

# Hot Corrosion Behaviors of CoCrFeNiTi<sub>0.5</sub> High Entropy Alloy in the Mixture Salt of Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25%NaCl at 750°C

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**Abstract:** Hot corrosion behaviors of CoCrFeNiTi<sub>0.5</sub> high entropy alloy pre-coated various mixture salt in air at 750°C were investigated respectively by using weight change kinetics, X-ray analyses, SEM equipped with EDS and EPMA. The results indicate that CoCrFeNiTi<sub>0.5</sub> alloy exhibits relatively high corrosion resistance in Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub> molten salts. The cross-section is divided into three parts: the oxide scale composed of various oxides, the corrosion affected zones with some micro-pores as well as minor of sulfides and the matrix. The addition of NaCl to Na<sub>2</sub>SO<sub>4</sub> destroys seriously the integrity and compactness of the oxide scale and induces the formation of more micro-pores as well as sulfides in the corrosion affected zone, which accelerates the propagation of hot corrosion. As a result, the alloy suffers from more severe corrosion in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl than in Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub>. Hot corrosion of the alloy in Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub> is explained based on the oxidation and the basic fluxing of Cr<sub>2</sub>O<sub>3</sub> in molten Na<sub>2</sub>SO<sub>4</sub>. However, hot corrosion process in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl is dominated by the interaction of oxidation and chlorination. In addition, the internal sulfidation of Fe and Ni also contributes to hot corrosion of the alloy in both Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25% NaCl mixture salt.

**Keywords:** High Entropy Alloys (HEAs), Alkali Metal Sulfate, Low Melting Point Eutectic, Sulfidation, Chlorination

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## 1. Introduction

Compared with the conventional practical alloys, high entropy alloys (HEAs) exhibit a series of excellent performance, such as the superior resistance to corrosion, oxidation, wear and high temperature [1-5] as a result of their simple solid solution structures and ease of amorphization or nanoprecipitation [6-8]. Hence, HEAs are widely used in academic research as well as industrial application and expected to be recognized as a potential candidate for high temperature structural materials because of their combinations of high melting point, low density, high elastic modulus and excellent creep and oxidation resistance.

At present, the studies of HEAs are focused on the composition design, preparation process, microstructure and properties [9-11]. Some scholars find HEAs containing Cr or Al at 1100°C have excellent resistance to corrosion and oxidation in the environment of the acid and alkali salts at

room temperature. Compared with pure oxidation, hot corrosion of metals or alloys is a type of accelerated damage caused by the deposition of a thin film of molten salts on the material surfaces in the temperature interval between 650°C and 1000°C [12-14]. The existence of such corrosive condensation layer on the surface can considerably reduce the service life of high temperature components [15]. It has been found that the aero/marine engines and boiler power plants exposed in offshore industrial rigs are prone to undergo attack from alkali halides and sulphides [16-17], moreover, it is also observed that the corrosive attack in the presence of both chlorides and sulphates is more aggressive than in sulphates alone [18]. At present, hot corrosion studies induced by mixtures of NaCl/Na<sub>2</sub>SO<sub>4</sub> have been generally focused on Ni/Co base super alloys and Ni/Cr alloys which are used in turbine engines [19-21]. A few data on hot corrosion behaviors of HEAs in aggressive environment, such as high temperature, corrosive servicing gases and deposition of

condensed phases, are not available.

The aim of the present study is to investigate hot corrosion resistance and highlight the mechanisms of CoCrFeNiTi<sub>0.5</sub> alloy pre-coated Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25% NaCl in air at 750°C. In order to achieve the objective, the environment is carefully controlled and thin corrosion specimens are prepared to get a sufficiently high ratio between the surface exposed hot corrosion and the total volume of the samples. Particular attention is paid to the phase identification of corrosion products, the cross-sectional morphologies and element distribution of samples corroded. Finally, we discuss hot corrosion mechanism of the alloy exposed in the mixture salt environment consisting of Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25% NaCl in air at 750°C based on the previous results.

## 2. Experimental Procedure

The corrosion specimens with a dimension of 10 mm x 6 mm x 2 mm were cut from CoCrFeNiTi<sub>0.5</sub> ingot melted by arc melting from a mixture of high purity (99.99%) of Co, Cr, Fe, Ni, Ti metals under argon atmosphere. The surfaces of the specimens were ground with SiC papers down to 800-grid, cleaned sequentially in alcohol and distilled water in an ultrasonic bath and then dried in hot air.

An air gun was used to spray the saturated aqueous salt solutions to produce the coating of fine salt particles on the specimen surface after the water evaporated. The process was repeated until the dry salt particles were evenly deposited up to a total coating weight of 5mg/cm<sup>2</sup> with a coating of 100μm in thickness. The samples deposited Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>-25% NaCl mixtures were then put into the dried Al<sub>2</sub>O<sub>3</sub> crucibles and placed in a tube furnace. The corrosion tests were performed in air at 750°C for some interval time (the longest endurance time to 150 h) respectively, then retrieved at regular interval and followed by air cooling.

Both of the specimens before and after corrosion tests were measured as a function of time using an electronic weighting balance machine with a sensitivity of 0.1mg. The weight change per unit area was measured with respect to time, and the corrosion products exfoliated were also retained to determine the total corrosion rate. During the measurement of weighting change, at least three parallel samples were tested simultaneously.

The samples corroded were subjected to the characterization studies by using XRD, SEM equipped with EDS and EMPA. The phase compositions of corrosion products were determined by X-ray diffraction (XRD) using monochromatic CuK radiation operated at 40kV and 100mA. XRD data were compared with JCPDS standard files to identify the various phases. A part of specimens were mounted in a plastic resin in order to reserve the surface products layer after hot corrosion, ground and polished for SEM analysis. The characterizations of the cross-sectional morphologies and compositions were investigated with Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS) and Electron Probe Micro Analyzer

(EMPA) techniques.

## 3. Results

### 3.1. Corrosion Kinetics Curves

The corrosion kinetics curves of CoCrFeNiTi<sub>0.5</sub> high entropy alloy pre-coated Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25% NaCl in air at 750°C are illustrated in Figure 1. Compared the overall mass gain per unit surface area with respect to time in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl, the alloy pre-coated Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> exhibits better hot corrosion resistance, moreover, the corrosion rate during the first 100 h is relatively high and thereafter slows down. However, the alloy suffers from slight severe attack in the environment of Na<sub>2</sub>SO<sub>4</sub>-25%NaCl mixture, the corrosion rate of CoCrFeNiTi<sub>0.5</sub> alloy seems to higher and follows a nearly linear law, indicating the addition of NaCl accelerates the corrosion of the alloy.

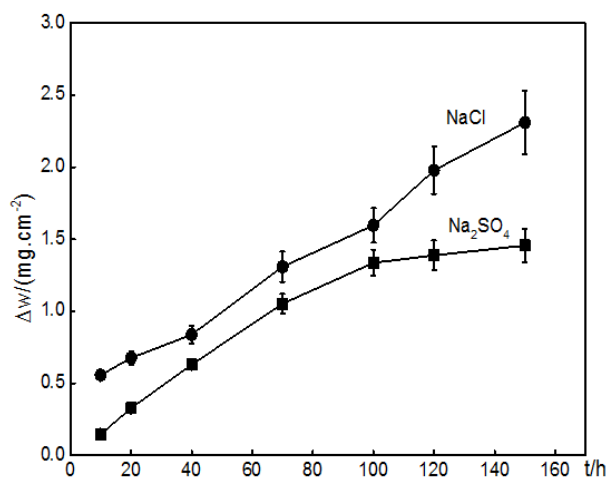


Figure 1. Corrosion kinetics curves of CoCrFeNiTi<sub>0.5</sub> alloy exposed Na-salts in air at 750°C.

### 3.2. X-ray Diffraction Analysis of Corrosion Products

Figure 2 presents the X-ray diffraction patterns of samples corroded in the various mixture salts. The addition of NaCl to Na<sub>2</sub>SO<sub>4</sub> has not result in distinct difference in the corrosion products. The corrosion products consist predominantly of Ti, Cr as well as Fe oxides, and minor of Fe, Ni sulfides is discovered on the surface of specimens corroded. In addition, some relatively strong characteristic peaks of spinel oxides AB<sub>2</sub>O<sub>4</sub> are also detected in the present experimental environments.

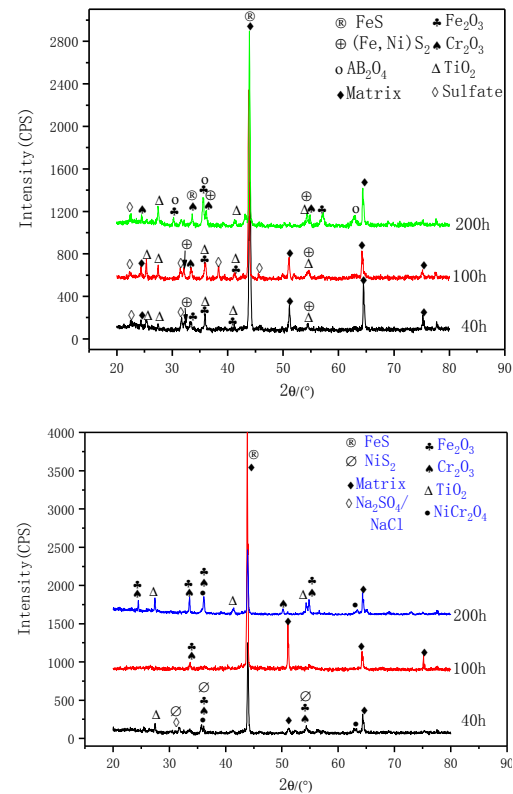
### 3.3. Cross-Sectional Morphology and Element Distribution

The cross-sectional morphologies of the alloy pre-coated Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> mixture salts after hot corrosion for 20 h and 100 h at 750°C are shown in Figure 3. A multi-layer structure like sandwich is composed of the relatively continuous and compact outer layer with the thickness of 2 μm, the middle layer called as the corrosion affected zone with some micro-pores and the matrix. With the corrosion proceeding, the outer layer is thickened obviously and the

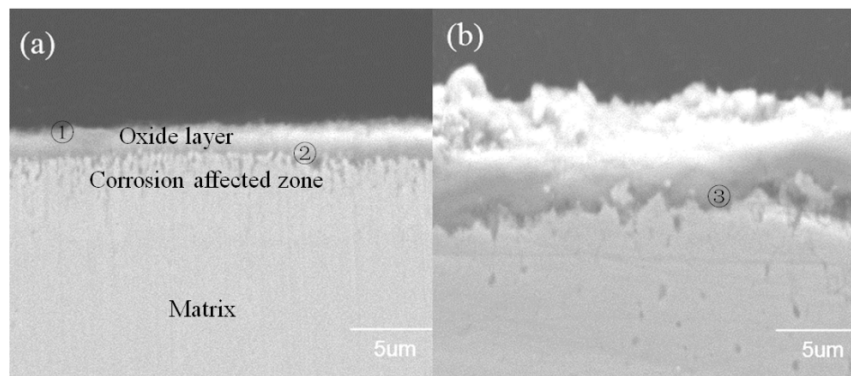
middle layer is widened deeply to 10  $\mu\text{m}$ . Combining XRD pattern with the corresponding EMPA as seen in the Figure 4, it is analyzed that the outer layer consists of various oxides, such as Ti (1: 28.25%), Cr (2: 31.41%) oxides and spinel oxides  $\text{AB}_2\text{O}_4$ . In Comparison with the outer layer, the corrosion affected zone is rich in Co (3: 15.54%), Fe (3: 14.73%) and Ni (3: 11.53%), meanwhile, there arises minor of sulfur (3: 0.44%;1: 0.08%). According to the XRD result, the sulfates of Fe, Ni form in the region, indicating that the region has experienced internal sulfidation.

In contrast, both cracking and spalling of corrosion products occur on a large scale after hot corrosion in  $\text{Na}_2\text{SO}_4$ -25% NaCl molted salts, as shown in Figure 5, revealing the corrosion is more severe in  $\text{Na}_2\text{SO}_4$ -25% NaCl than in  $\text{Na}_2\text{SO}_4$ -25%  $\text{K}_2\text{SO}_4$ . A relatively compact corrosion layer with the average thickness of 10  $\mu\text{m}$  is observed after corrosion only for 20 h in  $\text{Na}_2\text{SO}_4$ -25% NaCl. Combining with the EDS analysis, the oxide layer is mainly composed of Cr (30.87%), Ti (25.45%) and O (38.98%). There exists S (0.92%) and O (1.68%) around the pores in the corrosion affected area, in which Ni (27.74%), Fe (22.96%) and Co (32.28%) were rich. The corrosion layer becomes porous considerably and even exfoliates from the surface of the alloy after the endurance of 200 h. In addition, there are more voids forming in the corrosion affected zone with the thickness of 100  $\mu\text{m}$ . Compared with the matrix, there are rich in Ni (31.56%), Fe (25.06%) and Co (33.57%) around voids with the composition of O (2.52%) and S (1.09%) while Cr (4.75%)

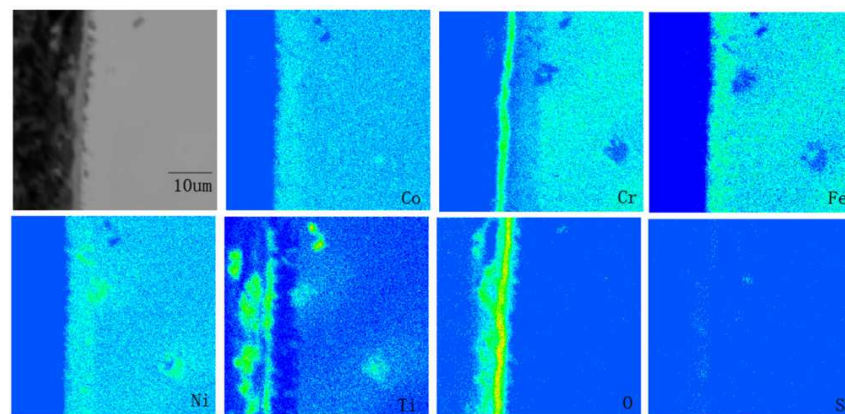
and Ti (1.27%) are significantly poor.



**Figure 2.** XRD patterns of CoCrFeNiTi<sub>0.5</sub> alloy exposed at 750°C in (a)  $\text{Na}_2\text{SO}_4$ -25% $\text{K}_2\text{SO}_4$  (b)  $\text{Na}_2\text{SO}_4$ -25% NaCl.

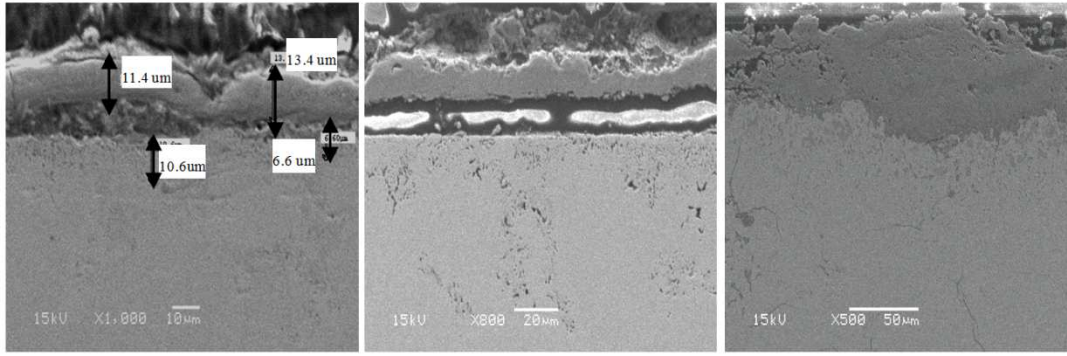


**Figure 3.** Cross-sectional micrographs of the alloy exposed in  $\text{Na}_2\text{SO}_4$ -25% $\text{K}_2\text{SO}_4$  mixture salt for 20 h (a) and 100 h (b) at 750°C.



**Figure 4.** EMPA of the alloy exposed in  $\text{Na}_2\text{SO}_4$ -25% $\text{K}_2\text{SO}_4$  mixture salt at 750°C for 20 h.

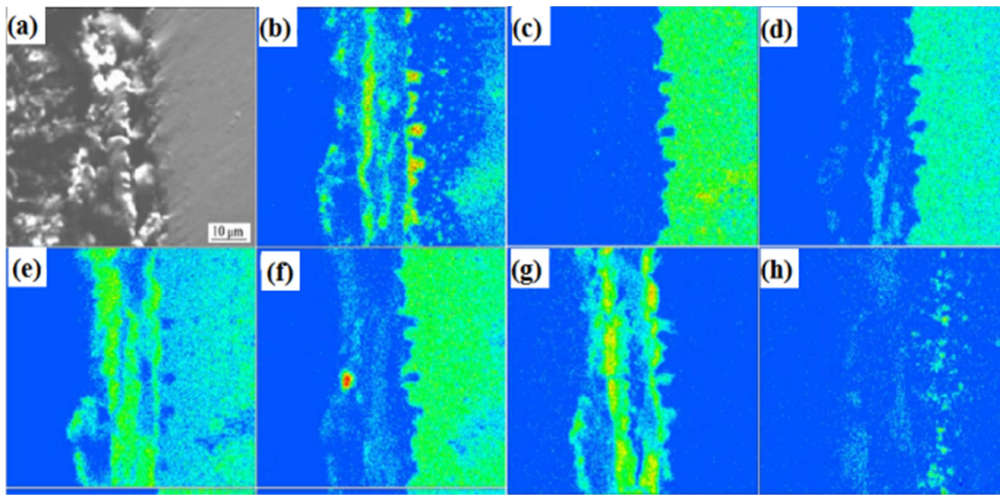




**Figure 5.** Cross-sectional micrographs of the alloy exposed in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl for 20 h (a) 70 h (b) and 200 h (c) at 750°C.

According to the element map scanning results of the alloy as seen in Figure 6, a rather wide corrosion layer, which is rich in Cr, Ti, O is formed. The corrosion products are similar to those formed in Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> salt, composing of TiO<sub>2</sub>,

Cr<sub>2</sub>O<sub>3</sub> and spinel oxides AB<sub>2</sub>O<sub>4</sub>. The element map scanning results show that a little of S dops with in the corrosion affected zone with Cr-depletion, and the detailed study indicates that a small quantity of sulfides still exist.



**Figure 6.** Element map scanning results of CoCrFeNiTi<sub>0.5</sub> alloy corroded in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl at 750°C for the exposure of 40h (a) SEM image (b) Ti (c) Co (d) Fe (e) Cr (f) Fe (g) O (h) S.

## 4. Discussion

### 4.1. High Temperature Oxidations of the Alloy at the Beginning of the Corrosion

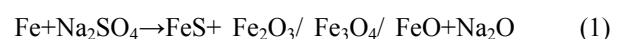
Combined with the corrosion kinetics curve, XRD analysis of corrosion products and the cross-sectional morphology, it is noticed that various oxides generate on the surface of the alloy under different corrosion environments. The formation of oxides can be described as following:

The alloy pre-coated mixed salts is firstly oxidized by inward diffusion of oxygen in air through the sulfate gap on the surface of the alloy in the initial stage of corrosion [22]. Compared with others elements, Ti has a high affinity for oxygen and diffuses outward to form TiO<sub>2</sub>. Similarly, Cr is also oxidized preferentially to form Cr<sub>2</sub>O<sub>3</sub> on the surface of the alloy. In addition, the spinel oxides AB<sub>2</sub>O<sub>4</sub> are produced by the interaction (Fe, Co, Ni) oxides forming simultaneously, which is helpful to restrain the further contact of the alloy with the mixture salt and the development of corrosion to some extent. Therefore, with respect to CoCrFeNiTi<sub>0.5</sub> alloy corroded in the

mixed salts, high temperature oxidation occurs and the formation of various oxides protects the matrix from the corrosion damage of sulfate salt at the initial stage of the corrosion.

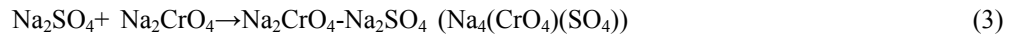
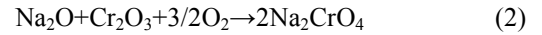
### 4.2. Hot Corrosion of CoCrFeNiTi<sub>0.5</sub> Alloy in Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub>

With respect to the alloy pre-coated Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub>, the formation of the low melting point eutectic Na<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>O (whose melting point is no more than 580°C) results in the localized melting of the mixture salt on the surface of the alloy in the subsequent corrosion proceeding, which is vital for hot corrosion [23]. The reaction process is followed as the reaction (1):



The Na<sub>2</sub>O generated in the above reaction can react with the previous oxide Cr<sub>2</sub>O<sub>3</sub> to form the yellow volatile Na<sub>2</sub>CrO<sub>4</sub> [24]. By the XRD identification, Na<sub>2</sub>CrO<sub>4</sub> exists in the form of Na<sub>4</sub>(CrO<sub>4</sub>)(SO<sub>4</sub>) in this investigation, which is explained as

following [25-26]:

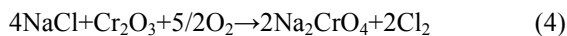


The volatilization of  $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$  damages the compactness and integrity of mixed oxide scale, which is helpful to the inward diffusion of sulfur element and the occurrence of internal sulfidation during the further corrosion.

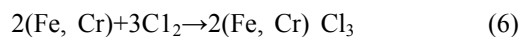
#### 4.3. Hot Corrosion of $\text{CoCrFeNiTi}_{0.5}$ in $\text{Na}_2\text{SO}_4\text{-25\% NaCl}$

Compared with hot corrosion in  $\text{Na}_2\text{SO}_4\text{-25\%K}_2\text{SO}_4$ , hot corrosion of the alloy in  $\text{Na}_2\text{SO}_4\text{-25\%NaCl}$  is more complicated besides oxidation as mentioned above. It is reported that the melting point of the mixture salt is no more than  $650^\circ\text{C}$  when the ratio of  $\text{Na}_2\text{SO}_4$  to  $\text{NaCl}$  in the mixture salt reaches 3:1 [27], indicating the occurrence of the localized melting of  $\text{Na}_2\text{SO}_4\text{-25\% NaCl}$  mixture salt on the surface under the current experiment condition. Hence, the corrosion of the alloy is accelerated by cyclic chlorination/oxidation process described as follows:

On the one hand, the molten  $\text{NaCl}$  destroys the protective  $\text{Cr}_2\text{O}_3$  layer by the direct reaction with  $\text{Cr}_2\text{O}_3$  formed at the beginning of the corrosion, on the other hand,  $\text{Fe/Cr}$  can also dissolve into the molten salt and react with oxygen existing on the surface [28-29]. According to the calculation of thermodynamic data [30], the possible reactions are listed as below:

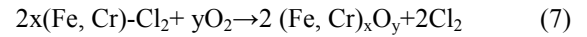


Some of  $\text{Cl}_2$  generated from the above reaction (4-5) escapes to the atmosphere along the cracks or pores of the oxide layer, and the rest reacts with element  $\text{Cr}$ ,  $\text{Fe}$  or  $\text{Ni}$  in the substrate to form the volatile chlorides. According to the thermodynamics data [31],  $\text{Cr}$  has the greatest driving force and is prone to react with chlorine to form chloride in comparison with  $\text{Fe}$  as well as  $\text{Ni}$ , moreover, nickel has the least tendency to react with chlorine and is apt to be left in the alloy substrate. Hence,  $\text{Cl}_2$  formed in the above reactions further diffuses inward through the pores and generates chlorides by the reaction with alloy element  $\text{Fe}$ ,  $\text{Cr}$  according to the following reactions (6).



Since the oxides are the ultimate stable phase in the oxygen-metal-chlorine system, the oxidation reaction between metal chlorides and oxygen can occur when the former chloride with high vapor pressure volatilizes to an area with essential activity of oxygen [32]. Due to the oxygen potential at the top surface of the scales is high, the volatile chlorides may diffuse outward through the cracks or pores to the outer surface and be re-oxidized according to the reaction (7). It is worth mentioning that  $\Delta G$  of the reaction of chromic chloride with oxygen is small, so the chromium oxides is apt to form preferentially, subsequently  $\text{Fe}$  oxides also form and cover on

the chromium oxides.

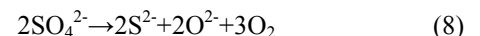


It is noted that the volatilization of various chlorides during corrosion damages the compactness and continuity of oxide scale and results in the formation of loose and porous oxide layer which is easily peeled off the substrate in the hot corrosion process of  $\text{NaCl}$  participating, as shown in Figure 5, which accelerates the inward diffusion of sulfurs as well as oxygen to the matrix and the occurrence of internal sulfidation.

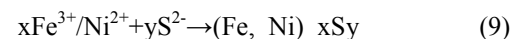
#### 4.4. Internal Sulfidation of $\text{CoCrFeNiTi}_{0.5}$ Alloy During Corrosion

In the present study, element  $\text{S}$  exists primitively on the surface of the alloy in the form of sulfate salt. With the corrosion processing, we have detected the sulfides of  $\text{Fe}$ ,  $\text{Ni}$  occurring in the corrosion affected zone beneath the oxide scales in the case of two mixture salts, which means that sulfur has diffused inward to the matrix and reacted with the  $\text{Fe}$ ,  $\text{Ni}$  by internal sulfidation. In theory,  $\text{Cr}$  has a high affinity with sulfur and can form a more stable sulfide compared with element  $\text{Ni}$  or  $\text{Fe}$ , however, due to the preferential oxidation/chlorination, the element  $\text{Ni}$ ,  $\text{Fe}$  is prone to be left in the corrosion affected zone and reacts with sulfur to form the sulfide phases  $(\text{Fe, Ni})_x\text{S}_y$  as detected by XRD in this study. The possible mechanisms perhaps are explained as followings:

The sulfate ions in molten mixture salt can be dissociated according to the following reaction (8) [33]:



The formation of the oxides on the surface of the alloy lowers the  $p(\text{O}_2)$  in the salts and increases the sulphur potential, accelerating the inward transportation of  $\text{S}$  through the oxide scale and the formation of sulfides at the corrosion affected zone [34]. Firstly, the nucleating of sulfides at the oxide/alloy interface and the diffusion of  $\text{Fe}^{3+}/\text{Ni}^{2+}$  outward and  $\text{S}^{2-}$  inward through the oxide layer lead to the formation of the corrosion affected zone. Subsequently, the  $\text{S}$  ions further transport inward and the cations diffuse outward simultaneously through the oxide scale, resulting in the formation of the sulfides beneath the oxide scale. With continued exposure to the sulfidizing environment, more  $\text{S}$  ions diffuse through the oxide layer and the growth of sulfide takes place at the oxide/metal interface. The possible sulfidation process is expressed by the reaction (9):



Above in all, the formation of the low melting point eutectic  $\text{Na}_2\text{O-Na}_2\text{SO}_4$  and the basic fluxing of  $\text{Cr}_2\text{O}_3$  in molten  $\text{Na}_2\text{SO}_4$  as well as sulfidation will contribute to the corrosion

of the alloy in Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub>. However, with respect to the alloy corrode in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl, hot corrosion is dominated by the interaction of oxidation, chlorination and sulfidation. Compared with hot corrosion in Na<sub>2</sub>SO<sub>4</sub>-25%K<sub>2</sub>SO<sub>4</sub>, the alloy in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl suffers from more severe attack, and Cl<sup>-</sup> is more deteriorate than SO<sub>4</sub><sup>2-</sup> to the alloy.

## 5. Conclusion

From the experimental studies, some important conclusions are obtained:

1. CoCrFeNiTi<sub>0.5</sub> alloy exhibits relatively good hot corrosion resistance in Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> molten salts. The addition of NaCl to Na<sub>2</sub>SO<sub>4</sub> accelerates dramatically the cracking and spalling of the oxide layer and promotes the formation of sulfides in the corrosion affected zones. Hence, the alloy suffers from more severe corrosion in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl mixture salt.
2. The cross-section of the alloy corroded is divided into three parts: the outer layer composed of various oxides, the corrosion affect zone containing minor of sulfides as well as a large number of micro-pores and the matrix.
3. Hot corrosion of the alloy in Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> is explained based on the preferential oxidation of Ti, Cr, the basic fluxing of Cr<sub>2</sub>O<sub>3</sub> in molten Na<sub>2</sub>SO<sub>4</sub>. In contrast, hot corrosion in Na<sub>2</sub>SO<sub>4</sub>-25% NaCl is dominated by the interaction of oxidation and chlorination.
4. The internal sulfidation of Fe, Ni also contributes to hot corrosion of the alloy in both Na<sub>2</sub>SO<sub>4</sub>-25% K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-25% NaCl salts.

## Acknowledgements

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