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

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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 investigations²⁻⁷⁾ 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 Cr_2O_3 scale. At and below 1273 K, this Cr_2O_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 CrCl_2 from the reaction between Cr_2O_3 and chlorine. However, SiO_2 scale is well-known to have an excellent corrosion resistance against chlorine-containing atmospheres.⁹⁻¹⁰⁾ Additionally, materials that

form a SiO_2 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.¹¹⁻¹⁵⁾ However, a phase transformation in SiO_2 tends to occur depending on temperature and atmosphere.¹⁶⁾ Therefore, there is a problem with the degradation of the SiO_2 scale because of the generation of residual stress by this phase transformation.

We have tried to develop a material that forms a double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale for excellent high-temperature corrosion resistance. Our previous work found the formation of a SiO_2 scale on CrSi_2 compacts and a Cr_2O_3 scale on CrSi_2 -40mass%Ni compacts at 1273 K in air¹⁷⁾. Consequently it is expected that the addition of less than 40mass% Ni to Cr-Si-Ni compacts would result in a double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ 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 H_2O -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 5mm 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 40MPa, 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 α 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 N₂-2.4vol% O₂-19.7vol% H₂O. 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 CrSi₂ compacts fabricated by SPS. The CrSi₂ compact consisted of CrSi₂ and a small amount of SiO₂ inclusions formed during SPS, whereas the Cr-Si-Ni compacts consisted of a dark gray phase, bright gray phase, and small amount of SiO₂ inclusions. The dark gray phase was identified as the CrSi₂ 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 CrSi_2 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 CrSi_2 phase to total phase decreased, while that of the $(\text{Cr, Ni})\text{Si}$ increased.

3.2 Identification of oxide scale formed in air and H_2O -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 Cr_2O_3 and the substrate are observed. Low broadening peaks are observed in the 5 mass% and 10 mass% Ni compacts, indicating that an amorphous SiO_2 is also most likely to have formed. It is clear that the relative intensity of the Cr_2O_3 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 H_2O -containing atmosphere. In these patterns, only the reflections corresponding to Cr_2O_3 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 H_2O -containing atmosphere were mainly Cr_2O_3 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 $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scales. The $\text{SiO}_2:\text{Cr}_2\text{O}_3$ ratio changed with the Ni concentration. **Fig. 6** shows the relations between the Ni concentration and the ratios of the SiO_2 and Cr_2O_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 -5-20mass%Ni, and CrSi_2 -40mass%Ni form SiO_2 -based scale, the double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale, and Cr_2O_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_2O_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_2O_3 -based scale through the formation of a double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale with an increase in the Ni concentration. It is clear that Cr_2O_3 and SiO_2 do not have solubility to each other¹⁹⁾ 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 SiO_2 . Therefore, it could be assumed that the formation of the double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale is due to the formation of Cr_2O_3 scale by outward Cr diffusion and the formation of SiO_2 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 $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale.

Fig. 7 shows the cross-sectional TEM image and elemental maps of the oxide scale formed on a CrSi_2 -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 SiO_2 and Cr_2O_3 in the initial oxidation stage. The above results clearly show that CrSi_2 and (Cr, Ni)Si form SiO_2 and Cr_2O_3 , 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 SiO_2 and Cr_2O_3 (see Fig. 7). **Fig. 8(b)** shows that the Cr diffuses outward from the substrate through the Cr_2O_3 and its grain boundary preferentially, because the Cr diffusion coefficient in Cr_2O_3 at 1273 K is much larger than that in SiO_2 .²¹⁾ Therefore, the Cr_2O_3 layer preferentially grows on the outside of the scale. Likewise, the inward oxygen diffusion occurs preferentially through the SiO_2

because the oxygen diffusion coefficient in SiO_2 at 1273 K is much larger than that in Cr_2O_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_2O_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_2O_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_2O_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_2O_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_2O_3 layer grows very slowly. Consequently, the double layer scale consisting of an outer Cr_2O_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_{12-5} , 10, and 20mass%Ni oxidized at 1273 K for 180 ks in an H_2O -containing atmosphere. The oxide scale consists of an outer dark Cr_2O_3 layer

and an inner bright SiO_2 layer. In all of the specimens, the Cr_2O_3 layer is almost plain and continuous, whereas the SiO_2 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 CrSi_2 -10mass%Ni in the H_2O -containing atmosphere. The double layer $\text{SiO}_2/\text{Cr}_2\text{O}_3$ scale formed on the Cr-Si-Ni compact in air, while the oxide scale that formed on the Cr-Si-Ni in an H_2O -containing atmosphere consisted of a continuous Cr_2O_3 layer and a localized SiO_2 layer. It is well-known that water vapor promotes the inward oxidant diffusion through a scale in an H_2O -containing atmosphere.^{23,24)} In this case, the inward oxidant diffusion occurs easily. In addition, it is also well known that the crystallization of SiO_2 is promoted by the presence of water vapor.¹⁶⁾ The crystallization of SiO_2 leads to an acceleration of the localized SiO_2 growth. If we take this reason into consideration, we can conclude that the SiO_2 scale shows a partially continuous layer because of the promotion of inward oxygen diffusion and the crystallization of SiO_2 .

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 H_2O -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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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_2O -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_2O_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.

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

	Cr (mol%)	Si (mol%)	Ni (mol%)
CrSi ₂	33.3	66.7	-
CrSi ₂ -5mass%Ni	32.3	64.6	3.1
CrSi ₂ -10mass%Ni	31.2	62.4	6.4
CrSi ₂ -20mass%Ni	28.9	57.5	13.6

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 H_2O -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) CrSi₂-5mass%Ni, (b) CrSi₂-10mass%Ni and (c) CrSi₂-20mass%Ni.

Fig. 5 TEM image and EDS elemental maps of CrSi₂-5mass%Ni compact oxidized for 180 ks at 1273 K in air.

Fig. 6 Ratio of SiO_2 layer thickness and Cr_2O_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.

Fig. 7 TEM image and EDS elemental maps of CrSi₂-10mass%Ni compact oxidized for 0.9 ks at 1273 K in air.

Fig. 8 Schematic diagram showing the development of 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 H_2O -containing atmosphere; (a) CrSi_2 -5mass%Ni, (b) CrSi_2 -10mass%Ni and (c) CrSi_2 -20mass%Ni.

Fig. 10 TEM image and EDS elemental maps of CrSi_2 -10mass%Ni compact oxidized for 180 ks at 1273 K in H_2O -containing atmosphere.