot steam for $3.6 \times 10^3$ ks.

The phase constituents of the hot steam oxidation tested coating surfaces and the polished surfaces for comparison were examined by X-ray diffraction (XRD). The cross-sections of the sample were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The Vickers microhardness of the polished cross-sections was measured under a load of 0.098 or 0.25 N.

3. Results and Discussion

Figure 3 shows typical XRD pattern from the coated surface. It also shows the as-chromosiliconized coating was covered by a mixture of residual $\text{Al}_2\text{O}_3$ filler and $\text{Cr}_3\text{Si}$, which was formed because of the reaction between the master alloy of Cr and Si. Peaks of $\alpha$-Fe rather than $\gamma$-Fe were detected on the as-chromosiliconized surface, which was believed to be the inward diffusion of alpha stabilizer Cr during the chromosiliconizing treatment.

As can be seen from Fig. 4, the hot steam oxidation tested substrate (Side A) is dominated by $\text{Fe}_3\text{O}_4$, while the hot steam oxidation tested coating (Side B) is mainly composed of $\text{Fe}_{0.7}\text{Cr}_{1.3}\text{O}_3$ together with a trace of $\text{Fe}_3\text{O}_4$.

Figure 5 shows typical SEM cross-sectional micrographs of the substrate (Side A) after hot steam oxidation testing. It consisted of a top layer of about 15 $\mu$m followed by a sublayer of about 70 $\mu$m. This layer was found to be delaminated in many areas. The interface between the sublayer and the substrate is smooth. Moreover, many cracks parallel to the surface were observed in the sublayer.

A similar dual layer structure was observed in the cross-sections of the hot steam tested coating - Side B (Fig. 6). The interface between the surface layer and the substrate for Side B is zigzagged (Fig. 6(a)), which is believed to be related to the grinding during the initial sample preparation. The top layer was very thin (1–2 $\mu$m) and the sublayer...
(about 25 µm thick) was relatively dense with some pores (Fig. 6(b)).

Detailed EDX analyses were conducted to probe the element depth distribution following the hot steam oxidation tests for the substrate (Side A) and the coating (Side B). Figure 7(a) shows a typical SEM cross-sectional micrograph of Side A consisting of a porous top layer of 10 µm followed by a dense sublayer of about 70 µm. It can be seen from Fig. 7(b) that the top layer is rich in O, indicative of an iron oxide layer. The oxygen content reduced gradually with depth of the sublayer as shown in Fig. 7(b).

Quantitative EDX measurements were also conducted. The results are summarized in Fig. 7(c). It was found that the top layer contained 30.5 mass% O and 68.2 mass% Fe together with 1.26 mass% Cr. The measured oxygen content was very close to that of Fe$_3$O$_4$ (which is 27 mass% O) in view of the margin of error of the EDX technique for such light elements as oxygen. This confirms the XRD results (Fig. 4), i.e., Fe$_3$O$_4$ dominated the top layer of Side A after the hot steam oxidation treatment.

The composition of the sublayer is similar to that of the bulk material but with a high content of oxygen. The oxygen content at the area near the interface between the sublayer and the substrate (Point 3 in Fig. 7(a)) is still as high as 8.62 mass% (Fig. 7(c)). This implies that the sublayer is an oxygen diffusion zone produced by inward diffusion of oxygen during the long-time hot steam oxidation treatment. This increased the hardness of the sublayer (see the microhardness results) but reduced the toughness of the material, which may account for the parallel cracks observed in the sublayer.

The EDX analyses results of the oxidation-tested coating are shown in Fig. 8. Figure 8(a) shows that it is difficult to identify the very thin surface layer as shown in Fig. 6 under low magnification. The quantitative EDX results given in Fig. 8(c) indicate that Cr and Si have been successfully introduced into the surface coating during the chromosiliconizing pack cementation.

The surface oxide layer formed on the uncoated substrate (Side A) is about 10 times that of the coated surface (Side B). In addition, the oxygen containing sublayer formed during the hot steam oxidation is about 25 µm while oxygen cannot diffuse into the stainless steel substrate in side B. The measured oxygen content 4.04 mass% at the position of Point 2 (Fig. 8(a)) is most probably caused by EDX quantitative measurement error of the light O element since the oxygen depth profiles (Fig. 8(b)) are almost constant across the substrate. Clearly, the coating containing Cr and Si has effectively protected the stainless steel from oxidation since Cr and Si can form dense and protective oxide films at high temperature.

Figure 9(a) shows Vickers microhardness depth distribution with Side A after hot steam oxidation. The hardness decreased gradually with increasing distance from the surface without iron oxide and then reached a constant substrate value of approximately 280 Hv at a depth of about 170 µm. The continuous decrease of hardness to the substrate value suggests the presence of a diffusion zone. This is because without protective coating containing Cr and Si both surface oxide layer and oxygen diffusion case were formed during the hot steam oxidation tests.

On the other hand, Fig. 9(b) shows the microhardness depth profile across Side B. The hardness is almost constant, about 25 µm from the surface, which then sharply drops to the substrate value. This indicates that no diffusion zone was formed below the surface coating since the surface coating can effectively stop the inward diffusion of oxygen. One of authors reported that Cr–Si coating on austenitic stainless
steel has an advantage in a high temperature oxidation at 1123 K for $7 \times 10^2$ ks. In the present investigation, oxidation tests of the samples were carried out at 873 K for a longer time of $3.6 \times 10^3$ ks. These results indicate that the duplex chromizing-siliconizing coating demonstrated long-term durability of stainless steel at high temperature.

4. Conclusion

Duplex chromosiliconizing coating has been successfully applied to heat-resistant austenitic stainless steel by pack cementation. This coating containing Cr and Si can effectively improve the oxidation resistance of heat-resistant austenitic stainless steel in 873 K hot steam for $3.6 \times 10^3$ ks.

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REFERENCES