Influence of oxidation temperature on the oxide scale formation of NiCoCrAl coatings

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Abstract. Intermetallic coatings of NiCoCrAl have been successfully developed on low carbon steel substrate to improve oxidation resistance in extreme environments. The influence of oxidation temperature on the oxide scale formation was studied in the temperature range of 600-1000 °C. The measurements were made in air under isothermal oxidation test for 100 h. The surface morphology showed that a cauliflower like structure developed entire the oxide scale of sample oxidized at 800 °C and 1000 °C, while partly distributed on the surface of sample oxidized at 600 °C. The XRD analysis identified Cr₂O₃ phase predominantly formed on the oxidized sample at 600 °C and meta-stable Al₂O₃ with several polymorphs crystalline structures η, δ, θ, κ, and α-Al₂O₃ at relatively high temperatures, i.e. 800 °C and 1000 °C. A Cross-sectional microstructure showed that complex and porous structures formed on the top surface of 600 °C and 1000 °C samples. In contrast, a very thin oxide scale formed on 800 °C oxidized samples and it appeared to act as a diffusion barrier of oxygen to diffuse inward, hence could increase in the service life of carbon steel substrate.

1. Introduction

Coatings are the most commonly used material to protect substrate against aggressive environment. NiCoCrAl coatings are often used to protect the substrate from oxidation at high temperatures [1-3]. Further, oxidation resistance of several materials is very important for some high temperature applications. Coatings with sufficient amounts of aluminium or chromium can form an Al₂O₃ or Cr₂O₃ layer on their surface by reacting with oxygen, in order to protect the base material from interaction with the high temperature environment [4]. A dense, continuous, stable, and adherent either α-Al₂O₃ or Cr₂O₃ scale is always desirable because it offers excellent protection for the substrate due to its slow growth rate and thermodynamic stability at high temperatures [5].
It has been reported that the scale formed during oxidation at a temperature between 800 - 1000 °C is often complex, typically consisting of transient aluminum oxides of the γ, δ, and θ types to the stable α-Al₂O₃ phase as well as spinel NiAl₂O₄ [6-10]. Many researchers have reported that at a temperature below 800 °C, Cr₂O₃ are preferentially formed and generally considered to be more protective than Al₂O₃ [11]. Moreover, previous studies showed that the pack cementation temperature can affect the oxidation behavior and the scale structure of NiCoCrAl coatings at a temperature of 800 °C [12]. However, a detailed investigation from low to high temperature oxidation behavior of these coatings has not been extensively explored.

In the present study, the influence of oxidation temperature on the oxide scale formation of NiCoCrAl coatings during 100 h oxidation in air at elevated temperatures of 600, 800, and 1000 °C were investigated. The oxidation resistance of these coatings in the corresponding oxide scale growth was compared.

2. Experimental Procedures
Carbon steel substrates measuring 15 x10 x 1.5 mm were machined out of the plate and a hole of 3.5 mm diameter was drilled near one end of each substrate. The slices were ground with SiC polishing paper up to a mesh size of 1000 and ultrasonically cleaned. NiCoCrAl multilayer coating was used to coat the substrate by electroplating and pack cementation processes. The coating parameters have been described elsewhere [13]. Isothermal oxidation test was performed at 600, 800, and 1000 °C in ambient atmosphere. The oxidation period was determined from 1 h, 5 h, 15 h, 31 h, 46 h, 66 h, 90 h, to 100 h. In each period, more than one coated sample was oxidized to check the reproducibility of the oxidation kinetic. The weight gain was measured after the coated samples were cooled using a balance with a sensitivity of 10⁻⁵ g. The oxide morphology and oxide composition were determined by SEM (JEOL, JSM6380LA). The compounds of the oxides were identified by XRD using XPert Pro with Cu-Kα radiation generated at 40 kV and 40 mA (Philips, PANalytical). A cross-sectional microstructure and elemental distribution of the samples were characterized by FE-EPMA (JEOL, JXA-8530F).

3. Results and Discussions

3.1. Isothermal oxidation
Figure 1 shows the oxidation kinetics curve of NiCoCrAl sample oxidized at 600, 800, and 1000 °C for 100 h. The weight gain of sample oxidized at 600 °C was slower than that of sample oxidized at 800 and 1000 °C. The oxidation kinetic of sample oxidized at 600 °C exhibits a linear increase in mass gain with increasing oxidation time. It revealed that the oxide growth controlled by aluminium or chromium diffusion. On the contrary, the oxidation kinetic of sample oxidized at 800 and 1000 °C follows parabolic rate law. The oxide growth occurs by diffusion of oxygen to the coated layer at initial rapid growth rate of NiCoCrAl oxidation followed by a steady growth of alumina oxide layer.

Figure 1. Isothermal oxidation at (a) 600, (b) 800, and (c) 1000 °C.
The results exhibited the sample oxidized at 800 °C has better oxidation behavior than the sample oxidized at 1000 °C due to its very low oxidation rate. For the sample oxidized at 800 °C, the weight gain increased to value between 0.5 and 0.8 mg/cm² after 15 h. The kinetic constant of sample oxidized at 1000 °C is one order larger than that of sample oxidized at 800 °C with \( k_p = 3.01 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \) and \( k_p = 1.06 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1} \), respectively.

3.2. Surface morphology of oxide scale

Figure 2 shows SEM characterization on the surface of oxidized samples. The investigation at 600 °C implied the roughness of oxide scale entire the surface of the sample (figure 2a). It indicates the boundary structure on the surface should be related to the different phases formed in the oxide scale which has irregular dark area and diverse cauliflower like structure. In contrast, a very rough cauliflower like structure homogeneously observed on the surface of the sample oxidized at 800 °C (Figure 2b), while similar structure with much less fine was also appeared on the surface of coated sample exposed to a higher temperature of 1000 °C (figure 2c). With increasing oxidation temperature, the grain structure of oxide scale was finer and uniformly deposited on the surface of coated sample.

Figure 2. Surface morphology of coating samples oxidized for 100 h at (a) 600 °C, (b) 800 °C, and (c) 1000 °C.

Figure 3. XRD analysis of the substrate, NiCoCrAl coating samples before and after oxidation for 100 h at 600, 800, and 1000 °C.

3.3. Phase identification of oxide scale

Figure 3 shows the phase identification of NiCoCrAl coated samples before and after oxidation. The XRD pattern shows the phases to be a mixture of predominant \( \alpha-\text{Fe} \), \( \zeta-(\text{Al,Cr})\text{Ni} \) accompanied with \( \text{AlNi} \) phase identified in the as-coated sample before oxidation which has good agreement with
previous results [11]. The oxide scale was identified mainly consists of Cr$_2$O$_3$ and small amount of intermetallic phase of Al$_3$Ni and Al$_3$Ni$_2$ after oxidation at a low temperature of 600 °C. This result is correlated with the surface structure previously described with corundum structure of Cr$_2$O$_3$ as shown cauliflower like structure and intermetallic phases as shown irregular dark area. Moreover, the oxide scale was transformed from Cr$_2$O$_3$ to δ-Al$_2$O$_3$ and α-Al$_2$O$_3$ when oxidation slightly increased to 800 °C. It reveals the evolution of oxide scale structure from diverse to be more uniform for cauliflower like structure. Several polymorphs of alumina, i.e., η-Al$_2$O$_3$, δ- Al$_2$O$_3$, θ- Al$_2$O$_3$, κ-Al$_2$O$_3$, and α-Al$_2$O$_3$ phases were formed in the sample oxidized at 1000 °C. It indicates the formation of transient alumina at relatively high temperature of 1000 °C which has a very fine cauliflower like structure.

3.4. Microstructure of oxide scale
FE-EPMA characterization was performed in order to understand the oxide scale formation after oxidation test. Figure 4 shows a cross sectional FE-EPMA images together with composition map of oxidized sample after 100 h exposure time. The oxide scale was established with an approximate thickness of 15 μm, 6 μm, and 25 μm for the sample exposed at temperatures of 600, 800, and 1000 °C, respectively.

![Figure 4](image)

**Figure 4.** BSE images and elemental maps of NiCoCrAl coating sample oxidized for 100 h at (a) 600 °C, (b) 800 °C, and (c) 1000 °C.
A complex and porous oxide scale was developed at sample oxidized at 600 °C. Internal oxidation occurred between metal/oxide interfaces which are indicated as a dark precipitate beneath the oxide scale (figure 4(a)). It might cause by the high activity of oxygen to diffuse inward and reacted with the coating elements. It can be readily recognized from the intensity of oxygen either on the surface or metal layer of sample in figure 4(a). From the composition map, it clearly understands that aluminum reacted with nickel to form intermetallic phases such Al₃Ni, Al₃Ni₂ and β-NiAl as identified by XRD analysis. Furthermore, high intensity chromium content accompanied with oxygen might form chromia (Cr₂O₃) protective scale on the top layer.

In contrast, a relatively thin with localized porous was developed at the sample oxidized at 800 °C as shown in figure 4(b). The existence of high Al and O content on the top layer of sample oxidized at 800 °C producing the simple alumina (Al₂O₃) scale. Ni, Co and Cr are hardly to diffuse outward to the outermost layer because the alumina scale might play a role as a diffusion barrier for this temperature oxidation. Similar with the result of the sample oxidized at 600 °C, a thick and porous structure with large voids was developed at sample oxidized at 1000 °C as shown in figure 4(c). Low intensity chromium was diffused outward to the top layer reacting with aluminum and oxygen. Therefore, it might cause the formation of transient alumina phases with a complex structure from the initial oxidation state at 1000 °C. The intensities of nickel and cobalt were not observed on the outermost layer, thus other phases were also not identified by XRD for this sample.

![Figure 5](image)

**Figure 5.** Magnified FE-EPMA images of oxide scale on NiCoCrAl samples oxidized at a) 600 °C, (b) 800 °C, and (c) 1000 °C for 100 h.

| Sample Code | Point Analysis | Composition (at%) | Phase          |
|-------------|----------------|-------------------|----------------|
| 5a          | 1              | Ni 7, Co 2, Cr 9, Al 80, O 2 | ζ-(Al,Cr)Ni |
|             | 2              | Ni 22, Co 1, Cr 3, Al 74, O 2 | Al₃Ni         |
|             | 3              | Ni 47, Co 2, Cr 51 | Cr₂O₃         |
|             | 4              | Ni 41, Co 3, Cr 56 | Cr₂O₃         |
| 5b          | 1              | Ni 4, Co 5, Cr 49, Al 42 | α-Al₂O₃        |
|             | 2              | Ni 1, Co 51, Cr 48 | α-Al₂O₃        |
|             | 3              | Ni 2, Co 67, Cr 20 | δ-Al₂O₃        |
|             | 4              | Ni 2, Co 74, Cr 20 | δ-Al₂O₃        |
| 5c          | 1              | Ni 1, Co 41, Cr 58 | α-Al₂O₃        |
|             | 2              | Ni 4, Co 46, Cr 50 | α-Al₂O₃        |
|             | 3              | Ni 2, Co 15, Cr 35 | θ-Al₂O₃        |
|             | 4              | Ni 1, Co 74, Cr 19 | δ-Al₂O₃        |
The morphologies of the oxide scale formed on the top of coated sample were magnified as shown in figure 5. It is clearly understood how the difference of porosity on oxide scale structure. The porosity size is about 0.6 μm, 0.2 μm, and 2 μm for sample oxidized at 600, 800, and 1000 °C respectively. It revealed the porosity of alumina scale in sample oxidized at 800 °C was denser than the other two samples. In addition, point analysis as indicated by the circle marks in fig. 5a-c was carried out in order to understand the composition of oxide scale related to the phase formation. The results are shown in table 1. It determined that the phases formation are correspond to the phases identification which previously identified by XRD analysis.

4. Conclusions
The influence of oxidation temperature on oxide scale formation of NiCoCrAl coating was investigated. At a temperature of 600 °C, the oxidation rate was determined by Cr2O3 formation. Generally, Cr2O3 scale is ideal against the oxidation below 800 °C, however Cr2O3 formed in this oxidized sample would not act as a protective layer due to the formation of complex with porous oxide structure and the oxidation kinetic with almost linear growth. At temperature 800 °C, δ and α-Al2O3 scales were formed with a thin and localized porous structure. The oxidation kinetic obeys the parabolic rate law and its \( k_p \) value was about 1.06 \( \times 10^{-9} \) g² cm⁻⁴ s⁻¹. At temperature 1000 °C, a transformation from \( \eta \)-Al2O3, δ-Al2O3, \( \theta \)-Al2O3, κ-Al2O3, to α-Al2O3 occurred from the initial to final stage of 100 h oxidation time. Transition of polymorph alumina phases might cause the formation of complex structure with thick and porous oxide scale. Consequently, the kinetic constant of this sample is one order larger than the sample oxidized at 800 °C and its \( k_p \) value was about \( 3.01 \times 10^{-8} \) g² cm⁻⁴ s⁻¹. Therefore, corresponding to the above described by XRD analysis and FE-EMP A results as well as the kinetic constant of oxidation, it concluded that sample oxidized at 800 °C had better oxidation resistance than the other two oxidized samples.

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