High Temperature Corrosion of CoNiCrAlY–Si Alloys in the Liquid Phase of Na₂SO₄–NaCl

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As an extension of our previous work to develop a high corrosion resistant alloy for coating applications, a fundamental study of high temperature corrosion behavior of spark plasma sintered CoNiCrAlY alloys with varying Si content as 0, 10, 20 and 30% by mass has been performed. The high temperature corrosion tests were carried out in the liquid phase (melted salt) of Na₂SO₄–NaCl at elevated temperatures of 923 and 1073 K for up to 720 ks and at 1273 K for 72 ks. Our results demonstrate that the CoNiCrAlY alloy suffers from internal corrosion attack at these temperatures. On the other hand, the addition of 30 mass% Si leads to beneficial effects not only in the suppression of the formation of internal corrosion products, but also in reducing the growth of external oxide layer. In this paper, the high temperature corrosion behavior of CoNiCrAlY–Si alloys and the influences of Si addition on the corrosion resistance are intensely discussed.

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1. Introduction

When the metallic components in the fireside of coal-fired power plants interact with corrosive gases and molten deposits such that O₂, SO_x, HCl, NO_x, CO_x, H₂O, Na₂SO₄, K₂SO₄, NaCl and V₂O₅ resulting from the combustion of coal, the high temperature corrosion can potentially take place.^{1–5)} Under such conditions, three types of corrosion: gas phase corrosion, liquid phase corrosion and/or a combination of both are liable to occur. On the other hand, recent advances in the development of boiler for coal-fired power plants have also been designed to operate at higher temperatures and pressures to achieve a high thermal efficiency and reduce CO₂ emission.^{6–9)} This approach may enhance the rapid degradation or catastrophic failure of fireside components. Consequently, the development of newly alloy or coating material that can promote the formation of a protective oxide scale is becoming increasingly important in order to avoid the diffusion of aggressive elements of the salt and the penetration of molten deposit to the alloy substrate.

In response to the needs of material as described above, we have carried out a preliminary study of high temperature corrosion behavior of STBA21 steel at 923 K under simulated extreme boiler conditions. Our results have indicated that STBA21 steel was susceptible to the severe corrosion attack in the atmosphere containing Na₂SO₄ and NaCl attributed to the formation of mainly Fe-sulfides with a minor amount of Cr in a thick Fe-oxides layer and at the oxide/alloy interface.¹⁰⁾ Further works have also been done to develop a high corrosion resistant alloy for coating applications by considering the addition of Si of up to 30 mass% to the CoNiCrAlY alloy. Their resistance in an air–Na₂SO₄–NaCl gas atmosphere over the temperature range of 923–1273 K was investigated and clarified. One of the most

significant current results is the formation of oxide scale consisting of Al₂O₃ and SiO₂ on the CoNiCrAlY–30 mass% Si alloy provides an excellent protection from aggressive elements of the salt.^{11,12)} However, several studies have pointed out that the formation and establishment of a protective oxide scale also depend on several factors including alloy composition, atmospheric condition and corrosion temperature.^{13,14)} Accordingly, it is necessary here to clarify the corrosion behavior of CoNiCrAlY–Si alloys exposed to the different atmospheres and temperatures.

The present paper includes fundamental study of high temperature corrosion behavior of spark plasma sintered CoNiCrAlY–Si alloys in the liquid phase (melted salt) of Na₂SO₄–NaCl at the same temperature range with our previous work. Moreover, the influences of Si addition on the corrosion resistance are intensely discussed.

2. Experimental Procedures

2.1 Specimen preparation

The CoNiCrAlY alloys with varying Si content as 0, 10, 20 and 30% by mass were prepared by a spark plasma sintering technique. The nominal composition of respective elements and the preparation conditions of the sintered alloy have been described in more detail elsewhere.¹¹⁾ The sintered CoNiCrAlY–Si alloys were then cut into dimensions of about 11.4 mm × 5.8 mm × 1.5 mm by a rotary cutting machine, polished down to 1 μm diamond finish, prior to ultrasonically cleaned in an ethanol solution.

2.2 High temperature corrosion test

For the high temperature corrosion test, the test specimens were put in an alumina crucible with a lid and completely buried by Na₂SO₄ + 25.7 mass% NaCl, as shown schematically in Fig. 1. The crucible was then placed in a muffle furnace for up to 720 ks at elevated temperatures of 923 and

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Fig. 1 Schematic of specimen setup for the high temperature corrosion test of CoNiCrAlY–Si alloys in a mixture of Na₂SO₄–NaCl melts.

1073 K and for 72 ks at 1273 K. The salt composition used in this study is close to the eutectic composition of a Na₂SO₄–NaCl salt mixture, which has a melting point of about 901 K.¹⁵⁾ Therefore, during the test, all specimens would be subjected to the quasi-eutectic melt of Na₂SO₄ and NaCl. After the test, the specimens were taken out of the furnace and cooled down to room temperature. Finally, for metallographic examinations, corroded specimens were washed in water to remove remained salt on the specimen surface.

2.3 Evaluation and characterization

In order to evaluate the corrosion kinetics of CoNiCrAlY–Si alloys, their consumed thickness of alloy which is the sum of thickness loss of the alloy substrate and the maximum thickness of an internal corrosion attack zone was carefully measured. The evaluation was conducted in the area which is considered to be representative for the morphology conditions of the internal corrosion attack zones that often appeared in the alloy. The phase compositions and microstructures of the specimen before and after the high temperature corrosion test were analyzed by X-ray diffraction (XRD JEOL JDX-3500, Japan) and a scanning electron microscope attached with an energy dispersive X-ray analysis (FE-SEM JEOL JSM-7001FA, Japan).

3. Results and Discussion

3.1 High temperature corrosion behavior of CoNiCrAlY–Si alloys

3.1.1 High temperature corrosion at 923 K

The corrosion kinetics of CoNiCrAlY–Si alloys corroded for up to 720 ks in a mixture of Na₂SO₄–NaCl melts is presented in Fig. 2. Cross-sectional SEI micrographs of CoNiCrAlY alloys with 0, 10, 20, and 30 mass% Si content after 720 ks exposure are shown in Fig. 3, respectively.

The results, as can be seen from Fig. 2, indicate that the CoNiCrAlY alloy suffers from a high corrosion rate in comparison with the CoNiCrAlY alloy containing Si attributed to the formation of internal precipitates of Al-oxide and probably Cr-sulfide (Fig. 3(a)). The results of metallographic observation also reveal that the area around internal products became depleted in Al. On the other hand, the addition of Si leads to decrease in the consumed thickness of alloy, which is associated with the suppression of the formation of internal products. Mainly, Al-oxide is identified as the products of localized internal corrosion in the CoNiCrAlY alloys with 10 and 20 mass% Si content, as shown in Figs. 3(b) and 3(c). The existence of this internal Al-oxide in the CoNiCrAlY–Si alloys is remarkably sup-

Fig. 2 Corrosion kinetics curve of CoNiCrAlY–Si alloys corroded for up to 720 ks at 923 K in a mixture of Na₂SO₄–NaCl melts.

pressed by the addition of 30 mass% Si (Fig. 3(d)). These results imply that the addition of high Si content can significantly improve the corrosion resistance of CoNiCrAlY alloy.

According to the results of scale structural analysis, CoNiCrAlY alloys with 0, 10, and 20 mass% Si content form mainly an Al₂O₃ scale. However, the presence of Cr in the oxide scale is also identified, mostly in the oxide scale of CoNiCrAlY alloy without Si addition. A difference in the oxide scale structure is found on the CoNiCrAlY–30 mass% Si alloy. The addition of 30 mass% Si promotes the formation of thin oxide scale containing mainly of Al-oxide and Si-oxide. It is believed that this oxide scale acts as barrier for the inward diffusion of oxygen and constituents of the salt or the penetration of melted salt to the alloys substrate. Interestingly, the cross-sectional images indicate that the oxide thickness of the CoNiCrAlY alloy is significantly decreased by the addition of 30 mass% Si (from μm order to nm order).

3.1.2 High temperature corrosion at 1073 K

Figure 4 shows the corrosion kinetics of CoNiCrAlY–Si alloys corroded for up to 720 ks in a mixture of Na₂SO₄–NaCl melts. Figure 5 shows the cross-sectional SEI micrographs of CoNiCrAlY alloys with 0, 10, 20, and 30 mass% Si content after 720 ks exposure.

From the corrosion kinetic curve, it can be seen that with increase in corrosion temperature, the CoNiCrAlY–10 mass% Si alloy is more susceptible to high temperature corrosion similarly to the CoNiCrAlY alloy without Si addition. The high consumed thickness of both alloys is ascribed to the formation of localized internal corrosion composing mainly of Al, Cr, O, S, and Na (probably Cr-sulfide and Al-oxide containing Na) in the CoNiCrAlY–10 mass% Si alloy, as far as of internal precipitates of Al-oxide and YS in the CoNiCrAlY alloy without Si, as shown in Figs. 5(a) and 5(b), respectively. The results of EDS analysis indicate that both alloys form the external oxide scale composed mainly of Al₂O₃.

On the other hand, the addition of 20 and 30 mass% Si demonstrates much better corrosion resistance than that of 10 mass% Si and seems to improve the corrosion resistance of CoNiCrAlY alloy. The CoNiCrAlY alloy with 20 mass%

Fig. 3 Cross-sectional SEI micrographs of CoNiCrAlY alloys with (a) 0, (b) 10, (c) 20, and (d) 30 mass% Si content after 720 ks exposure at 923 K in a mixture of Na_2SO_4 – NaCl melts.

Fig. 4 Corrosion kinetics curve of CoNiCrAlY–Si alloys corroded for up to 720 ks at 1073 K in a mixture of Na_2SO_4 – NaCl melts.

Si content formed the oxide scale composed mainly of Al_2O_3 . However, as shown in Fig. 5(c), an Al-depleted zone beneath the oxide scale can also be observed. In the case of CoNiCrAlY alloy with 30 mass% Si content, the addition of Si leads to the formation of oxide scale consisting of Al_2O_3 and SiO_2 , resulting in an excellent corrosion protection, as shown in Fig. 5(d). The formation of SiO_2 scale may also play an important role in reducing the supply of Al ions to form the external Al_2O_3 scale. As a result, an Al-depleted zone in this alloy has become negligible.

3.1.3 High temperature corrosion at 1273 K

The consumed thickness of CoNiCrAlY alloys as a function of Si content corroded for 72 ks in a mixture of Na_2SO_4 – NaCl melts is presented in Fig. 6. Cross-sectional SEI micrographs of CoNiCrAlY alloys with 0, 10, 20, and

30 mass% Si content after 72 ks exposure are shown in Fig. 7, respectively.

As well as at 1073 K, the CoNiCrAlY–10 mass% Si alloy experienced a high corrosion rate, followed by CoNiCrAlY alloy without Si addition. This is again due to the formation localized internal corrosion composed mainly of Cr-sulfide and Al-oxide with a minor amount of Na. In the case of CoNiCrAlY alloy, EDS analysis reveals that the products of internal corrosion are mainly yttrium sulfide. The surface of the CoNiCrAlY alloy beneath the oxide scale also became depleted in Al. This could be due to the outward diffusion of Al to retain the formation of external Al_2O_3 scale. Moreover, there is a difference in scale structure between CoNiCrAlY alloys with 0 and 10 mass% Si content. The CoNiCrAlY alloy without Si addition forms a duplex oxide layer consisting of $\text{Al}_5\text{Y}_3\text{O}_{12}$ in the outer layer and Al_2O_3 in the inner layer (Fig. 7(a)), while the CoNiCrAlY–10 mass% Si alloy forms the oxide scale composed mainly of Al_2O_3 (Fig. 7(b)).

The good effects of Si addition in improving the corrosion resistance of CoNiCrAlY alloy can be seen in the CoNiCrAlY alloys with 20 and 30 mass% Si content. These alloys form a denser Al_2O_3 scale containing trace element of Si and the oxide scale consisting of Al_2O_3 and SiO_2 , respectively. Comparing the two scales shown in Figs. 7(c) and 7(d), the oxide scale of the CoNiCrAlY–30 mass% Si alloy exhibits much better adherence to the alloy substrate than that of the CoNiCrAlY–20 mass% Si alloy.

3.2 Effect of Si addition

The schematic illustrations of cross-sectional scale structures formed on the CoNiCrAlY–Si alloys in a mixture of Na_2SO_4 – NaCl melts over the temperature range of 923–

Fig. 5 Cross-sectional SEI micrographs of CoNiCrAlY alloys with (a) 0, (b) 10, (c) 20, and (d) 30 mass% Si content after 720 ks exposure at 1073 K in a mixture of Na₂SO₄–NaCl melts.

Fig. 6 Consumed thickness of CoNiCrAlY–Si alloys corroded for 72 ks at 1273 K in a mixture of Na₂SO₄–NaCl melts.

1273 K are shown in Fig. 8. Table 1 summarizes the crystal structures of the external oxide scales, which were detected by X-ray diffraction analysis. However, there are still undecided crystal structures of an Al₂O₃ and Al₂O₃/SiO₂ scales due to the fact that it has spalled from the alloy surface and the oxide thickness is sufficiently thin, respectively. Therefore, X-ray diffraction analysis failed to identify their crystal structures. The structures of oxide scales were then obtained by EDS analysis. From the results of X-ray diffraction analysis, it is apparent that the crystal structures of an Al₂O₃ and SiO₂ scales on the CoNiCrAlY–Si alloys are affected by the alloy composition and corrosion temperature.

As described above, the high consumed thickness of alloy in the CoNiCrAlY and the CoNiCrAlY alloy with 10 mass% Si content is primarily caused by the formation of serious

internal corrosion products (mainly sulfides and oxides). The mechanism for the formation of internal sulfide is similar to that of internal oxidation, which can take place when the inward diffusion of sulfur in the alloy substrate is much faster than that the outward diffusion of the alloying elements in the alloy substrate to form their external oxide scale.^{16–18)}

The difference in the products of internal corrosion can be found in the CoNiCrAlY alloy without Si addition with increase in corrosion temperature, as mentioned above and shown schematically in Fig. 8. For examples, at 923 K Al-oxide and Cr-sulfide are formed, while at 1273 K mainly YS is preferentially formed. This difference might be due to the formation of a denser external oxide layer with increase in corrosion temperature. The Cr content (21 mass%) in the CoNiCrAlY alloy is much higher than Y content (0.5 mass%). However, the standard free energy of formation of YS at elevated temperatures is more negative than CrS.¹⁹⁾ The formation of a denser external oxide layer seems to significantly reduce the inward diffusion flux of sulfur. Therefore, at higher temperatures, even a very small amount of inward sulfur diffusion, yttrium will be sulfidized. In contrast, at 923 K, the CoNiCrAlY alloy did not form a dense and protective oxide layer. Consequently, the inward diffusion flux of oxygen and constituents of the salt through the oxide layer can be considerably higher than that at 1273 K. This leads to the internal oxidation of Al and sulfidation of Y firstly and Cr gradually occurs.

The beneficial effect of Si addition on the corrosion resistance of CoNiCrAlY alloys in the liquid phase corrosion is similar with in the gas phase corrosion, which depends on the alloy composition and corrosion temperature. At 923 K, the addition of Si improves the corrosion resistance of

Fig. 7 Cross-sectional SEI micrographs of CoNiCrAlY alloys with (a) 0, (b) 10, (c) 20, and (d) 30 mass% Si content after 72 ks exposure at 1273 K in a mixture of Na_2SO_4 – NaCl melts.

Fig. 8 Schematic illustrations of cross-sectional scale structures formed on CoNiCrAlY–Si alloys in a mixture of Na_2SO_4 – NaCl melts at elevated temperatures of (a) 923, (b) 1073, and (c) 1273 K.

CoNiCrAlY alloy. However, with increase in corrosion temperature (at 1073 and 1273 K), the addition of 10 mass% Si makes this alloy susceptible to the localized internal formation of Cr-sulfide and Al-oxide, mainly. The consumed thickness of this alloy is also higher than that of 0 mass% Si alloy. This might be related to the formation of fragile oxide scale on the 10 mass% Si alloy, which can probably lead to the generation of localized fine cracks. It then becomes

transport paths for the inward diffusion of oxygen and constituents of the salt to the alloy substrate. Diffused constituents then react with the alloy components to form mainly internal Cr-sulfide and Al-oxide. However, the reason for the role of 10 mass% Si addition in promoting the formation of fragile oxide scale is still unclear at present.

With increase in Si content (20 and 30 mass%), the corrosion resistance of CoNiCrAlY alloy increases. Never-

Table 1 Crystal structures of external oxide scales formed on CoNiCrAlY–Si alloys in a mixture of Na₂SO₄–NaCl melts at elevated temperatures of 923, 1073, and 1273 K.

Alloys (mass%)	Crystal structures of external oxide scales		
	923 K	1073 K	1273 K
CoNiCrAlY	Al ₂ O ₃	Al ₂ O ₃	Al ₅ Y ₃ O ₁₂ , α -Al ₂ O ₃
CoNiCrAlY–10 Si	θ -Al ₂ O ₃ , α -Al ₂ O ₃	θ -Al ₂ O ₃ , α -Al ₂ O ₃	α -Al ₂ O ₃ , θ -Al ₂ O ₃
CoNiCrAlY–20 Si	α -Al ₂ O ₃ , θ -Al ₂ O ₃	α -Al ₂ O ₃	α -Al ₂ O ₃
CoNiCrAlY–30 Si	Al ₂ O ₃ , SiO ₂	α -Al ₂ O ₃ , Monoclinic SiO ₂	α -Al ₂ O ₃ , Quartz SiO ₂

theless, a minor localized internal Al-oxide and Al-depleted zone is still observed in the CoNiCrAlY alloy with 20 mass% Si content. On the other hand, the CoNiCrAlY alloy with 30 mass% Si content shows the highest corrosion resistance over the temperature range of 923–1273 K. This is attributed to the formation of a protective oxide scale consisting of Al₂O₃ and SiO₂. Another interesting result could also be found in the liquid phase corrosion, that is, the oxide thickness in the CoNiCrAlY–Si alloys tends to decrease especially with the addition of 30 mass% Si, as can be seen in Figs. 3, 5 and 7. The same possible reason for this phenomenon has been explained briefly in our previous paper.¹¹⁾

The results of this study, as presented above, reveal that the corrosion products beneath the outer oxide scale are mainly oxides and sulfides. The other important corrosion product as chlorides is not detected by X-ray diffraction or EDS analysis. Thermodynamically, the chlorides of aluminum, chromium, cobalt or nickel show a negative free energy of formation in the range temperature of 923–1273 K.²⁰⁾ This means that the formation of those chlorides during the high temperature corrosion test are likely to occur. However, due to the high volatility and water solubility of most metal chlorides,^{21–23)} the chlorination products may evaporate during the high temperature corrosion test and dissolve into water during metallographic preparations. For that reason, they are not detected by metallographic analysis.

4. Summary

In this paper, the high temperature corrosion behavior of CoNiCrAlY–Si alloys in the liquid phase (melted salt) of Na₂SO₄–NaCl was investigated and clarified. The following conclusions can be drawn:

- (1) The CoNiCrAlY alloy suffers from internal corrosion in the current temperature region. Internal corrosion products consisting of Al-oxide, Cr-sulfide and/or YS are formed beneath an Al₂O₃ scale, depending on the corrosion temperature.
- (2) The beneficial effect of Si addition on the corrosion resistance of CoNiCrAlY alloy depends on the Si content and corrosion temperature.
- (3) The formation of oxide scale consisting of Al₂O₃ and SiO₂ on the CoNiCrAlY–30 mass% Si alloy shows an

excellent corrosion resistance in a mixture of Na₂SO₄–NaCl melts.

- (4) The formation of SiO₂ scale plays a significant role in suppression of the growth of external oxide scale and hindering the penetration of molten salt or the diffusion of constituents of the salt to the alloy substrate. As a result, internal corrosion is remarkably suppressed.

The results of this study support the idea that the CoNiCrAlY–30 mass% Si coating on STBA21 steel is very effective for improving the high temperature corrosion resistance of STBA21 steel in coal-fired boiler.

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