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Microstructure and Analysis of Oxide Scales Formed on Cr-Si-Ni Compacts in Air and H₂O-containing Atmosphere

Akira Yamauchi¹, Yoshio Suzuki², Norihito Sakaguchi¹, Seiichi Watanabe¹, Shigeji Taniguchi¹ and Kazuya Kurokawa¹,*

1 Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Sapporo 060-8628, Japan

2 Graduate student, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan (Present address: Kobe Steel, Ltd.)

*Corresponding author: Tel.: +81-11-706-7572 Fax: +81-11-706-7119

E-mail address: kurokawa@eng.hokudai.ac.jp (K. Kurokawa)
Abstract: The purpose of this study was to characterize the oxide scales formed on various Cr-Si-Ni compacts at 1273 K in air and H₂O-containing atmospheres by TEM. It was found that CrSi₂-(5-20) mass%Ni compacts form double layer scales, consisting of an outer Cr₂O₃ layer and an inner SiO₂ layer. The oxide scale changed from SiO₂- to Cr₂O₃-based scale with an increase in the Ni concentration. However, it was observed that the oxide scale formed in H₂O-containing atmospheres showed local SiO₂ growth into the substrate. This result suggests that the inward oxidant diffusion promotes the local growth of SiO₂ in the H₂O-containing atmospheres.

Keywords: High temperature oxidation, Cr-Si-Ni alloys, scale structure, double layer SiO₂/Cr₂O₃ scale
1. Introduction

Recently, the introduction of the waste-to-energy plants has been promoted with the goals of environmental protection and energy conservation. Such plants are characterized by the following features: no additional environmental load, a location close to the market, and a stable and continuous supply of power. To improve the power generation efficiency, prevent the generation of dioxins and reduce ash, the such plants are designed to use steam at temperatures of up to around 773 K.\(^1\) Their atmospheres contain aggressive oxidants such as oxygen, water vapor, chlorine, sulfur, and molten salts, and consequently conventional materials are subject to severe high-temperature corrosion.

Several relevant investigations\(^2\text{-}^7\) have been conducted on attractive material systems for high-temperature corrosion-resistant coatings that can be formed by using various thermal spray techniques on cheap carbon steels. For example, Ni-Cr coatings provide good high-temperature corrosion resistance by forming a \(\text{Cr}_2\text{O}_3\) scale. At and below 1273 K, this \(\text{Cr}_2\text{O}_3\) scale has excellent corrosion resistance against vanadium, sulfur, water vapor, and oxygen attack, but poor corrosion resistance against chlorine. This is due to the formation of volatile \(\text{CrCl}_2\) from the reaction between \(\text{Cr}_2\text{O}_3\) and chlorine. However, \(\text{SiO}_2\) scale is well-known to have an excellent corrosion resistance against chlorine-containing atmospheres.\(^9\text{-}^{10}\) Additionally, materials that
form a SiO₂ scale in high-temperature atmospheres containing various oxidants are attractive materials. Examples of such materials with good corrosion resistance in atmospheres including chlorine have been reported.\textsuperscript{11-15} However, a phase transformation in SiO₂ tends to occur depending on temperature and atmosphere.\textsuperscript{16} Therefore, there is a problem with the degradation of the SiO₂ scale because of the generation of residual stress by this phase transformation.

We have tried to develop a material that forms a double layer SiO₂/Cr₂O₃ scale for excellent high-temperature corrosion resistance. Our previous work found the formation of a SiO₂ scale on CrSi₂ compacts and a Cr₂O₃ scale on CrSi₂-40mass%Ni compacts at 1273 K in air\textsuperscript{17}. Consequently it is expected that the addition of less than 40mass% Ni to Cr-Si-Ni compacts would result in a double layer SiO₂/Cr₂O₃ scale. In order to observe the scale and discuss its formation mechanism, a study was conducted at 1273 K. Although this is higher than the actual steam temperature of waste-to-energy plants, it is likely to promote the formation of the protective oxide scale. This preliminary work involved observation of the protective oxide scales and a discussion of the oxidation mechanism of Cr-Si-Ni compacts. The purpose of this study was to characterize the oxide scales formed on various Cr-Si-Ni compacts at 1273 K in air and an H₂O-containing atmosphere using TEM-EDS.
2. Experimental Procedure

The starting materials were Cr, Si, and Ni powders. Their purities were 99.9 mass%. The
powder grain sizes of the Cr and Si were 75 µm or less and that of the Ni was 63 µm or less. The
mixed Cr-Si-Ni powders consisting of Cr-(64-57) mol%Si-(6-14) mol%Ni were referred to as
CrSi₂-(5, 10, 20) mass%Ni. Table 1 shows the nominal chemical compositions of these Cr-Si-Ni
mixed powders. Mechanical alloying was carried out with a mini-planetary ball mill at a
ball-to-powder mass ratio of five, and a rotation speed of 350 rpm for 180 ks. The mixed powders
were put into a 45 ml tungsten carbide vial filled with tungsten carbide balls with a diameter of
5 mm in an acetone atmosphere. In order to fabricate dense compacts, the spark plasma sintering
(SPS) method was applied. The as-mechanically alloyed powders and CrSi₂ powder, which had an
average grain size of about 3 µm, were packed into a graphite die under a compressive stress of
40 MPa, and then a pulsating current was passed through the mixed powders and graphite die
within a chamber evacuated to less than 10 Pa. The sintering temperature was measured by a
digital radiation thermometer. The heating rate was 0.17 Ks⁻¹ and the maximum sintering
temperature was 1223 K. The compacts then had 10×5×2 mm specimens cut from them for
oxidation tests. Their surfaces were polished with SiC paper up to #1500, and then with a 1-µm
diamond abrasive to provide a mirror finish. Prior to the oxidation tests, the specimens were
ultrasonically cleaned in ethanol. Phase and microstructural characterizations of the compacts were performed by scanning electron microscopy (SEM), Cu-K \( \alpha \) X-ray diffractometry (XRD), and electron probe microanalysis (EPMA).

Isothermal oxidation tests were performed at 1273 K for up to 180 ks in the laboratory air and N\(_2\)-2.4vol\%O\(_2\)-19.7vol\%H\(_2\)O. The oxidized specimens were characterized by using XRD and EPMA. The microstructures of the oxide scales formed on the Cr-Si-Ni compacts were observed by using a transmission electron microscope (TEM) and were analyzed by energy dispersive X-ray spectroscopy (EDS). A focused ion beam (FIB) instrument was used for the preparation of TEM specimens with thicknesses of less than 100 nm.

3. Results and Discussion

3.1 Structure of Cr-Si-Ni compacts

**Fig. 1** shows back scattered electron (BSE) images of the microstructures of Cr-Si-Ni and CrSi\(_2\) compacts fabricated by SPS. The CrSi\(_2\) compact consisted of CrSi\(_2\) and a small amount of SiO\(_2\) inclusions formed during SPS, whereas the Cr-Si-Ni compacts consisted of a dark gray phase, bright gray phase, and small amount of SiO\(_2\) inclusions. The dark gray phase was identified as the CrSi\(_2\) phase and the bright gray one as (Cr, Ni)Si. All of the specimens fabricated by MA-SPS
showed fine microstructures. The XRD showed that the peak intensities of the CrSi₂ decreased with an increase in the Ni concentration. This is consistent with the results of SEM observations of the compacts. Thus, as the Ni concentration increased, the area ratio of the CrSi₂ phase to total phase decreased, while that of the (Cr, Ni)Si increased.

3.2 Identification of oxide scale formed in air and H₂O-containing atmosphere

The XRD results for the Cr-Si-Ni compacts oxidized at 1273 K for 90 ks in air are shown in Fig. 2. In these patterns, only the reflections corresponding to Cr₂O₃ and the substrate are observed. Low broadening peaks are observed in the 5 mass% and 10 mass% Ni compacts, indicating that an amorphous SiO₂ is also most likely to have formed. It is clear that the relative intensity of the Cr₂O₃ peak increases with an increase in the Ni concentration. Fig. 3 shows the XRD patterns of the Cr-Si-Ni compacts oxidized at 1273 K for 90 ks in an H₂O-containing atmosphere. In these patterns, only the reflections corresponding to Cr₂O₃ and the substrate are observed, with none of the broad peaks found in Fig. 2. These results indicate that the oxide scales formed on the Cr-Si-Ni compacts at 1273 K in air and an H₂O-containing atmosphere were mainly Cr₂O₃ scales.
3.3 Influence of Ni concentration on microstructure of oxide scale

The above results indicated that the oxide scales formed in air and an H₂O-containing atmosphere consisted mainly of Cr₂O₃, and that the scales formed in air also included an inner SiO₂ layer as identified by X-ray diffraction. Next, FIB-TEM was used for a microstructure analysis of the oxide scales formed on the Cr-Si-Ni compacts. Fig. 4 shows cross-sectional TEM images of the oxide scales formed by the oxidation at 1273 K for 180 ks in air. The top black layers in the upper images are deposited W layers for the protection of the scales. Dense and protective 1-µm thick oxide scales were formed on these Cr-Si-Ni compacts. The Cr-Si-Ni compacts could form scales with a duplex structure consisting of an outer dark scale and an inner bright scale. Thus, such scales with a duplex structure were characterized by EDS mapping. Fig. 5 shows a cross-sectional TEM micrograph and elemental maps of the oxide scale formed on CrSi₂-5mass%Ni compacts by oxidation at 1273 K for 180 ks in air. The inner layer of the scale consists of Si and O, and the outer layer consists of Cr and O. Cr, Si, Ni, and O elements were also detected in the area of the W deposit. Since this phenomenon is caused by noise, the elemental maps in the area of the W deposit can be neglected. XRD (Fig. 2) and TEM-EDS analyses showed that the inner layer was SiO₂ and the outer layer was Cr₂O₃.

Similarly, EDS mapping was also used for microstructure analyses of the oxide scales formed
on the other Cr-Si-Ni compacts. As a result, the oxide scales formed on all of the Cr-Si-Ni compacts in this study were found to be double layer SiO$_2$/Cr$_2$O$_3$ scales. The SiO$_2$:Cr$_2$O$_3$ ratio changed with the Ni concentration. Fig. 6 shows the relations between the Ni concentration and the ratios of the SiO$_2$ and Cr$_2$O$_3$ layer thicknesses to the total oxide scale thickness. The relative thickness of the SiO$_2$ layer decreases with an increase in the Ni concentration. From these results and the results of our previous studies,$^{17-18}$ it is concluded that CrSi$_2$, CrSi$_2$-5-20 mass%Ni, and CrSi$_2$-40 mass%Ni form SiO$_2$-based scale, the double layer SiO$_2$/Cr$_2$O$_3$ scale, and Cr$_2$O$_3$-based scale, respectively. The oxide scale formation is closely related to the microstructure of the compact. Namely, the main constitutional phase of a compact changes from CrSi$_2$ to (Cr, Ni)Si with an increase in the Ni concentration; in other words, the primary scale changes from SiO$_2$ to Cr$_2$O$_3$.

3.4 Oxidation mechanism at 1273 K in air

The above results show that the oxide scale formed on a Cr-Si-Ni compact changes from SiO$_2$-based scale to Cr$_2$O$_3$-based scale through the formation of a double layer SiO$_2$/Cr$_2$O$_3$ scale with an increase in the Ni concentration. It is clear that Cr$_2$O$_3$ and SiO$_2$ do not have solubility to each other$^{19}$ and thus the outward Si diffusion in SiO$_2$ is almost neglected.$^{20}$ For this reason,
there is no reason to think that Cr diffuses in SiO₂. Therefore, it could be assumed that the formation of the double layer SiO₂/Cr₂O₃ scale is due to the formation of Cr₂O₃ scale by outward Cr diffusion and the formation of SiO₂ scale by inward oxygen diffusion. However, as described later, there is no reason to assume that this assumption is correct. Next, we considered the growth mechanism of oxide scale based on the observation of the double layer SiO₂/Cr₂O₃ scale.

**Fig. 7** shows the cross-sectional TEM image and elemental maps of the oxide scale formed on a CrSi₂-10mass%Ni compact by oxidation at 1273 K for 0.9 ks in air. The TEM observation revealed that the thin scale had a thickness of less than about 100 nm. This scale occupies an area consisting of Si and O, and another area consisting of Cr and O. This demonstrates the formation of the scales consisting of SiO₂ and Cr₂O₃ in the initial oxidation stage. The above results clearly show that CrSi₂ and (Cr, Ni)Si form SiO₂ and Cr₂O₃, respectively. On the basis of these results, an oxidation mechanism for the Cr-Si-Ni compacts at 1273 K in air was proposed, as shown in **Fig. 8**. 

As seen in **Fig. 8(a)**, the oxide scale formed in the initial oxidation stage is a mixture of SiO₂ and Cr₂O₃ (see Fig. 7). **Fig. 8(b)** shows that the Cr diffuses outward from the substrate through the Cr₂O₃ and its grain boundary preferentially, because the Cr diffusion coefficient in Cr₂O₃ at 1273 K is much larger than that in SiO₂.²¹ Therefore, the Cr₂O₃ layer preferentially grows on the outside of the scale. Likewise, the inward oxygen diffusion occurs preferentially through the SiO₂
because the oxygen diffusion coefficient in SiO$_2$ at 1273 K is much larger than that in Cr$_2$O$_3$.$^{21}$ Consequently, the SiO$_2$ layer preferentially grows at the inside of the scale. Fig. 8(c) shows that after a period of time has elapsed, the outer Cr$_2$O$_3$ layer grows by the outward Cr diffusion and the inner SiO$_2$ layer by the inward oxygen diffusion through the grain boundary of the Cr$_2$O$_3$. At that time, the Cr concentration at the scale/substrate interface decreases by the outward Cr diffusion, while the concentrations of Si and Ni increase. It is reasonable to think that a substitution reaction occurs in the interface between this Ni and Si concentrated area and the Cr$_2$O$_3$, as illustrated by the expression in Fig. 8. This is because the affinity of Si for oxygen is higher than that of Cr and that of Ni is lower than that of Cr.$^{22}$ As a result of the substitution reaction, SiO$_2$ forms. Fig. 8(d) shows that when the Cr$_2$O$_3$ forms a continuous layer, a SiO$_2$ layer grows beneath it owing to the substitution reaction. Moreover, after the inner SiO$_2$ has formed a continuous layer, the outer Cr$_2$O$_3$ layer grows very slowly. Consequently, the double layer scale consisting of an outer Cr$_2$O$_3$ layer and an inner SiO$_2$ layer was formed on the Cr-Si-Ni compact.

3.5 Influence of water vapor on microstructure of oxide scale

Fig. 9 shows cross-sectional TEM images of CrSi$_2$-5, 10, and 20 mass%Ni oxidized at 1273 K for 180 ks in an H$_2$O-containing atmosphere. The oxide scale consists of an outer dark Cr$_2$O$_3$ layer
and an inner bright SiO₂ layer. In all of the specimens, the Cr₂O₃ layer is almost plain and continuous, whereas the SiO₂ is discontinuous forming the irregular and rough interface with the substrate. This result agrees with the result of EDS mapping as shown in Fig. 10 that obtained from the scale formed on the CrSi₂-10mass%Ni in the H₂O-containing atmosphere. The double layer SiO₂/Cr₂O₃ scale formed on the Cr-Si-Ni compact in air, while the oxide scale that formed on the Cr-Si-Ni in an H₂O-containing atmosphere consisted of a continuous Cr₂O₃ layer and a localized SiO₂ layer. It is well-known that water vapor promotes the inward oxidant diffusion through a scale in an H₂O-containing atmosphere.²³,²⁴ In this case, the inward oxidant diffusion occurs easily. In addition, it is also well known that the crystallization of SiO₂ is promoted by the presence of water vapor.¹⁶ The crystallization of SiO₂ leads to an acceleration of the localized SiO₂ growth. If we take this reason into consideration, we can conclude that the SiO₂ scale shows a partially continuous layer because of the promotion of inward oxygen diffusion and the crystallization of SiO₂.

4. Conclusions

In the present study, the microstructures of the oxide scales formed on the Cr-Si-Ni compacts at 1273 K in air and an H₂O-containing atmosphere were observed and analyzed by TEM-EDS. The
influence of water vapor and the Ni concentration in the compact were clarified, and the oxide scale formation mechanism was discussed. The following results were obtained.

1. The microstructure of a Cr-Si-Ni compact changes from a CrSi₂-based structure to a (Cr,Ni)Si-based structure with an increase in the Ni concentration.

2. The oxide scales formed on CrSi₂-(5-20) mass%Ni compacts at 1273 K in air consist of an outer Cr₂O₃ layer and an inner SiO₂ layer. The structure of the oxide scale changes from an SiO₂-based scale to a Cr₂O₃-based scale with an increase in the Ni concentration.

3. The oxide scales formed on Cr-Si-Ni compacts at 1273 K in an H₂O-containing atmosphere consist of an outer continuous Cr₂O₃ layer and an inner localized SiO₂ layer. These structures can be explained by the promotion of inward penetration of oxidant by water vapor and the crystallization of SiO₂.

4. We proposed the formation mechanism for a duplex structure scale consisting of an outer Cr₂O₃ layer and an inner SiO₂ layer.

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References


(23) A. Yamauchi, K. Kurokawa, H. Takahashi, Y. Takada, High Temperature Oxidation of

Figure Caption

Table 1 Chemical compositions of the Cr-Si-Ni specimens

Fig.1 BSE images of the sintered Cr-Si-Ni specimens before oxidation: (a) CrSi$_2$, (b) CrSi$_2$-5mass%Ni, (c) CrSi$_2$-10mass%Ni, and (d) CrSi$_2$-20mass%Ni.

Fig. 2 XRD patterns of the sintered specimens oxidized for 90 ks at 1273 K in air: (a) CrSi$_2$-20mass%Ni, (b) CrSi$_2$-10mass%Ni, and (c) CrSi$_2$-5mass%Ni.

Fig. 3 XRD patterns of the sintered specimens oxidized for 90 ks at 1273 K in an H$_2$O-containing atmosphere: (a) CrSi$_2$-20mass%Ni, (b) CrSi$_2$-10mass%Ni, and (c) CrSi$_2$-5mass%Ni.

Fig. 4 Cross-sectional TEM images of the sintered specimens oxidized for 180 ks at 1273 K in air: (a) CrSi$_2$-5mass%Ni, (b) CrSi$_2$-10mass%Ni, and (c) CrSi$_2$-20mass%Ni.

Fig. 5 TEM image and EDS elemental maps of CrSi$_2$-5mass%Ni compact oxidized for 180 ks at 1273 K in air.

Fig. 6 Ratio of SiO$_2$ layer thickness and Cr$_2$O$_3$ layer thickness to the total scale thickness as a function of the Ni concentration in Cr-Si-Ni compacts oxidized for 180 ks at 1273 K in air.

Fig. 7 TEM image and EDS elemental maps of a CrSi$_2$-10mass%Ni compact oxidized for 0.9 ks at 1273 K in air.
Fig. 8 Schematic diagram showing the development of the structure of the oxide scales on the Cr-Si-Ni compacts during the oxidation in air.

Fig. 9 Cross-sectional TEM images of sintered specimens oxidized for 180 ks at 1273 K in an H₂O-containing atmosphere: (a) CrSi₂-5mass%Ni, (b) CrSi₂-10mass%Ni, and (c) CrSi₂-20mass%Ni.

Fig. 10 TEM image and EDS elemental maps of a CrSi₂-10mass%Ni compact oxidized for 180 ks at 1273 K in an H₂O-containing atmosphere.
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<th>CR (mol%)</th>
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Table 1. Chemical compositions of the Cr-Si-Ni specimens
Fig. 1 BSE images of the sintered Cr-Si-Ni specimens before oxidation: (a) CrSi₂, (b) CrSi₂-5 mass% Ni, (c) CrSi₂-10 mass% Ni and (d) CrSi₂-20 mass% Ni.
Fig. 2 XRD patterns of the sintered specimens oxidized for 90 ks at 1273 K in air: (a) CrSi2-20mass%Ni, (b) CrSi2-10mass%Ni and (c) CrSi2-5mass%Ni.

- Substrate
- Amorphous SiO2
- Cr2O3
- CrSi2
Fig. 3 XRD patterns of the sintered specimens oxidized for 90 ks at 1273 K in H₂O-containing atmosphere: (a) CrSi₂-20mass%Ni, (b) CrSi₂-10mass%Ni, and (c) CrSi₂-5mass%Ni.
Fig. 4 Cross-sectional TEM images of the sintered specimens oxidized for 180 ks at 1273 K in air:

(a) CrSi$_2$-5mass%Ni, (b) CrSi$_2$-10mass%Ni and (c) CrSi$_2$-20mass%Ni.

(a) W-depo W-depo
(b) W-depo
(c) W-depo
Fig. 5 TEM image and EDS elemental maps of CrSi$_2$-5mass%Ni compact oxidized for 180 ks at 1273 K in air.

\[ \text{scale} \]

substrate

TEM

W-depo
Fig. 6 Ratio of SiO$_2$ layer thickness and Cr$_2$O$_3$ layer thickness to the total scale thickness as a function of Ni concentration in the Cr-Si-Ni compacts oxidized for 180 ks at 1273 K in air.
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