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Title:

Structure and Oxidation Resistance of plasma sprayed Ni-Si Coatings on Carbon Steel

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Abstract:

Ni-Si coatings consisting of mainly NiSi_2 and NiSi were deposited on a carbon steel by air plasma spraying. Isothermal oxidation tests of the carbon steel substrates with the Ni-Si coatings at 500 °C to 800 °C have been carried out. The result indicated that a protective SiO_2 -based oxide scale was formed on the surface of the coatings after oxidation. On the other hand, during oxidation, phase transformation occurred among the NiSi_2 , NiSi and Ni_2Si phases constructing the Ni-Si coatings. This was caused by the extraction of silicon from the silicides and the reformation of silicides at the silicide/Si-blocks interface. Above 700 °C, the outward diffusion of iron and carbon became very fast and consequently decarburization happened at the coating/substrates interface, which induced the formation of pores in the substrates near the interface. In addition, grain boundary oxidation of Cr in the steel substrate observed above 700 °C.

Keywords:

Plasma sprayed Ni-Si coatings, Structure of coating layer, High-temperature oxidation, Interfacial reaction.

1. INTRODUCTION

In coal-, heavy oil-, and waste-fired power generation systems, carbon steels being used in the reactor walls and heat exchanger tubes are subject to severe oxidation, hot corrosion and erosion, resulting in the tube and wall thinning and then premature failure [1]. One way to protect the walls and tubes against failure is to perform surface coatings. In balance of density, strength and oxidation and corrosion resistance, nickel silicides are one of the promising candidate materials for coating applications. In fact, NiSi_2 showed excellent high-temperature corrosion resistance in a complex

atmosphere containing oxygen, sulfur and chlorine, in our some preliminary experiments. It has been also reported that the Ni-Si coatings obtained on a carbon steel through laser cladding can improve corrosion and wear resistance [2-4]. However, thermal spraying rather than laser cladding is more favorable for the preparation of relatively thick Ni-Si coatings. Therefore, in the present study, the preparation of the Ni-Si coatings by thermal spraying was done on a carbon steel and high temperature performance of the coatings was investigated.

In the present study, the oxidation resistance of the plasma sprayed Ni-Si coatings on the carbon steel substrates was discussed in the temperature range of 500 °C to 800 °C, including the growth mechanism of oxide scales. Phase transformation in the coatings and diffusion of elements between the coatings and substrates during oxidation were also studied.

2. EXPERIMENTAL PROCEDURES

The carbon steel substrate (SS400, C:0.17, Si:0.01, Mn:0.34, P:0.015, S:0.014, balance Fe in weight%) was degreased and sand-blasted with Al₂O₃ particles before air plasma spraying. The powder material used for spraying was NiSi₂ with an average grain size of about 3 μm. Ni-Si coatings were deposited on the carbon steel through air plasma spraying with a thickness of 45-65 μm. For the oxidation tests, the substrates with Ni-Si coatings were cut with the dimensions of 7mm×10mm×5mm.

Isothermal oxidation tests were carried out in the temperature range of 500 °C to 800 °C in static air. The phases in Ni-Si coatings before and after oxidation were identified by the X-ray diffraction method. The morphology of surface and cross-section of the Ni-Si coatings was observed by an field emission scanning electron microscope (JSM-6500F). The concentration profile of each

element in the cross-section of the oxidized specimens was measured by an electron probe microprobe analyzer (JXA-8900M).

3. RESULTS AND DISCUSSION

3.1 Structure of as-deposited Ni-Si coatings on the carbon steel substrate

The Ni-Si coatings were deposited on the carbon steel by air plasma spraying with a thickness of 45-65 μ m. XRD patterns for the plasma sprayed Ni-Si coatings are shown in **Fig. 1**. The main phases were identified as NiSi₂ and NiSi, except for a few oxides (SiO₂ and NiO). In addition, existence of a few black blocks (called “Si-blocks”) inside the coatings is observed in **Fig. 2**. Alumina powders used for sand-blasting surface of substrate also remained in the substrates.

During plasma spraying, the high temperature of plasma (maximum value: about 15000 K) is generally sufficient to melt the NiSi₂ particles completely. According to the binary phase diagram, the following reactions is respected during the cooling.

Therefore, the main phases in as-deposited coatings were NiSi₂ and NiSi. Because the plasma spraying process is characterized by a high enthalpy heat source in combination with a high quenching rate ($\sim 10^6$ K/s [5]), the upper phase transformations (eq. (1) and (2)) is tend to occur, resulting in formation of Si-blocks during the solidification process after plasma spraying. During plasma spraying, the extraction of Si from the NiSi₂ powder by selective oxidation of Si also induced the formation of NiSi phase [6].

3.2 Oxidation behavior of Ni-Si coatings

Figure 3 shows XRD patterns for specimens oxidized for 1 hr and 100 hrs at various temperatures. After oxidation for 1 h (Fig.3(a)), the oxide scale is mainly consisting of SiO₂ at all temperatures. After oxidation for 100 hrs (Fig.3(b)), the phases of oxides was same as those after 1h, except for the disappearance of NiO at 500 °C. These results demonstrate that selective oxidation of Si occurs on the Ni-Si coatings to form a protective SiO₂ scale.

Figure 4 shows the cross-sectional morphology of the SiO₂ scale formed in oxidation at 600 °C for 100hrs. The thickness values of SiO₂ scales formed at different temperatures are shown in **Fig. 5** as a function of oxidation time. After 100 hrs oxidation, the thickness values were in the range of 120-520 nm and showed an increase with the increase in temperatures. At 800 °C, the thickness of oxide scale was about 2.5 times of those at lower temperatures. The kinetics results also indicate that the increase of oxide thickness is obviously quick in the early stage of oxidation. With the increase in oxidation time, the growth rate of oxide scale becomes smaller.

The oxidation kinetics of silicide films on the silicon substrate have been modeled using the parabolic rate law [12] and a linear-parabolic (LP) model [13,14]. The linear-parabolic model can be written as

$$(L^2 - L_0^2) / k_p + (L - L_0) / k_l = t - t_0 \quad (6)$$

where L is the oxide thickness, t is the oxidation time, k_p is the parabolic rate constant, k_l is the linear rate constant, and L_0 and t_0 are offsets to the Deal-Grove model [15] and account for the initially rapid regime. The oxidation kinetics of the plasma sprayed Ni-Si coatings on the carbon steel is different from the above models, especially in the early stage.

In the early stage, because of the pores that were already existence in the Ni-Si coatings after

plasma spraying, there were a lot of diffusion channels for silicon and oxygen. The fast outward diffusion of silicon and the reaction between silicon and oxygen induced the rapid growth of SiO_2 scale during early oxidation stage. Once a continuous SiO_2 scale was formed, the oxidation rate would depend on the diffusion of oxygen through the oxide film. Therefore, in the steady oxidation stage, the growth rate of SiO_2 scale is very small and the oxidation kinetics is probably similar to that of the silicide film on a Si substrate.

3.3 Phase change in Ni-Si coatings

Table 1 indicates that NiSi_2 phase transforms into NiSi and Ni_2Si phases during oxidation. The characteristic peaks of NiSi_2 phase were very strong in the deposited Ni-Si coatings. However, after oxidation for 100 hrs at 500°C and 600°C , Ni_2Si became the main phase in the coatings, while the peaks of NiSi phase became very strong at 700°C and 800°C .

It has been reported that, for the Ni-Si films on Si substrates, the oxidation proceeds by selective oxidation of silicon at the silicide/oxide scale interface, with the diffusion of nickel toward the silicon substrate to reform silicide [7-9]. In this study, the plasma sprayed Ni-Si coatings were composed of NiSi_2 , NiSi phases and the Si-blocks. During oxidation at low temperatures ($<700^\circ\text{C}$), the growth of SiO_2 scales depend on the selective oxidation of silicon from NiSi_2 and NiSi . Therefore, NiSi_2 transformed into Ni_2Si and NiSi phases, while NiSi transformed into Ni_2Si . In 1 hr oxidation at 500°C and 600°C , NiSi and Ni_2Si became the main phases in the coatings (Table 1). With the increase in oxidation time, the main phase in the coatings became Ni_2Si .

At higher oxidation temperatures ($\geq 700^\circ\text{C}$), the Si-blocks inside the coatings began to provide a silicon supply for the reformation of silicide at the silicide/ Si-blocks interface. Therefore, the peaks

intensity of NiSi and NiSi₂ phases was stronger than that at 500°C and 600°C due to the reactions, $Ni_2Si + Si \rightarrow NiSi$ and $NiSi + Si \rightarrow NiSi_2$. A similar reaction ($NiSi + Si \rightarrow NiSi_2$) between the Ni-Si films and the Si substrates has also been observed during oxidation around 750°C [10,11]. Therefore, the phase transformation of the Ni-Si coatings during oxidation is summarized as follows:

Once the Si-blocks depleted, Ni₂Si probably reforms and becomes the main phase with increase in oxidation time.

3.4 Interface analysis between the Ni-Si coatings and substrate

Figure 6 shows the line analysis of each element, in cross section of the Ni-Si coatings before and after oxidation at different temperatures. The diffusion of carbon and iron from the substrate into the coatings increases with the increase in temperature, especially at 700°C and 800°C. In the diffusion zone, iron reacted with Si and Ni to form new phases (such as Fe₅Ni₃Si₂, FeSi, FeSi₂, FeNi₃ which were speculated from EPMA analysis). Carbon diffused into the Ni-Si coatings is oxidized to form the CO/CO₂ mixture. The voids existing in the coatings provided a space to store the CO/CO₂ mixture and acts as the channels for the escape of carbon-bearing gases, as shown in **Fig. 7**. Chen et.al. have summarized the behavior of carbon during steel oxidation [16]. At lower temperatures (<700°C), the oxidation rate of carbon may be lower than that of iron. Because carbon has virtually no solubility in the oxide scale, solid-state diffusion of carbon through the scale is inconsequential. Above 700°C, decarburization is normally observed near the surface of carbon steel [17-19]. During the oxidation of carbon steel substrates deposited with the Ni-Si coatings,

decarburization also happened near the coating/substrates interface above 700°C. This is testified by the fast diffusion of carbon from the substrates into the coatings and the existence of pores in the steel. In addition, Fig. 7 demonstrates that grain boundary oxidation of Cr, which was confirmed by EPMA analysis, occurred inside the steel substrate. This phenomenon would lead to degradation in mechanical properties of the substrate.

In contrast, the diffusion of Ni and Si from the coatings into the substrate was little detected in oxidation at 500 °C to 800 °C.

4. CONCLUSIONS

The oxidation behavior of plasma sprayed Ni-Si coatings, consisting of NiSi₂, NiSi and Si-blocks, on the carbon steel substrate have been discussed. During oxidation, the phase transformation among Ni₂Si, NiSi and NiSi₂ occurred in the coatings. This was caused by the extraction of silicon from the silicides and the reformation of silicides at the silicide/Si-blocks interface. The continuous SiO₂ scales formed, with the thickness of 120-520 nm, on the surface of the coatings after oxidation at 500 to 800°C. After the very fast growth in the early stages (within 1 h), the growth rate of the SiO₂ scales became slow in the steady oxidation stage. At 500°C to 700°C, the thickness of oxide scale was very thin, only one third of that at 800°C. Above 700°C, the outward diffusion of iron and carbon became very fast and decarburization occurred at the coating/substrates interface, which induced the formation of pores in the substrates near the interface. In addition, grain boundary oxidation of Cr in the steel substrate occurred. The results demonstrated that a diffusion barrier layer at the coatings/substrates interface was desired in order to hinder the diffusion of iron and carbon, especially during oxidation above 700°C.

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Table 1 Comparison of the peaks intensity of the Ni-Si phases before and after oxidation.

		NiSi ₂	NiSi	Ni ₂ Si
As-deposited		<i>ss</i>	<i>w</i>	<i>-</i>
500 °C	1h	<i>m</i>	<i>ss</i>	<i>ss</i>
	100 hrs	<i>m</i>	<i>-</i>	<i>ss</i>
600 °C	1 h	<i>m</i>	<i>ss</i>	<i>ss</i>
	100 hrs	<i>m</i>	<i>w</i>	<i>ss</i>
700 °C	1 h	<i>s</i>	<i>ss</i>	<i>ss</i>
	100 hrs	<i>s</i>	<i>ss</i>	<i>s</i>
800 °C	1 h	<i>s</i>	<i>ss</i>	<i>m</i>
	100 hrs	<i>s</i>	<i>ss</i>	<i>m</i>

* ss:very strong, s:strong, m:middle, w:weak

Fig. 1 XRD pattern for the plasma sprayed Ni-Si coatings.

Fig. 2 Morphology in cross section of the plasma sprayed Ni-Si coatings (1:Si, 2: NiSi₂, 3:NiSi, 4: Al₂O₃).

Fig.3 XRD patterns for the Ni-Si coatings before and after oxidation at different temperatures for 1 h (a) and 100 hrs (b)

Fig. 4 Cross-sectional morphology of oxide scale formed on the Ni-Si coatings after oxidation at 600°C for 100 hrs.

Fig. 5 Relationship between oxide scale thickness and oxidation time at different temperatures.

Fig. 6 Line analysis along the cross section before and after oxidation at different temperatures
(C: Ni-Si coatings; S: Carbon steel substrates; D: Fe diffusion area).

Fig. 7 Cross-sectional morphology of the coatings/substrate interface after oxidation for 100 hrs at 700°C.

Figure Captions:

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