

Hot Corrosion of a Single Crystal Ni-Base Superalloy by Na-Salts at 900°C

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The hot corrosion behaviors of a single crystal (SC) Ni-base superalloy coated with Na₂SO₄ and 75 wt.% Na₂SO₄-25 wt.% NaCl mixture were studied in air at 900°C. The results showed that the corrosion productions were laminar structure, porous and easily spalled. And sulfides formed quickly in the deep SC superalloy under the corrosion production. The addition of NaCl into Na₂SO₄ considerably accelerated the corrosion of the SC superalloy, and the corrosion scale became more porous. The hot corrosion process was explained based on sulfide formation and its subsequent oxidation.

KEY WORDS: single crystal Ni-base superalloy; hot corrosion; molten salt; microstructure.

INTRODUCTION

The majority of nickel-base superalloy development efforts have been directed toward improving high-temperature strength with relatively minor concern for high temperature corrosion resistance. Subsequently, the mechanical properties are severely affected during service due to hot corrosion attack that, in turn, results in considerably reducing the lifetime of turbines. The corrosion attack is further accelerated for marine applications by the aggressiveness of an environment, which includes sulfur, vanadium, and sodium from the fuel and the various halides present in seawater. Hence,

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for effective and efficient functioning of turbine components, it is highly essential to develop alloys with high-temperature strength as well as good hot corrosion resistance. Fortunately, protective coatings, such as aluminides, NiCrAlY and thermal barrier coatings,¹⁻⁵ were developed and applied to superalloys to control high temperature corrosion of superalloys.

A single-crystal (SC) Ni-base superalloy developed recently is found to exhibit excellent high-temperature strength and it may be possible to use this material for gas turbine blades. Since high temperature corrosion is one of the major limitations in selecting the materials for gas turbine engines, it is essential to study in detail the high temperature corrosion behavior of the candidate alloy. Recently, the oxidation behavior of the SC superalloy has been studied in different conditions, the results revealed that the SC superalloy exhibited good oxidation resistance up to 1000°C.^{6,7} In this paper, the hot corrosion behavior of the SC Ni-base superalloy was investigated in the presence of pure sodium sulfate and salt mixtures of sodium sulfate and sodium chloride, with the aim of providing data for predicting its hot corrosion life and for determining a suitable protection method.

EXPERIMENTAL PROCEDURES

Circular specimens of ϕ 15 mm \times 5 mm were machined from SC Ni-base superalloy bars, which contain mainly Ni with 6.3 wt% Al, 6 wt% Cr, and some Co, Ti, Mo, W and Ta. The specimens were ground down to 600-grit SiC paper, degreased in acetone, ultrasonically cleaned in alcohol, and dried in hot air.

For the hot corrosion test, the specimens were placed on a warm plate (\sim 200°C) and brushed with a saturated aqueous solution of Na₂SO₄ or 75 wt.% Na₂SO₄-25 wt.% NaCl mixture to form a uniform coating of deposit salt. The melting points of these salts are 884°C and 620°C, respectively.⁸ The specimens with Na₂SO₄ coating or 75 wt.% Na₂SO₄-25 wt.% NaCl mixture were suspended and inserted into a muffle furnace with a temperature of 900°C separately, and then were taken out at certain intervals. After cooling to room temperature, they were cleaned in boiling water for removing the salt left on the surface, dried in hot air, and then weighed with an electronic balance with a resolution of 2×10^{-5} g. After mass measurement, the specimens were re-coated with Na₂SO₄ salts and the test was continued for another run. All kinetics data were normalized per unit area. Five specimens were simultaneously tested at each case and the average values of mass change were used.

The surface morphologies and polished cross sections of the corroded specimens were examined with SEM (JSM-6301F) equipped with energy dispersion analytical X-ray spectroscopy (EDAX). The compositions and the phases of the corrosion scales were analyzed by EDAX and X-ray diffraction, respectively.

RESULTS

Hot Corrosion Kinetics

Figures 1 and 2 show the hot corrosion kinetics of the SC Ni-base superalloy in the environment of Na_2SO_4 or 75 wt.% Na_2SO_4 -25 wt.% NaCl mixture at 900°C. In the environment of Na_2SO_4 , significant mass gain was associated with rapid hot corrosion attack of the superalloy, followed by considerable mass loss due to the corrosion scale spallation after 10 hr. While in the environment of 75 wt.% Na_2SO_4 -25 wt.% NaCl mixture, only mass loss was observed in the whole process due to the scale spallation when the specimens were cleaned in boiling water.

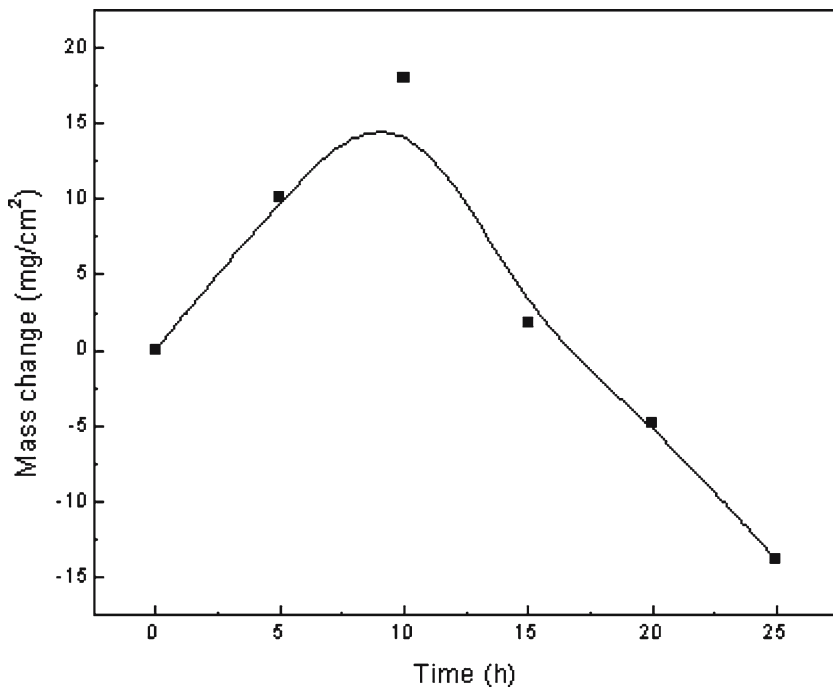


Fig. 1. Hot corrosion kinetics of the SC superalloy coated with Na_2SO_4 at 900°C.

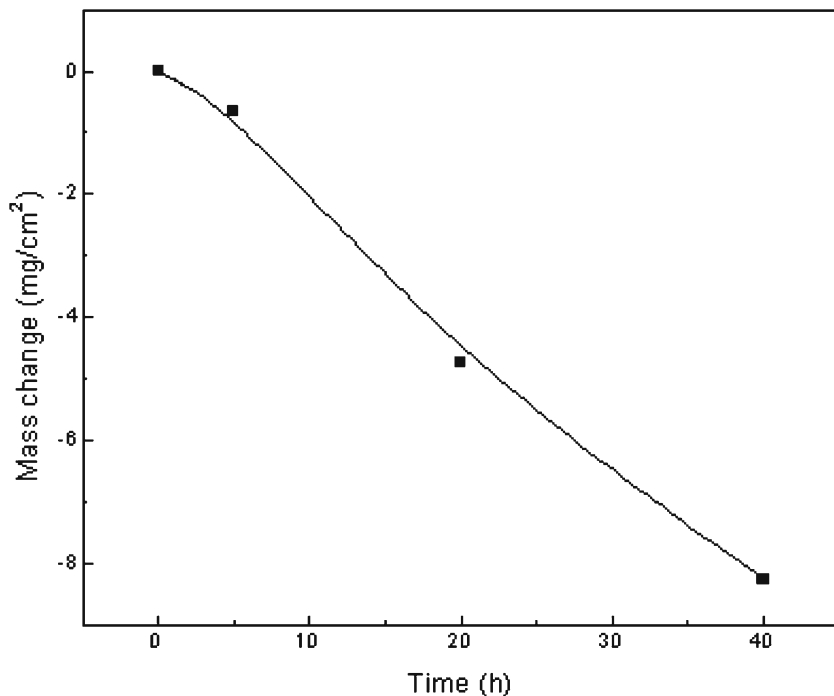


Fig. 2. Hot corrosion kinetics of the SC Ni-base superalloy coated with 75 wt% Na_2SO_4 -25 wt% NaCl mixture at 900°C .

X-ray Diffraction

The X-ray diffraction (XRD) spectra for surfaces of the SC superalloy specimens after hot corrosion are illustrated in Fig. 3. In the case of the superalloy coated with Na_2SO_4 , the corrosion scale phases were predominant NiO with a little other oxides and sulfides after 10 hr corrosion at 900°C (Fig. 3a). However, relatively strong peaks of Al_2O_3 , NiAl_2O_4 , Cr_2S_3 , Al_2S_3 , Ni_3S_2 and TiS were detected in the XRD spectra after 100 hr (Fig. 3b). While in the case of the superalloy coated with Na_2SO_4 -25 wt.% NaCl mixture, relatively strong peaks of Cr_2S_3 , Al_2S_3 and Ni_3S_2 were detected only after 5 hr (Fig. 3c).

Microstructure of Corrosion Products

Figures 4 and 5 show the surface morphologies of the corrosion scale for the SC superalloy after hot corrosion at 900°C , with corresponding

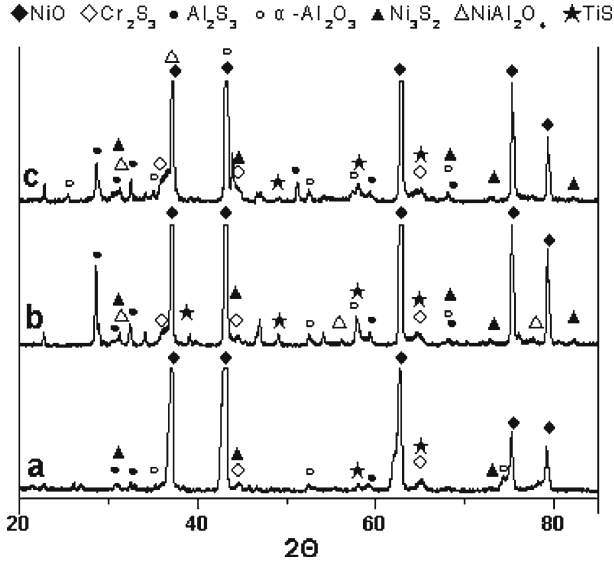


Fig. 3. XRD spectra for surfaces of the SC superalloy after hot corrosion in the environment of (a) Na_2SO_4 for 10 hr, (b) Na_2SO_4 for 100 hr, and (c) $\text{Na}_2\text{SO}_4\text{-NaCl}$ mixture for 5 hr.

representative EDAX results. In the case of the SC superalloy coated with Na_2SO_4 , cracks and some spallation were observed in the corrosion scale (Fig. 4a), and a subscale appeared in the spalled areas (area B in Fig. 4a) after 100 hr. At higher magnification, the outer scale had a blocky morphology (Fig. 4b) and mainly consisted of NiO (Fig. 4c). The subscale showed a grain-like morphology (Fig. 4d); strong Ni and O peaks as well as Al, Cr and other alloying element peaks were obtained by EDAX (Fig. 4e), indicating that in addition to oxide of Ni, some oxides of Al, Cr and other alloying element formed in the subscale. While in the case of the superalloy coated with 75 wt.% $\text{Na}_2\text{SO}_4\text{-}25$ wt.% NaCl mixture after 20 hr at 900°C, cracks and spallation of the corrosion scale were more pronounced (Fig. 5a). Many pores were found in the outer scale and subscale (Fig. 5b, d). Compared with the case of the superalloy coated with pure Na_2SO_4 , the outer scale and the subscale were looser and more porous. According to the EDAX analysis, the outer scale was mainly oxide of Ni with some oxides of Cr, Co and Al (Fig. 5c), and the subscale was mainly oxide of Ni and Al (Fig. 5e).

The cross section of the superalloy coated with Na_2SO_4 after 10 hr at 900°C revealed the presence of multilayers of sulphide and oxide (Fig. 6). Based on X-ray and EDAX results, the outer layer (I) in the right of

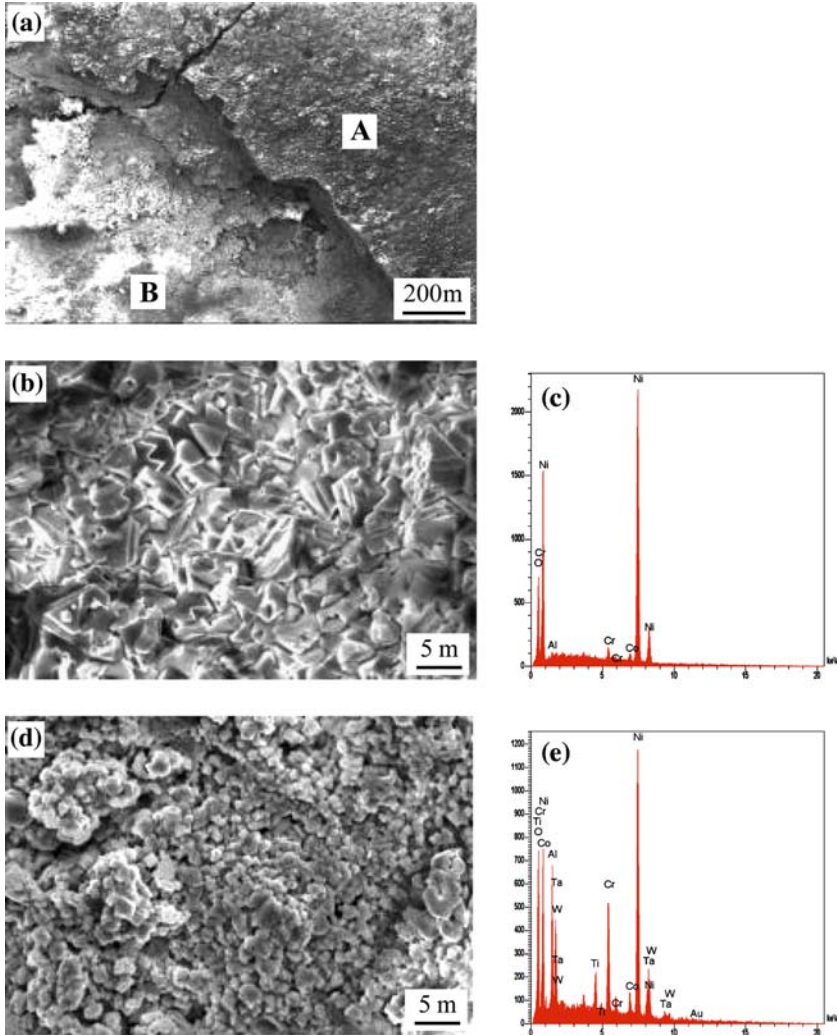


Fig. 4. The corrosion scale formed on the superalloy coated with Na_2SO_4 after 100 hr at 900°C . (a) surface morphology, (b) magnification and (c) EDAX results of area A, (d) magnification and (e) EDAX results of area B.

Fig. 6 was oxide scale and consists primarily of NiO with $\text{Ni}(\text{Al}, \text{Cr})_2\text{O}_4$ spinel (Point 1). The sublayer (II) just near the outer layer was a mixture of oxide, Na_2SO_4 (dark area in this layer, some of which has become ravine due to the dissolution of Na_2SO_4 in the SEM sample preparation

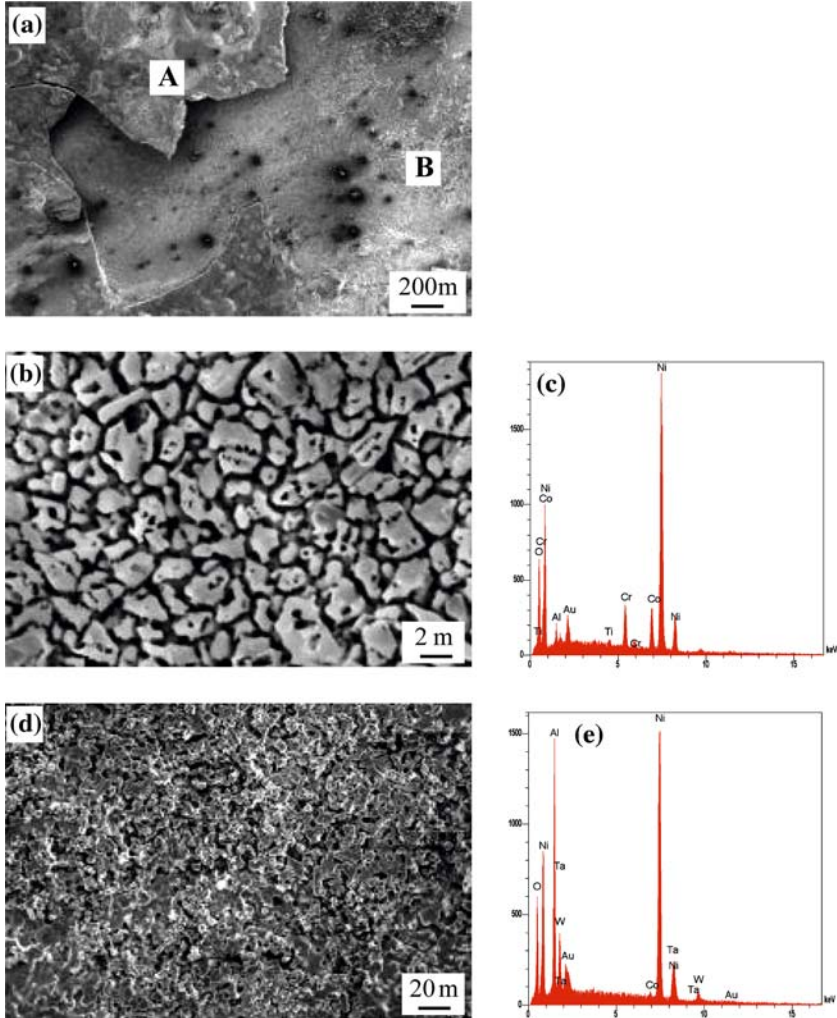


Fig. 5. The corrosion scale formed on the superalloy coated with 75 wt.%Na₂SO₄-25 wt.% NaCl mixture after 20 hr at 900°C. (a) surface morphology, (b) magnification and (c) EDAX results of area A, (d) magnification and (e) EDAX results of area B.

process) and a little of un-corroded alloy. The light-colored oxide in the inner zone of the outer layer I and in the sublayer II was enriched in tantalum (Point 2). The inner layer (III) in contact with the unaffected alloy (IV) was the affected alloy. It could be found that a lot of gray particles were scattered in the light-colored matrix. The light-colored matrix

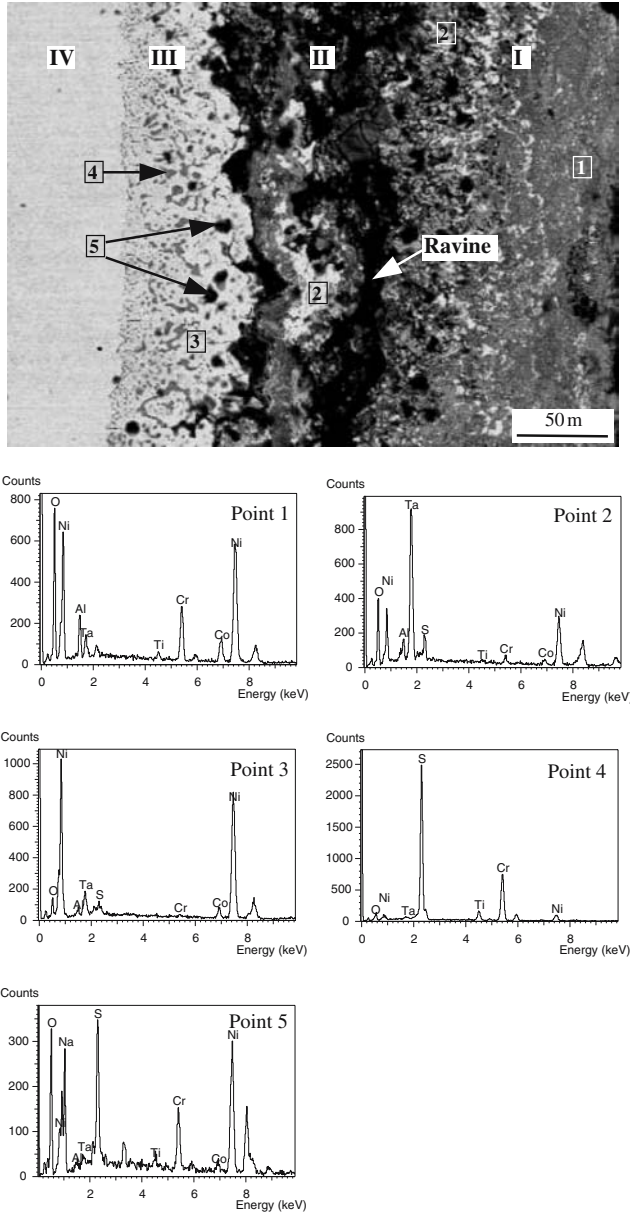


Fig. 6. Cross-sectional BS morphology of the SC Ni-base superalloy coated with Na_2SO_4 at 900°C for 10 hr, with corresponding representative EDAX results. I-outer layer, II-sublayer, III-affected alloy, IV-unaffected alloy.

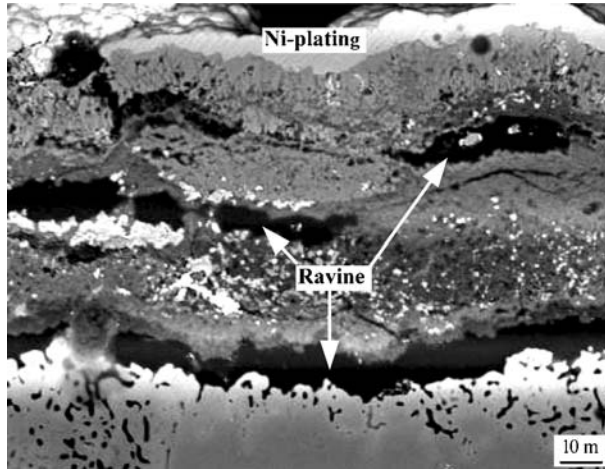


Fig. 7. Cross-sectional BS morphology of the SC Ni-base superalloy coated with 75 wt.% Na_2SO_4 -25 wt.% NaCl mixture after 5 hr at 900°C.

was identified as primarily nickel containing traces of aluminum, tantalum and cobalt (Point 3). Compared with the unaffected alloy, the matrix was depleted of chromium, aluminum and titanium. While the gray particles were identified as a phase containing chromium, titanium, nickel and sulfur (Point 4). According to the XRD result, this phase should be Cr_2S_3 , Ni_3S_2 and TiS . Some dark areas were also observed sporadically in the matrix. The dark areas were mainly Na_2SO_4 (Point 5).

The cross-sectional back-scattered electron image (BEI) of the superalloy coated with 75 wt.% Na_2SO_4 -25 wt.% NaCl mixture after 10 hr at 900°C is shown in Fig. 7. Compared with the scale formed on the superalloy coated with Na_2SO_4 , the corrosion scale was more porous and more ravines could be found in the corrosion scale. It was the formation of the ravines that led to a great deal of scale spallation when specimens were cleaned in boiling water, resulting in continuous mass loss.

Observation was conducted further to an area that the corrosion scale was relatively adherent to the alloy (Fig. 8). The outer light layer (in fact, most of this layer has been spalled off) in contact with the Ni-plating layer consists of NiO (Point A). The gray sublayer just below the outer NiO layer is a mixture of oxides containing oxides of Cr, Ni, Ti, Ta and Al, however the oxide of Cr is dominating (Point B). While the dark gray layer underneath the sublayer is composed of Al_2O_3 (Point C). An internal oxidation layer exists between the Al_2O_3 layer and the affected alloy, in which lots of bright and uncorroded alloy islands are found among

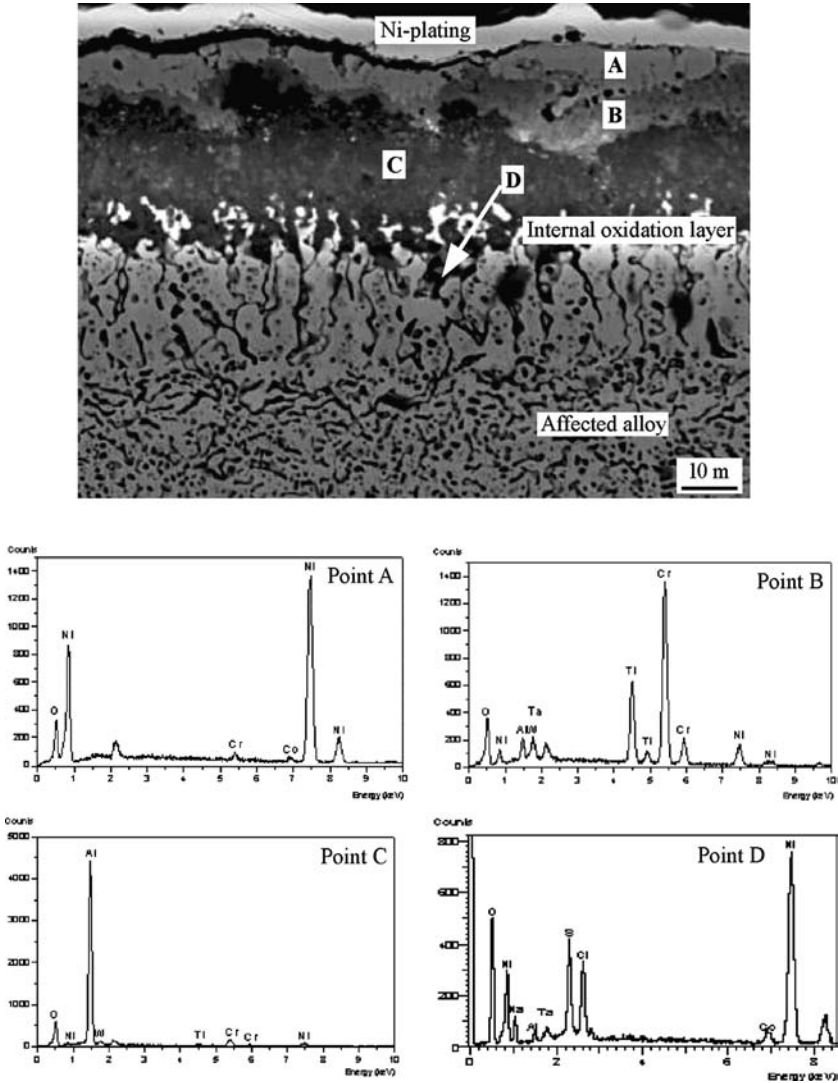


Fig. 8. Cross-sectional BS morphology of the SC Ni-base superalloy coated with 75 wt.% Na_2SO_4 -25 wt.% NaCl mixture after 5 hr at 900°C , with corresponding representative EDAX results.

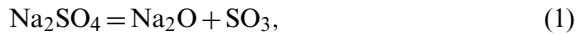
the internal oxide. Like the case of the superalloy coated Na_2SO_4 , a great deal of gray sulfides were observed in the affected alloy. And some dark areas may also be found near the internal oxidation layer. Using EDAX

analysis, relatively strong Cl peak is obtained from this phase besides O, Ni, Al, Ta, Na, Co and S peaks (Point D).

DISCUSSION

Hot corrosion studies on several commercial and experimental superalloys have shown that extensive corrosion can take place at higher temperatures due to change in salt chemistry^{9,10} and/or sulfur penetration through scales.^{11,12} Generally, a fluxing mechanism¹³ was proposed for explaining hot corrosion behavior of alloys. According to this model, the reaction of a metal with Na₂SO₄ and the removal of sulfur from the melt resulted in high melt basicity (defined as $\log a_{\text{Na}_2\text{O}}$), or the reaction of refractory metal oxides with the salt resulted in high melt acidity. The oxide formed on the alloy surface could dissolve into the molten salt.

The melting points of 100 wt.% Na₂SO₄ salt and 75 wt.% Na₂SO₄–25 wt.% NaCl salt are 884°C and 620°C, respectively.⁸ Therefore, the two salts are molten during corrosion tests at 900°C. Sodium sulphate may dissociate according to the following reactions:



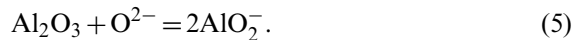
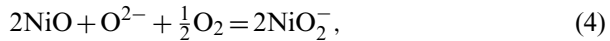
Based on Lewis acid-base concept, in reaction (1) Na₂O was basic component, and SO₃ was acidic component. SO₃ is in equilibrium with S₂ and O₂ as shown in reaction (2). Therefore, when the oxygen partial pressure decreases, the sulfur partial pressure will increase. This mechanism will result in the increasing of sulfur partial pressure in the molten salt, when the oxygen is consumed. The generated high sulfur partial pressure will either diffuse into the alloy substrate or diffuse toward the salt/gas interface. If the sulfur partial pressure in the gas phase is higher than this generated sulfur partial pressure, then the later phenomenon would not be the case. On the other hand, if the generated sulfur partial pressure is higher than that the gas phase then sulfur will either diffuse into the substrate to cause the sulfide formation again, or diffuse to the salt/oxide interfaces. If sulfide is formed under the oxide scale layer, the first case may not occur alone or even do not occur at all.¹⁴ Reaction (2) was favored by oxygen or sulfur consumption, leading to the basicity of molten salt increase, i.e. the activity of Na₂O ($a_{\text{Na}_2\text{O}}$) increased.

In this paper, the hot corrosion behavior of the SC superalloy could also be understood based on the fluxing mechanism. Because the melted salt film on the surface of the superalloy was very thin during the hot corrosion process, the oxygen could transport into the substrate through

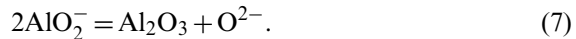
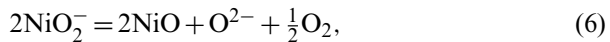
the salt film and react with alloy elements. For the SC Ni-base superalloy, the oxide scale consisted mainly of NiO and Al₂O₃ in the molten sulfate. According to the fluxing mechanism, oxide formation consumes oxygen in molten salt. The consumption of oxygen will reduce the oxygen and thereafter allow the sulfur partial pressure to increase at the interface between the molten sulfate and the oxide scale. Once the protective oxide scale is penetrated, sulfur reacts preferentially with chromium and, to a minor degree, with other elements normally found in superalloys, that is, aluminum, titanium, and nickel to form internal sulfides beneath the oxide scale according to reaction (3):



where M is the superalloy elements. According to the XRD and EDAX analysis results, several sulfides were formed in the superalloy (Fig. 3), however the mainly sulfide phase was sulfide of chromium (Point 4 in Fig. 6). The formation of sulfides in the superalloy resulted in the basicity increase because of the depletion of sulfur. Under this condition, the oxides on the surface of substrate suffered basic fluxing and were dissolved, for example as following reactions:



Because the basicity of molten salt increased gradually with the distance from the air/molten salt interface to substrate, NiO₂⁻ and AlO₂⁻ diffused outward through the molten salt, and part of them decomposed and precipitated as NiO and Al₂O₃ as follows:



A porous and nonprotective oxide scale consisted mainly of NiO, Al₂O₃ and other oxides formed on the outer corroded layer (Figs. 6 and 8).

The reaction (3), in effect, causes the adjacent metal to become impoverished of chromium and aluminum and, subsequently, prone to oxidation. The MS phase, in addition to the adjacent metal, react with oxygen to form oxides again. The reaction can be described as either:



or

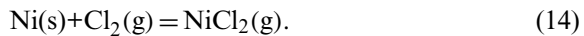
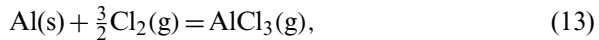
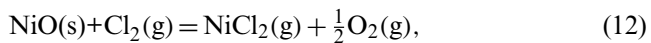
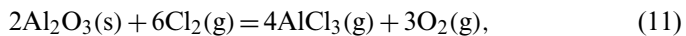


The released sulfur is free to react with alloying elements, primarily chromium, in the base alloy immediately ahead of the affected alloy layer. With hot corrosion continuing, the sulfides formed within the base alloy are also eventually converted to oxides due to the advancing scale-metal interface. And the released sulfur further penetrates the base alloy perpetuating the mechanism of attack. The repetition of oxidation and sulfidation by turns led to the sulfides go deep into the base alloy.

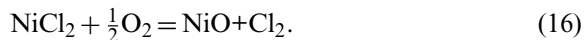
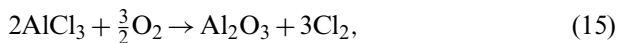
In 75%Na₂SO₄–25% NaCl corrodent, the SC superalloy suffered severe hot corrosion (Figs. 5 and 7). Obviously, the presence of NaCl significantly accelerated the corrosion of the superalloys. The corrosion mechanism is similar to the active oxidation mechanism.^{15,16} At the beginning of corrosion, NiO, Al₂O₃ and other oxides formed on the superalloy surface act as barrier layers, by separating the substrate surface from the aggressive deposits. However, in the molten Na₂SO₄–NaCl salts, it is possible that the oxide scales (e.g., Al₂O₃) react with NaCl:¹⁷



The Cl₂ produced is able to penetrate through oxide scales quickly along cracks or pores and then react with oxides and Ni, Al and other elements in the superalloy. Some volatile chlorides such as AlCl₃ and NiCl₂ would be formed:^{18,19}



The volatile chlorides may diffuse outward through the cracks or pores to the outer surface. At the surface of the scales, where the oxygen potential is high, the chlorides may reoxidize,



The Cl₂, except that which evaporated outward, reacted cyclically with Al, Ni and other elements in the superalloy, which increased the corrosion rate.

CONCLUSIONS

The hot corrosion tests of a SC Ni-base superalloy coated with Na₂SO₄ and 75 wt.% Na₂SO₄–25 wt.% NaCl mixture were studied in air

at 900°C. The corrosion productions were laminar structure, porous and easily spalled and sulfides formed quickly in the deep SC superalloy under the corrosion production. The possible sequence of attack in hot corrosion was proposed. The formation of sulfides resulted in nonprotective scales. The oxidation of sulfides releases sulfur, which again diffused inward into the SC superalloy to cause further attack. The repetition of oxidation and sulfidation by turns led to the penetration of sulfides deep into the base alloy. The accelerated corrosion of the SC superalloy coated with 75 wt.% Na₂SO₄-25 wt.% NaCl mixture was attributed to the formation of Cl₂, which reacted cyclically with oxides and Ni, Al and other elements in the superalloy and formed volatile chlorides.

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