The Influence of CoNiCrAlY Addition on the High Temperature Corrosion Behavior of CrSi₂ Alloy in an Air–Na₂SO₄–NaCl Gas Atmosphere

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In this study, an attempt has been made to improve the resistance of CrSi₂ alloy toward high temperature corrosion and promote the formation of a continuous and slow-growing SiO₂ scale on the alloy surface. For this purpose, spark plasma sintering was used to fabricate the CrSi₂ alloys containing various amounts of CoNiCrAlY. The sintered alloys were then corroded isothermally in an air–Na₂SO₄–NaCl gas atmosphere at three different temperatures of 923 and 1073 K for up to 720 ks and at 1273 K for 72 ks. XRD, SEM and SEM-EDS were utilized to examine the alloy structures and compositions before and after the high temperature corrosion test. The influence of CoNiCrAlY addition on the high temperature corrosion behavior of the CrSi₂ alloy was clarified. [doi:10.2320/matertrans.MAW201210]

(Received April 25, 2012; Accepted June 5, 2012; Published July 25, 2012)

Keywords: CrSi₂–CoNiCrAlY, high temperature corrosion, gas atmosphere, sodium sulfate, sodium chloride

1. Introduction

Owing to its high melting point (1750 K), relatively low density (4.6 g cm⁻³) and outstanding resistance to oxidation in air, chromium disilicide (CrSi₂) has become an attractive material for energy-related high temperature applications.¹,² The excellent oxidation resistance of this material is ascribed to the formation of a protective SiO₂ scale. In our study, CrSi₂ has been taken into consideration as a candidate coating material of commercial alloys for use in corrosive boiler atmospheres. However, the previous results indicated that at temperature of 1073 K and in the corrosive atmosphere containing Na₂SO₄ and NaCl, the CrSi₂ alloy was susceptible to severe internal corrosion because they didn’t serve the formation of a continuous SiO₂ layer.³,⁴ Accordingly, a considerable amount of additional elements is necessary to improve the corrosion resistance of this alloy.

In further study, we have succeeded in developing a continuous, dense and protective SiO₂ scale on the surface of CrSi₂ alloys under the same atmospheric conditions by adding varying Ni content.³,⁴ The establishment of (Cr,Ni) Si and (Cr,Ni)₂Si phases in the CrSi₂–Ni alloys seems to have a strong influence in promoting the growth of a continuous SiO₂ scale. As a result, an internal corrosion (sulfides and chlorides formation) was completely suppressed. However, there is still a noticeable concern that the thickness of a SiO₂ scale appears to increase with the content of Ni in the alloys.³,⁴ Thus, an attempt to find out how to develop a slow-growing SiO₂ scale has become an essential feature, especially for long exposure times.

To elucidate the above problems, we deal with the addition of alumina-forming material (CoNiCrAlY)⁵,⁶ to the CrSi₂ alloy. We expect that the presence of Ni and Co elements can result in the generation of Ni or Co-silicides phases, which may play a role in promoting the formation of a continuous SiO₂ scale, and the presence of Al element can contribute to the formation of an Al₂O₃ scale at the SiO₂/alloy interface. Expectingly, this oxide layer has a good effect in suppressing the growth of a SiO₂ scale by retarding the inward diffusion of oxygen.

In the present study, the influence of CoNiCrAlY addition on the high temperature corrosion behavior of CrSi₂ alloy exposed to an air–Na₂SO₄–NaCl gas atmosphere is clarified.

2. Experimental Procedures

The nominal compositions of respective elements of CrSi₂–CoNiCrAlY powders (in mass%) used in this study are shown in Table 1. The CrSi₂–CoNiCrAlY alloys were prepared by applying the same procedures and technique as that for fabrication of the CrSi₂–Ni alloys.³,⁴ The powders were fully sintered for 1.98–2.88 ks in a temperature range of 1123–1273 K.

Cut specimens with average dimensions of length 11.4 mm, width 5.8 mm and thickness 1.5 mm were ground to 1 µm diamond paste finish and then cleaned ultrasonically.

Table 1: Nominal compositions of respective elements of CrSi₂–CoNiCrAlY powders.

<table>
<thead>
<tr>
<th>Powder compositions (mass%)</th>
<th>Components content (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrSi₂</td>
<td>Co</td>
</tr>
<tr>
<td></td>
<td>48.07</td>
</tr>
<tr>
<td>CrSi₂–10 CoNiCrAlY</td>
<td>3.85</td>
</tr>
<tr>
<td>CrSi₂–20 CoNiCrAlY</td>
<td>7.70</td>
</tr>
<tr>
<td>CrSi₂–30 CoNiCrAlY</td>
<td>11.55</td>
</tr>
</tbody>
</table>

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in an ethanol solution for 0.9 ks. The experimental set-up for the high temperature corrosion test is similar to the one that has been already reported schematically in our previous study.7) The test specimens were put in a lidded alumina crucible containing a salt mixture of \( \text{Na}_2\text{SO}_4 + 25.7 \text{ mass}\% \text{NaCl} \) and then corroded isothermally in a muffle furnace for up to 720 ks at elevated temperatures of 923 and 1073 K and for 72 ks at 1273 K. The salt mixture used in this study is near to the eutectic composition of \( \text{Na}_2\text{SO}_4 \) and \( \text{NaCl} \) which has a melting point of 901 K.8) Accordingly, the test specimen would be exposed to an air containing salt vapor of a quasi-eutectic melt of \( \text{Na}_2\text{SO}_4 \) and \( \text{NaCl} \). After completion of the corrosion test, the specimens were then removed from a muffle furnace and cooled to room temperature.

To measure the thickness loss of alloy substrate and observe the depth of an internal attack zone, the corroded alloys were fractured in liquid nitrogen. For elemental mapping analysis, some specimens were mounted in the epoxy resin, sectioned and polished down to 1 µm diamond paste finish. XRD, SEM and SEM-EDS analysis were utilized to examine the structure and composition of the alloys before and after the high temperature corrosion test. Finally, based on the corrosion kinetic data and structures of the oxide scales formed on the alloy surface, the influence of \( \text{CoNiCrAlY} \) addition on the high temperature corrosion behavior of \( \text{CrSi}_2 \) alloy is discussed.

3. Results and Discussion

3.1 Structures and compositions of sintered alloy

The microstructures of \( \text{CrSi}_2-\text{CoNiCrAlY} \) alloys before the high temperature corrosion test fabricated by spark plasma sintering are shown in Fig. 1. In the \( \text{CrSi}_2 \) alloy, small precipitations of \( \text{CrSi} \) phase are dispersed in the alloy matrix. On the other hand, in the \( \text{CrSi}_2 \) alloys with various \( \text{CoNiCrAlY} \) content, the alloys comprise two major regions: the dark area composed primarily of \( \text{CrSi} \) phase and the light area composed of \( \text{CrSi}_2 \) and \( \text{Co-Ni} \) silicides phases. As can be seen from Figs. 1(b), 1(c) and 1(d), the volume fraction of light area increases with increase in \( \text{CoNiCrAlY} \) content.

The results of EDS semi-quantitative analysis also indicate that the Al content in the light areas increases with increase in \( \text{CoNiCrAlY} \) content. For instance, in the \( \text{CrSi}_2 \) alloys with 30 mass\% \( \text{CoNiCrAlY} \) content, it is around 2–4\% by molar amount. Furthermore, the localized grey area in this alloy is confirmed as \( \text{Cr}_2\text{Si} \).

3.2 High temperature corrosion behavior of \( \text{CrSi}_2-\text{CoNiCrAlY} \) alloys

3.2.1 High temperature corrosion at 923 K

Figure 2 shows the kinetic curves of corrosion of \( \text{CrSi}_2-\text{CoNiCrAlY} \) alloys exposed to an air–\( \text{Na}_2\text{SO}_4–\text{NaCl} \) gas atmosphere at 923 K for up to 720 ks. Figure 3 shows the
fractured cross-sectional SEI micrographs of CrSi₂ alloys with 0, 10, 20 and 30 mass% CoNiCrAlY content after 720 ks exposure.

The kinetic results reveal that the CrSi₂ alloy exhibits somewhat higher consumed thickness of alloy compared with the CoNiCrAlY-added CrSi₂ alloys. Moreover, the corrosion kinetics have a tendency to decrease with increase in CoNiCrAlY content in the alloys. As can be seen in Fig. 2, in the CrSi₂ alloys with 20 and 30 mass% CoNiCrAlY content, a slight increase in the consumed thickness of alloy is observed after 72 ks exposure.

The metallographic observation indicates that the structures of the oxide scale depend on the CoNiCrAlY content. The CrSi₂ alloys with 0 and 10 mass% CoNiCrAlY content form mostly a SiO₂ scale. However, according to the results of X-ray diffraction analysis, there is a difference in the crystal structure of a SiO₂ scale on the both alloys. The CoNiCrAlY-free alloy forms mainly trydimite-SiO₂ while the CrSi₂ alloy with 10 mass% CoNiCrAlY content forms mainly cristobalite-SiO₂. Accordingly, a high consumed thickness of the CrSi₂ alloy may be caused by the fact that oxygen can diffuse inward easily through trydimite-SiO₂ than that of cristobalite-SiO₂. On the other hand, the CrSi₂ alloys with 20 and 30 mass% CoNiCrAlY content form the oxide scales composed of SiO₂ and Al₂O₃.

At this temperature, a continuous, compact and protective oxide scales are formed on the surface of CrSi₂–CoNiCrAlY alloys. Consequently, these four alloys exhibit a high resistance against internal corrosion and oxidation.

### 3.2.2 High temperature corrosion at 1073 K

Figure 4 shows the kinetic curves of corrosion of CrSi₂–CoNiCrAlY alloys exposed to an air–Na₂SO₄–NaCl gas atmosphere for up to 720 ks at 1073 K. The fractured cross-sectional SEI micrographs of CrSi₂ alloys with 0, 10, 20 and 30 mass% CoNiCrAlY content after corroded for 720 ks are shown in Fig. 5.

As can be seen, the CoNiCrAlY-free alloy suffers the highest consumed thickness of alloy compared with the other three alloys. A significant difference in the consumed
thickness of alloy at 1073 K is attributed to the formation of severe internal products beneath a SiO₂ scale. As explained previously, the CrSi₂ alloy doesn’t form a continuous SiO₂ scale at this temperature. As a result, the aggressive elements of the salts can easily diffuse inwardly and react with the alloy components to form the internal products of sulfide and chloride.

On the contrary, the corrosion resistance of CrSi₂ alloy is improved by the addition of CoNiCrAlY because they can promote the formation of more uniform a SiO₂ scale on the CrSi₂–10 mass% CoNiCrAlY alloy and the oxide scale consisting of SiO₂, Al₂SiO₅ and Al₂O₃ on the CrSi₂–20 and 30 mass% CoNiCrAlY alloys. Accordingly, a high protection to the inward diffusion of oxygen and aggressive elements of the salt is provided for these alloys. Additionally, the results also clearly demonstrate that the addition of 20 and 30 mass% CoNiCrAlY leads to decrease in the consumed thickness of CrSi₂–CoNiCrAlY alloys. The formation of Al₂SiO₅ scale on these alloys is resulted from the reaction of SiO₂ and Al₂O₃ scales.

3.2.3 High temperature corrosion at 1273 K

The consumed thickness of CrSi₂ alloys with 0, 10, 20 and 30 mass% CoNiCrAlY content exposed to an air–Na₂SO₄–NaCl gas atmosphere for 72 ks is shown in Fig. 6. The cross-
sectional micrographs of CrSi2–CoNiCrAlY alloys after 72 ks exposure are presented in Fig. 7.

From the graphs, we can see that the consumed thickness of CrSi2 alloys slightly rises with the addition of 10 mass% CoNiCrAlY. However, it tends to decrease by the addition of 20 and 30 mass% CoNiCrAlY.

The cross-sectional observation reveals that these four alloys offer a high corrosion resistance attributed to the formation mainly of a continuous and dense SiO2 scale on the CrSi2 alloys with 0 and 10 mass% CoNiCrAlY content, and a duplex oxide layer consisting mainly of SiO2 containing some amount of Al-oxide in the outer layer and Al2O3 in the inner layer on the CrSi2 alloys with 20 and 30 mass% CoNiCrAlY content.

The results also indicate that after 72 ks exposure, the effect of CoNiCrAlY addition on the corrosion resistance is not clearly seen. Accordingly, by considering the structure of the alloy, the thickness and structure of the oxide scale, we believe that an increase in the thickness of oxide scale on the CrSi2 alloy by the addition of CoNiCrAlY is influenced strongly by the alloy structure. As aforementioned, the volume fraction of new phases increases with increase in CoNiCrAlY content in the alloy. Their formation appears to play a key role in enhancing the growth of SiO2 scale. On the other hand, the effect of alumina formation at the SiO2/alloy interface on the CrSi2 alloys with 20 and 30 mass% CoNiCrAlY content may become visible in longer exposure time.

The results of EDS elemental maps also indicate that with increase in corrosion temperature, the distribution of sodium element in the SiO2 scales tends to be more noticeable. The same reason for this evidence has been described in our previous study.4) Interestingly, the sodium distribution is remarkably suppressed in an Al2O3 scale. This may be related to the eutectic temperature of sodium aluminate which is higher than that of sodium silicate and the corrosion temperature.10)

3.3 Influence of CoNiCrAlY addition

Summarizing the results of this study, the addition of CoNiCrAlY to the CrSi2 alloy leads to the formation of new phases as CrSi, Cr3Si and Co–Ni silicides in the CrSi2–CoNiCrAlY sintered alloys and promote the formation of a continuous and dense SiO2 scale and oxide scale consisting of SiO2, Al2SiO5 and Al2O3, depending on the alloy composition and temperature.

The major reason for why the establishment of new phases can promote the formation of a protective oxide scale may be explained by that the new phases and the phase boundaries in alloys seem to allow the higher flux of the outward silicon diffusion. As a result, they can lead to the promotion of the formation of a continuous and denser SiO2 scale on the alloy surface.

Next, we would like to consider the effect of Al on the formation of a protective scale. As mentioned before, with increase in the CoNiCrAlY content, the Al content in the
light areas also tends to increases and its effect on the corrosion resistance tends to be more pronounced in longer exposure times (for instance, after 72 ks exposure at 923 and 1073 K). The CrSi2–20 and 30 mass% CoNiCrAlY alloys form not only a protective SiO2 scale but also Al2O3 and Al2SiO5 scales, as described above. The formation of an Al2O3 scale on the alloy surface appears to play a role in suppressing the inward diffusion of oxygen, sulfur and chlorine. Accordingly, the consumed thickness of the alloy tends to decrease with the addition of 20 and 30 mass% CoNiCrAlY.

The mechanism of a duplex oxide layer formation on the surface of CrSi2 alloys with 20 and 30 mass% CoNiCrAlY content can be shown schematically in Fig. 8 and explained in more detail as follows. Initially, oxygen and aggressive elements of the salts react with the alloy substrate (Fig. 8(a)). Owing to the high content of Si in the alloys, Si is preferentially oxidized (Fig. 8(b)). This results in the formation of a SiO2 layer on the alloy surface (Fig. 8(c)). However, it is important to note that the alloy also contains Al element which has a strong affinity for oxygen. For that reason, Al element in the alloy substrate diffuses outwardly and reacts with SiO2 to form mainly Al2O3 at the SiO2/Alloy interface (Fig. 8(d)).

\[ 2\text{Al} + \frac{3}{2}\text{SiO}_2 \rightarrow \text{Al}_2\text{O}_3 + \frac{3}{2}\text{Si} \]  

(1)

The released Si is then gradually re-oxidized to form a SiO2 scale. At the oxide interfaces, the reaction between Al2O3 and SiO2 seems to take place, resulting in the formation of SiO2-Al2O3 scales (Fig. 8(e)).

**4. Summary**

The influence of CoNiCrAlY addition on the high temperature corrosion behavior of CrSi2 alloy was investigated and clarified in an air–Na2SO4–NaCl gas atmosphere. The obtained results can be summarized as follows:

1. The addition of CoNiCrAlY to the CrSi2 alloy contributes in the formation of a continuous and dense oxide scale on the alloy surface. As the result, the attack of aggressive elements of the salts doesn’t occur the underneath alloy.

2. The establishment of an Al2O3 scale at the SiO2/Alloy interface has beneficial effect in retarding inward diffusion of oxygen and other aggressive elements, leading to suppression of the consumed thickness of alloy in longer exposure time.

3. Considering the alloy fabrication, microstructure and corrosion resistance, the CrSi2 alloy with 20 mass% CoNiCrAlY content offers the highest performance as a candidate coating material.

**Acknowledgements**

The authors thank the Japan Society for the Promotion of Science (JSPS) for financial support and also Akira Yamauchi, Ph.D. for his excellent and valuable technical assistance.

**REFERENCES**