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Formation of Alumina Layer on Fe-Cr-Ni Alloy by Pack Cementation and Oxidation

Linlin Xing,[1] **Yanjun Zheng,**[1,*] **Lishan Cui,**[1] **Maohu Sun,**[1] **Mingzeng Shao**[1] **and Guiwu Lu**[1]

[1] Department of Materials Science and Engineering, China University of Petroleum, Beijing 102249, China

Abstract. To protect Fe-Cr-Ni based alloy from high temperature corrosion in carbon containing atmosphere at elevated temperature, alumina coating was prepared on the Fe-Ni-Cr alloy substrate by pack cementation and oxidation. Results showed that a surface FeAl layer formed after the pack cementation process, and an Al_2O_3 coating formed by selective oxidation of the FeAl layer. The coating adhered tightly to the FeAl layer without any cracks or porous inbetween them. By the oxidation process the catalytic elements such as Fe and Ni were remarkably reduced from the surface. Further anti-coking test indicated that the alumina scale could successfully inhibit the outward diffusion of catalytic elements and showed excellent coking resistance.

Keywords. High temperature alloy, coke deposition, oxidation, pack cementation.

1 Introduction

The deposition of carbon onto the external surfaces of critical metallic components in carbon-containing atmospheres is of particular concern in many industries [1, 2]. Take pyrolysis coils for example, the deposited coke on the coil surface is always a direct reason for the shut down of ethylene furnace. Catalytic coking is one major mechanism responsible for carbon deposition, by which catalytic elements such as Fe and Ni greatly facilitate the carbon deposition and accumulation. An effective way to prevent this is to prepare protective coatings which are free of Fe and Ni elements. For Fe-Ni-Cr high temperature alloy, a surface Cr_2O_3 layer usually acts as a protective coating which seals the Fe and Ni elements in the matrix and provides resistance to carburization and carbon deposition. However, chromia layer is protective in carbon containing atmosphere only when the temperature is below 1323 K, otherwise it will be quickly carburized and lose its protective property.

Al_2O_3 coating has excellent thermal stability at elevated temperatures [3–5], and can satisfy the requirements for high temperature protection. Some attempts have been made to use aluminized layer prepared by pack cementation for the prevention of carbon deposition [6]. However, pack cementated aluminum element usually exists in the form of Ni (Fe)-Al intermetallic compounds. High contents of catalytic elements still exist in the pack cementated layer, which remain as a major cause of considerable coke deposition [7].

Selective oxidation is one effective method to prepare a pure alumina layer on the aluminum-containing intermetallics. There is almost no studies on the formation of alumina scale on a pack aluminized high temperature alloy, although some research has been done on the oxidation of bulk intermetallics. Gao et al [8] reported the oxidation behavior of Ni_3Al and FeAl intermetallics and showed that an external Al_2O_3 scale forms on the surface under low oxygen partial pressures. Murata et al [9] also found that only Al_2O_3 was observed on the surface of Fe-40 at. % Al at 1273–1473 K for oxidation times from 5 min to 10 h under low oxygen partial pressures. For the pack cementated alloy, aluminum element has a gradual distribution along the coating thickness direction. This may cause different oxidation behaviors other than bulk intermetallics, since the diffusion of ions always plays a major role in the oxidation behavior. To obtain a compact Al_2O_3 layer with excellent coking resistance, a commercial Fe-Ni-Cr alloy was subjected to pack cementation and a following selective oxidation process under a low oxygen partial pressure atmosphere, prior to its application in carbon containing atmospheres. This Al_2O_3 protection layer is expected to control the carbon deposition or coke formation on this high temperature alloy in carbon-containing atmospheres.

2 Experimental

The substrates used for this study are a commercial Fe-Cr-Ni alloy, with a composition of 0.35 % C, 2.00 % Si, 2.00 % Mn, 0.04 % P, 0.04 % S, 25.00 % Cr, 35.00 % Ni (all in mass %), and Fe as the balance. The alloy sheet were cut into approximately $15 \times 10 \times 2$ mm^3 plates. The plate specimens were first mechanically ground on SiC abrasive paper down to 600 grades, and then ultrasonically cleaned in

Corresponding author: Yanjun Zheng, Department of Materials Science and Engineering, China University of Petroleum, Beijing 102249, China; E-mail: yanjun_zheng@hotmail.com.

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acetone, distilled water, followed by drying at room temperature.

The pack mixtures consist of 96.9 mass % diffusion metal with a composition of aluminum and iron (powders of 100 mesh) at a Fe : Al ratio of 48 : 52, 2.5 mass % Al_2O_3 (100 mesh) as the inert filler, and 0.6 mass % NH_4Cl as the activator. The pack cementation process was carried out in a horizontal tube furnace, at 1253 K for 8 h.

After the aluminizing process, the specimens were subjected to isothermal oxidation at 1273 K for 30 h in a thermobalance (TGA Cahn). The effects of different contents of water vapor on the oxidation of aluminized alloy had been investigated in our previously work [10], and the results show that a 2.23 vol. % water vapor content is favorable to the selective oxidation of Al. Coke deposition experiment were performed in a C_3H_8 cracking atmosphere at 1023 K for 1 h, 5 h and 10 h, respectively, with a flow rate of 30 ml/min. The coking rates of the coated and uncoated HP40 specimens were calculated by weighing the HP40 specimens before and after coking with a microbalance.

Observation of surface morphology and chemical composition of the oxide layer were carried out by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The specimens were Ni-plated prior to sectioning for cross-sectional observation. Cu-Kα radiation was used for X-ray diffraction.

3 Results and Discussion

Figure 1(a) is a typical surface morphology of the FeAl coating after the aluminizing process. The grain size is about 2–4 μm. The coating is continuous, although a few pores can be found occasionally. Figure 1(b) shows the morphology of oxides after oxidation in the H_2 + 2.23 vol. % H_2O atmosphere at 1273 K. The oxides appear as a network of ridges, and no obvious spallation is found.

XRD profile shown in Figure 2(a) indicates that the phases of the aluminized coatings are mainly FeAl and a small fraction of Fe_3Al. Figure 2(b) shows the XRD profile of aluminized samples after oxidation in H_2 + 2.23 vol. % water vapor at 1273 K for 20 h. Strong peaks of α-Al_2O_3, θ-Al_2O_3 and some weak peaks of FeAl and Fe_3Al are found in the figure. Obviously, Al has been selectively oxidized into α-Al_2O_3 and θ-Al_2O_3. Since the oxide scale is just about 3 μm in thickness, the FeAl and Fe_3Al phases beneath the alumina scale can still be detected by XRD. Results in Figure 2 indicate that the amount of catalytic elements such as Fe and Ni were significantly decreased. This is also confirmed by the EDS result which indicates that the surface composition after oxidation are Al 48.88 at. %, O 41.51 at. %, Fe 4.06 at. %, Ni 3.15 at. % and Cr 2.40 at. %.

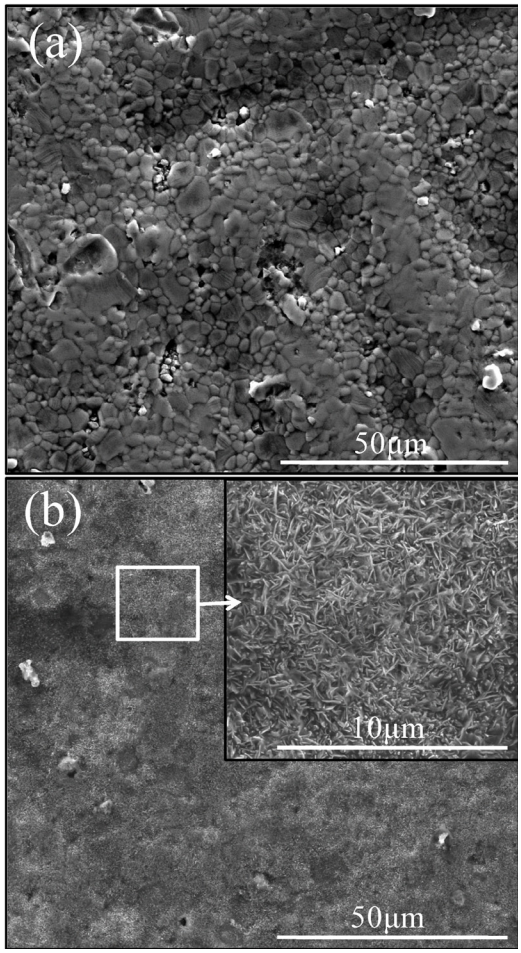

Figure 1. Scanning electron micrographs of the surface morphology of the specimen. (a) After pack cementation, and (b) after oxidation.

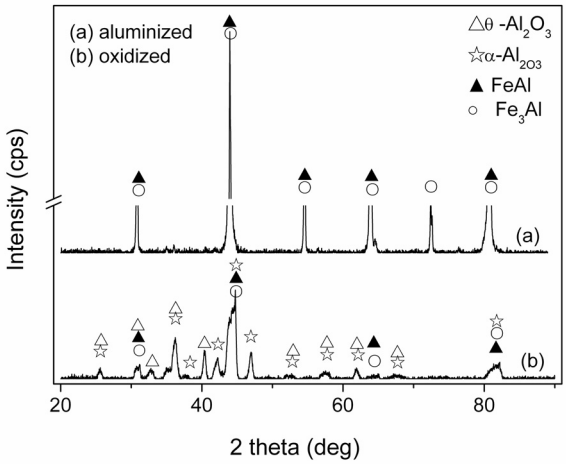

Figure 2. X-ray profiles of the specimen. (a) After pack cementation (b) after oxidation in H_2 + 2.23 vol. % water vapor at 1273 K for 20 h.

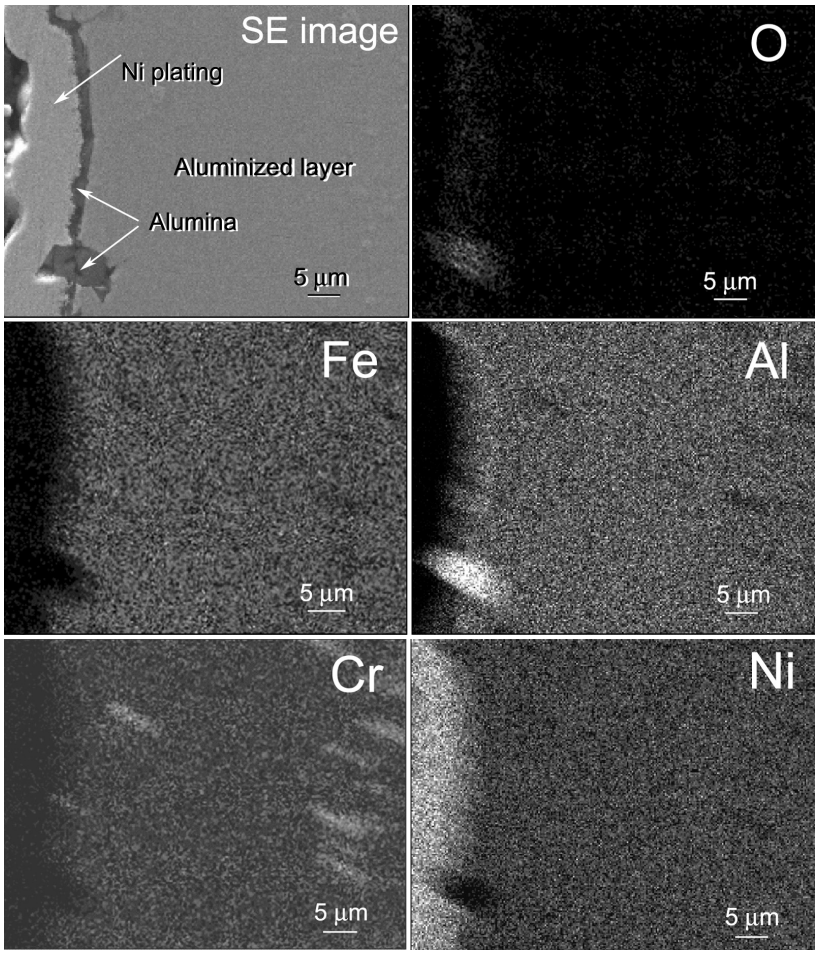

Figure 3. Cross-section EDS maps of O, Al, Fe, Cr, and Ni elements in alumina layer formed on aluminized Fe-Cr-Ni alloy after oxidation in H_2 + 2.23 vol. % water vapor at 1273 K for 30 h.

The formation of a protective oxide scale on alumina-forming alloys is generally described in terms of a two stage process. In the first stage "transient" aluminas form and the oxidation process is relatively fast. In the second stage the transient aluminas convert to α-Al_2O_3, which may decrease the oxidation rate [11–13]. Some reports claimed that the formation of α-Al_2O_3 can be promoted by the present of water vapor in the oxidizing atmosphere [12]. Some research also suggested that the $\theta \rightarrow \alpha$ alumina transformation can be accelerated by the presentation of water, resulting in a faster oxidation in humid air than in dry air [14]. In our research, XRD profile shown in Figure 2(b) indicates that the formed oxides are mainly stable α-Al_2O_3 and transient θ-Al_2O_3, seemly the selected condition promotes the formation of θ alumina and its transition to α alumina. Once a continuous α-Al_2O_3 is established, the role of water content in the atmosphere will become less important, for the molecule of water vapor can not penetrate a continuous α-Al_2O_3 [15].

EDS mapping analysis of element distribution along the cross-section direction of the oxide scale is shown in Figure 3. The oxide scale is generally well adhered, dense and continues, with a thickness about 3 μm. Element analysis revealed strong intensity of Al and O in the surface oxide layer. There are some nodules in the alumina layer, and its composition is also confirmed to be Al_2O_3. Some Cr rich areas are distributed in the Fe-Al layer, which are chromium carbides commonly found in high temperature alloys.

Figure 4 shows the coking weight gains of the coated and uncoated HP40 alloy after exposing in the cracking atmosphere for different time. The weight gains of the uncoated HP40 samples are systemically higher than the coated HP40 samples. Both the weight gain of the uncoated and coated HP40 samples increase with coking time in C_3H_8 at 1023 K. The coke on the coated HP40 sample is about 21.4 %, 26.1 % and 49.1 % (all in mass %) of that on the uncoated HP40 sample after 1h, 5 h and 10 h, respectively. These values are better than those reported in earlier papers [16–19].

Results in Figure 4 indicate that oxidation in low oxygen partial pressure atmospheres can successfully prepare a protective Al_2O_3 layer. Theoretically, under such a low

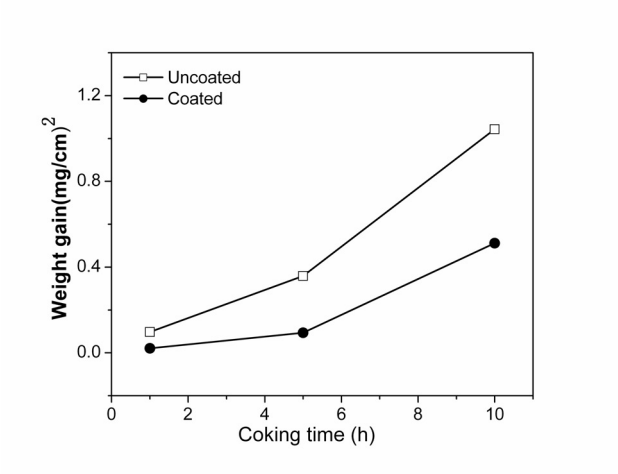

Figure 4. Weight gains of coated and uncoated HP40 steels in C_3H_8 for 1 h, 5 h and 10 h.

oxygen partial pressure (lower than 10^{-20} Pa), aluminum should be oxidized exclusively. However, Fe and Ni oxides are always found in the surface. Some reports indicated that small bare nickel particles are always found on top of the Al_2O_3 layer when a Ni-Al intermetallic is oxidized in low oxygen partial pressure atmospheres [8]. The reason is that formerly formed NiO may eventually reduced to pure Ni under a low oxygen partial pressure. These nickel particles may not harm the protection ability of the Al_2O_3 layer as long as the Al_2O_3 layer is continuous, so there is almost no report on how to prevent the formation of these pure Ni particles. In carbon-containing atmosphere, however, a small amount of bare nickel or iron particles will cause serious carbon deposition and coke formation, no matter how compact a beneath Al_2O_3 layer is. These arouse special attention to the surface treatment of high temperature alloys in carbon containing atmosphere.

Some research showed that no obvious pure metal particles are found on the oxidized FeAl surfaces [8], although no detailed explanation was provided. In this paper we use Fe-Al powder as the diffusion metal, instead of pure Al, because a Fe-Al intermetallic layer will form on the surface instead of Ni-Al intermetallic layer. Results in Figure 1 show that no bare metal particles existing on the surface. This may at least partly contribute to the absence of surface Ni-Al phase. It is generally accepted that less active elements may also form its oxides in the initial stages of oxidation, even if the oxygen partial pressure is low enough for a thermodynamic impossibility [8]. For the case of Ni-Al alloy, NiO or $NiAl_2O_4$ may always be found in the initial stage of oxidation. These oxides are p-type semiconductors and induce a growth by outward diffusion of cations. These Ni oxides may grow very fast and form a continuous layer, and partly hinder the formation of a continuous Al_2O_3 layer [20]. Excess amount of Ni oxides may eventually be reduced to pure Ni particles under low oxygen partial pressure atmospheres. For Fe-Al alloy, Fe_2O_3 or $FeAl_2O_4$ may forms as well in the initial stage. Fe_2O_3 is an n-type semiconductor, and growth by the inward diffusion of O^{2-}. This inward diffusion of oxygen also facilitates the formation of Al_2O_3 at the oxide-matrix interface, allowing a quick formation of a continuous Al_2O_3 layer [20]. Once a continuous Al_2O_3 is formed, the outward diffusion of metal ions will be greatly delayed. This may partly explains why Fe-Al intermetallics show a less tendency to form pure metal on the oxide surface than Ni-Al does.

4 Conclusions

Al_2O_3 coating was prepared on the surface of a HP40 alloy by the combination of pack cementation and selective oxidation process. The formed alumina coating is mainly consisted of α-Al_2O_3, θ-Al_2O_3 and is almost free of catalytic elements. The scale is compact and continues. Al_2O_3 coatings show excellent coke deposition resistance in the carbon containing atmosphere.

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