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REVIEW

Molten Salts Induced Hot Corrosion of High Temperature Protective Coatings: Research Progress

Li Xiaoya[1,2,3], **Zou Jianpeng**[1], **Shi Qian**[2,3], **Dai Mingjiang**[2,3], **Lin Songsheng**[2,3], **Tang Peng**[2,3], **Su Yifan**[2,3]

[1] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China; [2] National Engineering Laboratory of Modern Materials Surface Engineering Technology, Institute of New Materials, Guangdong Academy of Sciences, Guangzhou 510651, China; [3] Guangdong Provincial Key Laboratory of Modern Surface Engineering Technology, Guangzhou 510651, China

Abstract: High temperature hot corrosion is one of main failure modes for the hot components. The Na_2SO_4 and NaCl molten salts can accelerate the hot corrosion at high temperatures and even lead to the catastrophic accidents. Thus, this research discussed the molten salts (Na_2SO_4 or/and NaCl) induced hot corrosion with Na_2SO_4 as the main corrosion reactant. The corrosion behavior and performance characteristics of two typical types of hot corrosion were introduced. Several hot corrosion models and mechanisms were introduced, as well as the reaction formulas and corrosion mechanisms of Na_2SO_4, NaCl, and Na_2SO_4+NaCl molten salts. According to the current research status, the protective coating is an optimal approach in the hot corrosion reduction. The advanced progress of the *M*CrAlY coatings, NiAl coatings, thermal barrier coatings, and novel coatings was summarized. In addition, the methods to further improve the corrosion resistance of coatings were investigated. Finally, the development direction of protective coatings was predicted.

Key words: hot corrosion; molten salts; high temperature protective coatings

High temperature coatings are widely used to provide hot corrosion resistance and oxidation resistance for the hot-section components of gas turbine engine. However, these coatings fail quickly in the alkali or alkaline sulfate-containing atmosphere[1,2]. The SO_4^{2-}, Cl^-, and VO_3^-[3-5] may easily form once the exhaust containing Na, K, Cl, S, and O elements produced by gas combustion mixes with the moisture and salt fog of marine atmosphere, and they can adhere to the component surface, which aggravates the component properties. The components may rapidly fail due to the salt contaminants, and the typical corrosion salts are Na_2SO_4, NaCl, and Na_2SO_4+NaCl[5,6]. The mixed salts are deposited on surface of turbine blades and other components, and then the corrosion occurs, leading to the component failure. However, the protective coatings can effectively prevent the molten salt corrosion. The blade corrosion in the mixed molten salts near the coastal seawater is shown in Fig.1.

The simulation of the actual working condition has been widely investigated[7,8]. Many factors can influence the corrosion behavior of component, such as temperature, types of molten salts (Na_2SO_4, NaCl, V_2O_5, H_2O), alloy elements,

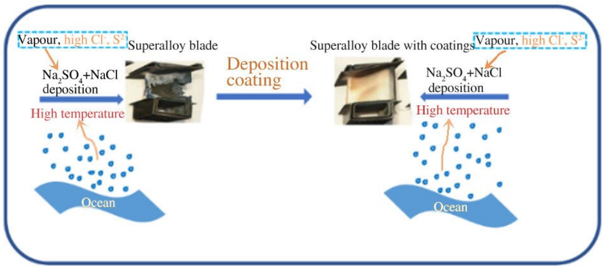

Fig.1 Blade corrosion in molten salts under the near sea environment

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Corresponding author: Zou Jianpeng, Ph. D., Professor, State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, P. R. China, Tel: 0086-731-88876630, E-mail: zoujp@csu.edu.cn

and external stress. Ma et al[3] studied the effect of different temperatures on the corrosion properties and found that the corrosion becomes more serious with increasing the temperature. Singh et al[9] researched the hot corrosion behavior of NiCrAlY-SiC and NiCrAlY-B_4C coatings prepared by the high velocity oxygen fuel-sprayed method in Na_2SO_4-60wt% V_2O_5 environment at 900 °C. The results prove that the NiCrAlY-20SiC coating can better protect the substrate than the NiCrAlY-20B_4C coating does, because the NiO, Al_2O_3, and Cr_2O_3 have better protective effects than B_2O_3 does. The external stress may also play a significant role in the corrosion process. Fu et al[10,11] found that the external stress can hinder the corrosion process when the molten salt layer (Na_2SO_4 and K_2SO_4) is deposited on the substrate surface. The Cr_2O_3 protective layer forms because the Cr atoms can diffuse along with the cracks and defects induced by the external stress. Although the corrosion behavior of components has been studied in many simulated environments, the lifetime of gas turbine engines cannot be accurately obtained due to the complicated service environment and technical restriction. With the implementation of the "deep blue strategy" and the "deep sea strategy", the hot corrosion of the hot-end components of aeroengine has attracted extensive attention.

The Na_2SO_4 molten salt can accelerate the oxidation of nickel-based alloys. Goebel et al[12] found that the Na_2SO_4 molten salt dissolves the protective oxide scales (Al_2O_3 and Cr_2O_3) and accelerates the protection failure. The presence of sulfur affects the adhesion property of the oxide scale, because the sulfur can weaken the bonding between the oxide scale and substrate and promote the formation of interfacial pores by reducing the surface energy of the pores[13].

NaCl can be deposited on the surface of turbine blades and react with the metal and oxygen, and then the volatile metal chlorides are generated, thereby leaving the pores[14,15]. It is found that the chlorine generated by the oxychlorination of NaCl and O_2 is one of main hot corrosion factors for the components under marine atmosphere[16]. The reactions[3] are expressed by Eq.(1) and Eq.(2), as follows:

$$4Cl^{-}+O_2=2O^{2-}+2Cl_2\uparrow \tag{1}$$

$$2M+xCl_2=2MCl_x\ (M=\mathrm{Ni, Co, Al, Cr}) \tag{2}$$

The eutectic salts of NaCl and Na_2SO_4 can accelerate the serious corrosion. Thus, the mechanisms of hot corrosion of different salts should be investigated[17]. The melting points of Na_2SO_4 and NaCl are 884 and 801 °C, respectively; whereas the melting point of mixed salt of Na_2SO_4 and NaCl is about 620 °C[18], indicating the broader temperature range of hot corrosion and oxidation. Thus, more consideration should be focused on the corrosion mechanisms of Na_2SO_4 and NaCl mixed molten salts, which is beneficial to the development of the hot corrosion resistance for the components.

In this research, the advanced progress of hot corrosion mechanism and anti-corrosion coatings was summarized. The methods for corrosion resistance improvement against the molten salt were discussed. This review can broaden the understanding of the molten salts-induced hot corrosion and provide the outlook for the future development directions of anti-corrosion coatings.

1 Types and Processes of Hot Corrosion

1.1 Hot corrosion types

The hot corrosion is a complex chemical reaction process involving both the sulfidation and oxidation[19,20] processes, and it can reduce the material lifetime and accelerate the failure. There are two hot corrosion types[21], namely Type I and Type II. The predominant hot corrosion mechanism changes with temperature[22,23], as shown in Fig. 2. The hot corrosion at high temperatures (815~980 °C) is referred as the Type I, whose typical characteristics are the uniform loose oxide scale and internal sulfurization. The hot corrosion at low temperatures (560~815 °C) is referred as the Type II, whose typical corrosion characteristic is the local pitting[23]. There is no obvious boundary between these two types of hot corrosion under actual reaction conditions, but their reaction mechanism, conditions, and process are different[4].

During the Type II hot corrosion, the localized corrosion occurs, as indicated by the red arrows in Fig. 3a. This corrosion with thickness of about 50 μm is less severe. However, during the Type I hot corrosion, the corrosion thickness increases greatly to about 108 μm. In addition, severe internal oxidation occurs. The corroded layer includes three layers, which seriously decreases the interfacial bonding between the coating and the substrate. The liquid eutectic salt not only dissolves the protective oxide scale, but also quickly enters the substrate along the grain boundaries. In conclusion, the liquid eutectic salt is more corrosive than the solid salt.

1.2 Molten salt hot corrosion

The molten salt-induced hot corrosion process contains two stages[5,22]: the incubation stage and the propagation stage. The initial incubation stage mainly involves the oxidation reactions in air: NiO, Cr_2O_3, and Al_2O_3 can be observed on the surface of materials which are rich in chromium and aluminum. In the propagation stage, the incubation period is decreased with the reaction proceeding, and the NiO and Al_2O_3 dissolve into the mixed molten salts. SO_3 diffuses near the metal substrate, so the sulphates are generated, aggravating the hot corrosion. The internal sulfides cause more

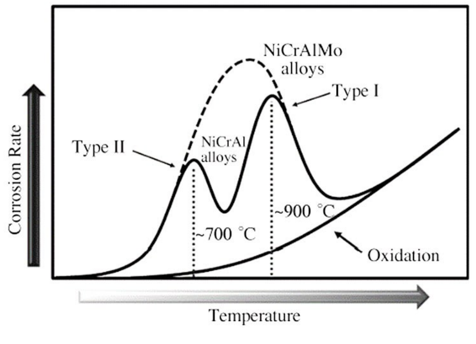

Fig.2 Schematic diagram of hot corrosion types at different temperatures[24]

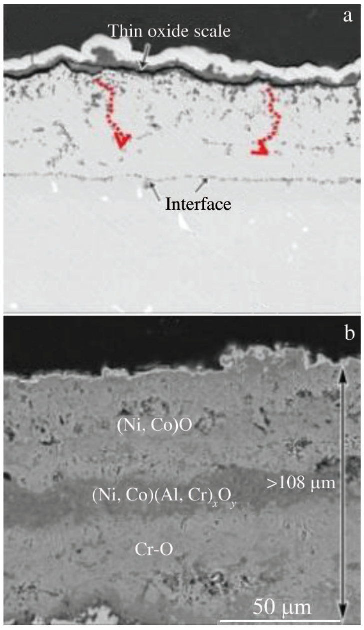

Fig.3 Cross section morphologies of protective coatings after Type I (a) and Type II (b) hot corrosion processes[3]

serious consumption of chromium and aluminum, resulting in the penetration of corrosion into the alloy substrate.

Balashadehi et al[25] found that the material surface shows the loose and porous morphology after the molten salt-induced corrosion. The thin thickness of corrosion products implies a good blocking effect of oxide scale against the internal diffusion and permeation of sulfur. The corroded coating has three layers: the outermost protective oxide scale (Al_2O_3, Cr_2O_3), the intermediate mixture oxide layer (NiO, $NiAl_2O_4$, $NiCr_2O_4$, Al_2O_3), and the innermost sulfide layer. In the serious corroded areas, a large amount of spinel and sulfide appears, which seriously affects the mechanical properties of material.

2 Mechanism of Hot Corrosion at High Temperatures for Ni-based Superalloys

The molten salt dissolution mechanism of hot corrosion has been widely researched. Several corrosion mechanisms have been proposed, including the classic sulphur-oxidation model[26], chlorination and oxidation model[27], and the acid-base melting model[28,29].

2.1 Sulphur-oxidation model

The gas turbines usually serve under the oxygen environment. The Na_2SO_4 deriving from the burning of aircraft fuel in gas turbines is deposited on the surface of turbines and can severely corrode the coating surface.

Simons et al[26] proposed a simplified sulphur-oxidation model mechanism, which assumed that the Na_2SO_4 is the primary oxidization agent, the initial triggering phase includes the reduction product of Na_2SO_4, namely the single sulfur, obtained through the reducing agent R, and the sulfur reacts with the metal M to form sulfide MS. The proposed mechanism can be expressed as follows:

$$\mathrm{Na_2SO_4}+3R=\mathrm{Na_2O}+3R\mathrm{O}+\mathrm{S} \tag{3}$$

$$M+\mathrm{S}=M\mathrm{S} \tag{4}$$

$$\mathrm{Na_2SO_4}+3M\mathrm{S}=4\mathrm{S}+3M\mathrm{O}+\mathrm{Na_2O} \tag{5}$$

$$4M+4\mathrm{S}=4M\mathrm{S} \tag{6}$$

The generated sulfide can accelerate the oxidation. Some eutectics are formed with their sulfides, which leads to the lower melting point of material. The liquid eutectic salts can penetrate the protective oxide scale, resulting in the faster diffusion of molten salt along the grain boundary. Meanwhile, the O_2 tends to diffuse into the substrate and reacts with the eutectic and substrate, leading to the eutectic oxidation and dissolution, as follows:

$$M+M\mathrm{S}=M\cdot M\mathrm{S} \tag{7}$$

$$M\cdot M\mathrm{S}+\frac{1}{2}\mathrm{O_2}=M\mathrm{O}+M\mathrm{S} \tag{8}$$

Mahini et al[30] found that the Al_2O_3 layer can protect the specimens from the Na_2SO_4 molten salt-induced corrosion by hindering the diffusion of oxygen and sulfur ions. The corrosion mechanism of Na_2SO_4 molten salt is shown in Fig.4. Al_2O_3 reacts with the Na_2SO_4 molten salt and Na_2SO_4 decomposes, as follows:

$$\mathrm{Na_2SO_4}=\mathrm{Na_2O}+\mathrm{SO_3} \tag{9}$$

$$2\mathrm{SO_3}=2\mathrm{S}+3\mathrm{O_2} \tag{10}$$

$$2\mathrm{SO_3}=2\mathrm{SO_2}+\mathrm{O_2} \tag{11}$$

The coating is corroded and the O_2 in the molten salt is consumed, causing the weak interfacial adhesion between the oxide scale and the coating, which leads to the sulfur penetration into the coating. The cracks are generated and the oxide scale peels off with the corrosion proceeding. The internal oxidation and sulfidation occur, and finally the coating fails, as shown in Fig.4.

In addition, when the reducing agent exists and Na_2SO_4 molten salt is sufficient, the corrosion reaction is more intense and the substrate is corroded rapidly.

2.2 Chlorination and oxidation model

NaCl has severe penetration and destruction effects. Thus, when the molten salts contain Cl^- ions, the anti-corrosion performance of superalloy is greatly reduced. NaCl can form the volatile chloride at high temperatures and release Cl_2, which may react with the metal substrate to form the new gaseous chloride. Therefore, the protective oxide scale becomes loose and porous, as expressed by Eq. (12), as follows:

$$4\mathrm{NaCl\ (l)}+\mathrm{O_2\ (g)}\leftrightarrow 2\mathrm{Na_2O}+2\mathrm{Cl_2\ (g)} \tag{12}$$

NaCl reacts with O_2 at high temperatures and then releases Cl_2 which diffuses into the superalloys along the defects. Then, Cl_2 is adsorbed to the metal surface with low partial pressure of oxygen (P_{O_2}). Meanwhile, Cl_2 reacts with the metallic elements, forming the volatile metal chlorides[25], as follows:

$$M+\mathrm{Cl_2\ (g)}\rightarrow M\mathrm{Cl}_x\ \mathrm{(s)}\rightarrow M\mathrm{Cl}_x\ \mathrm{(g)} \tag{13}$$

After the formation of gaseous metallic chlorides, the gaseous metallic chlorides diffuse to the salt/gas interface,

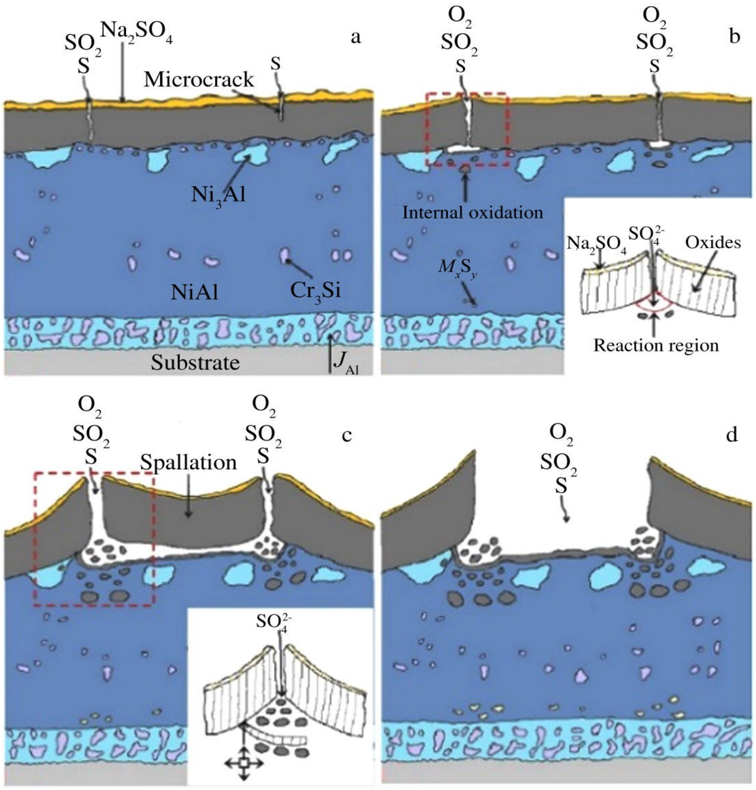

Fig.4 Schematic diagrams of corrosion mechanism of Na_2SO_4 molten salt: (a) Na_2SO_4 and other substances entering the oxide layer through microcracks; (b) $Al_2(SO_4)_3$ formation by reactions between Na_2SO_4 and Al_2O_3; (c) spallation of oxide layer; (d) formation of new oxide layer[31]

where the P_{O_2} is higher than the partial pressure of Cl_2 (P_{Cl_2}) and the metal oxides are more stable. Therefore, the metallic chlorides react with the oxygen, and the metal oxides are precipitated at the salt/gas interface[32], as follows:

$$M_xCl_y\,(g)+yO_2=2M_xO_y+\frac{1}{2}yCl_2\,(g) \tag{14}$$

The corrosion mechanism of NaCl molten salt is shown in Fig. 5. Al_2O_3 reacts with the NaCl molten salt to produce the $AlCl_3$ which is gaseous and can volatilize at high temperatures, thereby leaving voids and holes on the coating surface[33]. The cracks appear at the stress concentration locations with increasing the number of voids. Eventually, the coating fails.

Cl_2 may diffuse to the places with low P_{O_2} through the defects and it can react with the metal again. Thus, Cl_2 becomes a catalyst for the hot corrosion process. Different molten salts have different oxidation models. In the chlorination and oxidation model, the molten salts act as the catalyst. In addition, the molten salts are also related to the dissolution of oxides and metals.

2.3 Acid-based melting model

It is known that the hot corrosion does not depend on the alloy elements. Once the corrosion medium of Na_2SO_4 presents the characteristics of alkaline (excess Na_2O) or acidic (excess SO_3), the oxide scale is dissolved and destroyed. Jafari[32] and Bender[33] et al proposed the acid-based melting model of hot corrosion, which suggests that the dissolution of the protective oxide scale can be divided into the alkaline dissolution model and acid dissolution model[34,35]. In general, the pure Na_2SO_4 molten salt is neutral and its thermodynamic equilibrium is as follows:

$$Na_2SO_4=Na_2O+SO_3 \tag{15}$$

$$SO_3=\frac{1}{2}S_2+\frac{3}{2}O_2 \tag{16}$$

In this decomposition reaction process, Na_2O and SO_3 are regarded as the basic component and acid component of molten salt, respectively. The content ratio of Na_2O to SO_3 changes when the components are exposed under high temperature conditions, which leads to the alkaline or acidic Na_2SO_4 molten salt and the dissolution of oxide scale. The Ni-based superalloy suffers oxidation under the molten salt film and consumes oxygen, forming the protective oxide scale (Al_2O_3 or Cr_2O_3) on the superalloy surface at high temperatures. Meanwhile, the P_{O_2} at the oxide/molten salt interface decreases. According to Eq.(16), the partial pressure of S_2 (P_{S_2}) increases, which leads to formation of sulfides at the metal/oxide interface. Besides, the partial pressure of SO_3 (P_{SO_3}) at oxide/molten salt interface reduces. According to Eq.(15), the partial pressure of Na_2O (P_{Na_2O}) increases and the metal oxides thus undergo the alkaline dissolution. Therefore, the melting mechanism of the alkaline dissolution model is as follows. (1) The metallic elements in the superalloy react with the Na_2SO_4 molten salt. (2) The local alkalinity activity (O^{2-})

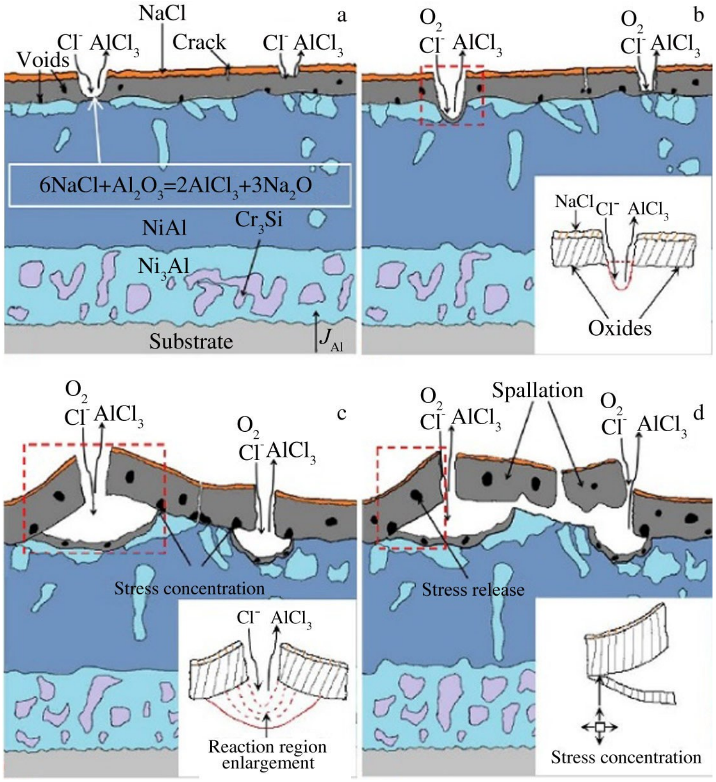

Fig.5 Schematic diagrams of corrosion mechanism of NaCl molten salt at 1050 °C in air: (a) $AlCl_3$ formation by reactions between NaCl and Al_2O_3 and surface hole formation by $AlCl_3$ vaporization; (b) further reactions between NaCl and Al_2O_3 and surface hole enlargement; (c) oxide layer bulges and stress concentration with increased internal stress; (d) spallation of oxides layer[31]

at the alloy/molten salt interface increases and the alkaline dissolution occurs at the metal oxides. (3) The MO_2^{2-} diffuses to the molten salt/gas interface from the alloy/melting salt interface with a concentration gradient. Then the alkalinity activity reduces and the MO_2^{2-} begins to decompose, resulting in the precipitation of the loose metal oxides at the melting salt/gas interface. (4) If the alloy contains the hot resistant elements, such as Mo, W, and V, their related oxides can react with Na_2SO_4, decreasing the alkalinity at the oxide/molten salt interface and thereby increasing the acidity of the molten salts. Therefore, the protective oxide scale suffers the acid dissolution. (5) In the molten salt zone near the molten salt/gas interface, the alkalinity is relatively high. Thus, the loose oxide particles are precipitated at the molten salt/gas interface. The corresponding reactions are expressed by Eq.(17~22), as follows:

$$4M+SO_4^{2-}=MS+3MO+O^{2-} \tag{17}$$

$$MO+O^{2-}=MO_2^{2-} \tag{18}$$

$$MO_2^{2-}=MO+O^{2-} \tag{19}$$

$$MO+Na_2SO_4=Na_2MO_2+SO_3\ (M=\text{Mo, W}) \tag{20}$$

$$Al_2O_3=2Al^{3+}+3O^{2-} \tag{21}$$

$$2Al^{3+}+3O^{2-}=Al_2O_3 \tag{22}$$

Besides, the activity of S decomposed from SO_3 is increased with the dissolution of acid oxide, promoting the S diffusion into the alloy. The internal sulfide occurs when the sulfur diffuses through the oxide scale on the alloy surface, where the oxygen activity is low and S reacts with the metal to form the sulfides.

It is obvious that the acid-based melting model involves the acid/alkaline dissolution and oxide precipitation. Particularly, the acid corrosion occurs spontaneously, causing more harmful hot corrosion. The alkaline corrosion cannot occur spontaneously, and its corrosion rate is slower than that of the acid corrosion. For the acid-based melting model, the hot corrosion process occurs continuously, abiding by the Rapp-Goto criterion[36], as follows:

$$\left[\frac{\mathrm{d}(\text{oxides solubility})}{\mathrm{d}x}\right]_{x=0} < 0 \tag{23}$$

This criterion proves that the solubility gradient of protective oxide at the oxide/molten salt interface is negative. The oxides are continuously precipitated at the molten salt/gas interface to maintain the local equilibrium between the oxide scale and the molten salt. The dissolution of metal oxides, including the basic and acid fluxing reactions of several typical oxides[37-40], can be used to explain this phenomenon. The dissolution reactions can be divided into the alkaline dissolution and acid dissolution, as expressed by Eq.(24~26) and Eq.(27~29), respectively:

$$Cr_2O_3+2Na_2O+\frac{3}{2}O_2=2Na_2CrO_4 \tag{24}$$

$$Al_2O_3+Na_2O=2NaNiO_2 \tag{25}$$

$$2NiO+Na_2O+\frac{1}{2}O_2=2NaNiO_2 \tag{26}$$

$$Cr_2O_3+3Na_2SO_4=Cr_2(SO_4)_3+3Na_2O \tag{27}$$

$$Al_2O_3+3Na_2SO_4=Al_2(SO_4)_3+3Na_2O \tag{28}$$

$$NiO+Na_2SO_4=NiSO_4+Na_2O \tag{29}$$

The establishment of these corrosion mechanism models provides guidance for the investigation of hot corrosion, and the acid-based melting model also has some restrictions.

Ma et al[3] investigated the corrosion properties of NiCoCrAlY-, AlSiY/NiCoCrAlY-, and AlSiY/NiCoCrAlY/Ni-Cr coated alloys under the corrosion condition of Na_2SO_4+ NaCl mixed molten salts. It is found that the corrosion process is serious because of the volatile MCl_x and the formation of molten voids. The corrosion level is positively correlated with the temperature. The formed molten voids indicate that the reactions of NaCl molten salt can produce Cl_2 and the volatile gas MCl_x. The coating failure mechanism includes two stages: the formation of oxide scale and the acid-based dissolution process. The corresponding corrosion mechanism is shown in Fig. 6. Firstly, $AlCl_3$ is generated and then volatilized, which results in the formation of voids and channels. Meanwhile, S and SO_2 pass through the channels and cracks, causing the internal oxidation and sulfidation. With the reactions proceeding, the stress concentration leads to more cracks and more serious spallation of the oxide scale, and the coatings fail finally.

The severe hot corrosion of the substrate leads to a rapid failure. Therefore, the protective coatings for substrate are essential. The diffusion coatings and overlay coatings are two typical coating systems, which are commonly used for the gas turbines.

3 High Temperature Protective Coatings Against Molten Salt-Induced Hot Corrosion

3.1 *M*CrAlY coatings

The hot corrosion behavior of *M*CrAlY coatings has been widely investigated. Luo et al[41] prepared NiCoCrAlYTa coating on the single crystal superalloy by low pressure plasma spraying, and found that NiCoCrAlYTa coating presents better corrosion resistance than the uncoated superalloy does in the Na_2SO_4 molten salt and the 75wt% Na_2SO_4+25wt% NaCl mixed molten salt atmospheres. The enhanced corrosion resistance is due to the formation of the dense and continuous Al_2O_3 layer. Zhang et al[42] prepared NiCrAlY and NiCoCrAlYTa coatings on the nickel-based alloy and found that the corrosion kinetic curves of NiCrAlY coating obeys the parabolic law and the NiCrAlY coating exhibits better corrosion resistance.

Zhang et al[43] researched the cyclic hot corrosion

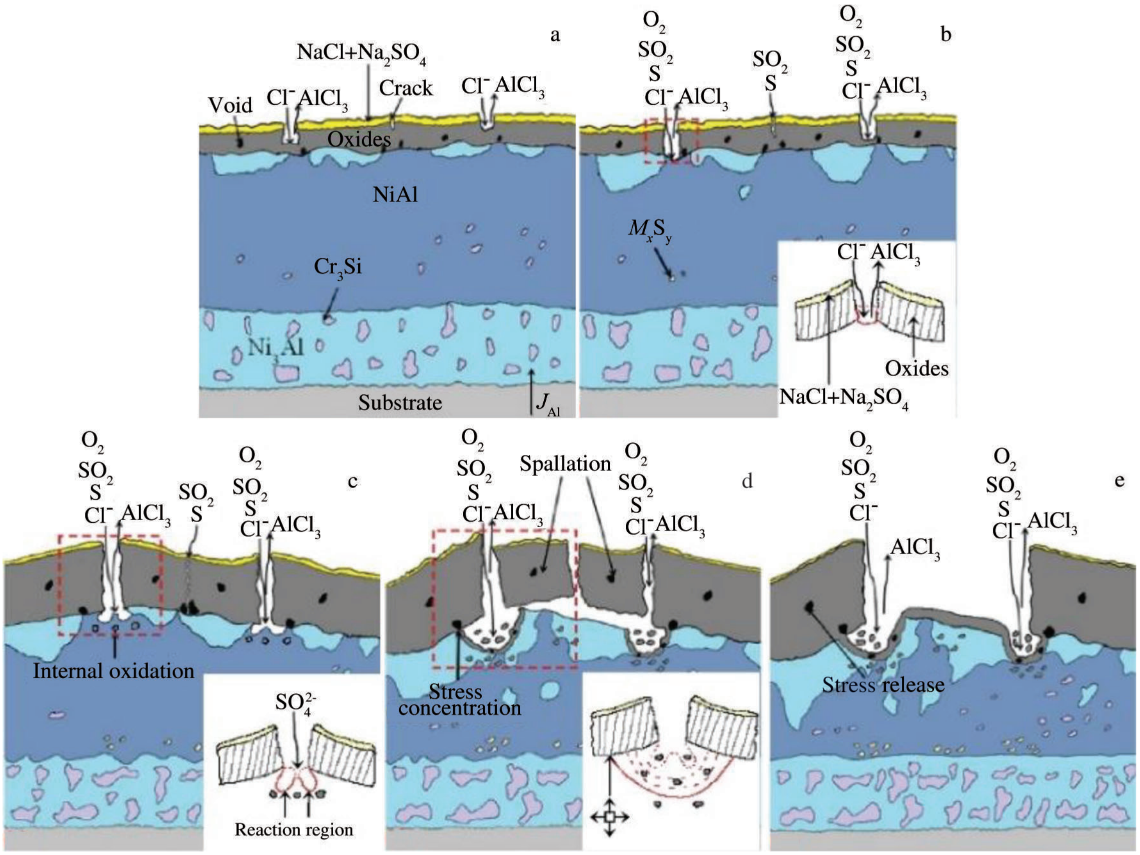

Fig.6 Schematic diagrams of corrosion behavior of NaCl+Na_2SO_4 mixed molten salts: (a) $AlCl_3$ formation by reactions between NaCl and Al_2O_3 and surface hole formation by $AlCl_3$ vaporization; (b) further reactions between NaCl and Al_2O_3 and surface hole enlargement; (c) oxide layer bulges, stress concentration with increased internal stress, and internal stress release by $Al_2(SO_4)_3$ through the channels formed by NaCl; (d) spallation of oxides layer; (e) formation of new oxide layer[31]

performance of the *M*CrAlFe$_x$ coatings in the mixed molten salts atmosphere (75wt% Na_2SO_4+25wt% NaCl), and revealed that the Fe addition can slow down the hot corrosion process. Based on the thermodynamic model, the high Fe content of *M*CrAlFe$_x$ coatings reduces the Al content in γ phase and thereby impedes the Cr diffusion from the coating to the substrate. Therefore, the hot corrosion resistance of coatings is enhanced and the substrate is well protected.

3.2 NiAl coatings

β-NiAl attracts much attention because of its high melting point and low density. However, the β-NiAl cannot serve in the sulphur-containing atmosphere at high temperatures. Generally, the sulphur can accelerate the pore formation and weaken the interface bonding strength.

Yang et al[44] found that Pt+Hf-modified NiAl coatings can promote the nucleation and growth of pores, which facilitates the low hot corrosion rate. The formation of slack Al_2S_3 and chloride bubbles results in the worm-like embossments. HfO_2 gradually dissolves because the molten salt is immersed into the Hf-rich zone. Zhang et al[45] found that Pt can reduce the negative effects of sulphur in the coatings and improve the corrosion resistance of coatings in the molten salt environment.

3.3 Thermal barrier coatings

The thermal barrier coatings usually play an important role as heat insulation in the gas flow, and they usually consist of an outmost ceramic coating with low thermal conductivity, an intermediate bonding layer of *M*CrAlY alloy or diffusion aluminide layer, and an inner oxidation/corrosion-resistant layer[46]. The zirconia with 7wt%~8wt% yttria (YSZ) is a commonly used top-coating material because of its excellent properties, such as high melting point, low thermal conductivity, and excellent mechanical properties[47,48]. But YSZ is weakened in the atmospheres containing V, Na, and S during the hot corrosion process. The deposited salts on the thermal barrier coating surface can react with YSZ, resulting in the strong Lewis acid[49], which therefore causes the loss of Y_2O_3, the formation of corrosion product (YVO_4 precipitation), ZrO_2 phase transformation, and finally the failure of thermal barrier coatings. Song et al[50] prepared the boron-doped silica (B-SiO_2) layer on YSZ coating surface, and found that the B-SiO_2 layer can improve the corrosion resistance and chemical stability of YSZ coating.

However, some researchers consider that the failure mechanism of thermal barrier coatings is primarily due to the crack formation and propagation in the oxide scale, instead of the degradation of the ceramic layer. Leyens et al[51] studied the hot corrosion of thermal barrier coatings at 950 °C, and found that the lifetime of thermal barrier coatings is related to the ceramic layer microstructure.

3.4 Novel coatings

Recently, the Pt-modified coatings are designed to improve the overall performance of the coatings by promoting the selective oxidation of aluminum, hindering the detrimental effects of sulphur, and reserving more aluminum substrate[52,53]. Besides, the corrosion resistance against the molten salts is also improved. Yang et al[54] studied the effect of Pt contents and pre-oxidation on hot corrosion behavior of alloys. It is revealed that the Pt-modified coatings exhibit better hot corrosion resistance by hindering the element diffusion from the substrate, and the Pt-modified coating with the thickness of 5 μm shows the optimal performance in the mixed molten salt atmosphere[55-57]. In addition, the composite coatings can improve the corrosion resistance against the molten salt-induced corrosion. Zhang et al[58] studied the oxidation and hot corrosion behavior of *M*CrAlY-Cr_2O_3 coating, and found that the as-deposited Cr_2O_3 coating acts as the barrier to restrict the element diffusion from the substrate. Thus, Cr_2O_3 can also improve the corrosion resistance against the molten salt-induced corrosion.

4 Corrosion Resistance Improvement Methods

The lifetime and hot corrosion resistance performance of high temperature coatings have been continuously investigated, and the pre-oxidation[59], element doping, and surface modification[60,61] methods are proposed.

4.1 Pre-oxidation method

The diffusion channels of oxygen and aluminum ions, such as grain boundaries, pores, and cracks, play an important role in the corrosion process. The failure of β-NiAl coating is mainly due to the external diffusion of aluminum and the internal diffusion of harmful elements. Therefore, reducing the diffusion channels and forming a dense protective oxide scale can effectively slow down the degradation rate of coatings. The protective alumina can form on the coating surface by pre-oxidation treatment under the conditions of high temperature and low oxygen pressure. Thus, the selective oxidation of coating and the growth of coarse grains can be controlled by adjusting the oxygen pressure.

4.2 Element doping

The element doping method can effectively improve the corrosion resistance of coating in molten salt atmosphere. The appropriate amount of Cr addition can improve the corrosion resistance of coating, because the resultant Cr_2O_3 can preferentially react with the molten salt and protect Al_2O_3 in molten salt atmosphere.

Zhang et al[62] used the first-principles calculation method to obtain the adsorption properties of different active elements with S at the oxide/metal interface. At the α-Al_2O_3/β-NiAl-S interface, the adsorption efficiency of the active elements with S is Y>La>Dy>Hf>Zr>no active element doping. The results provide theoretical guidance for the further study of corrosion of NiAl coatings at high temperatures in marine atmosphere.

Although various methods can improve the corrosion resistance of coatings, the complex service environment is still a problem for the gas turbine. With the continuous development of the “deep blue strategy” and the “deep sea strategy”, the molten salt-induced hot corrosion of gas turbine in marine atmosphere still needs further research.

5 Summary and Prospects

The hot corrosion problem of gas turbine is an important factor restricting the development of aeroengine. Several molten salt-induced corrosion mechanisms are proposed. Among them, the acid and alkaline corrosion mechanisms are widely recognized. To reduce the molten salt-induced corrosion of the coatings, the dense continuous oxide scale on coating surface and the coarse grain structure should be obtained by the pre-oxidation treatment. Thus, the internal diffusion of harmful elements and outward diffusion of substrate elements are hindered. The active element addition can pin the S on the metal/oxide interface, blocking the internal sulfide and improving the adhesion performance of metal/oxide interface. Both these two methods can effectively improve the resistance of coatings against the molten salt-induced corrosion.

In recent years, the service conditions of aeroengine are more and more complicated. The single-structure protective coatings or the single-function high temperature protective coatings cannot meet the engineering needs anymore. The simultaneous improvement in the high temperature oxidation resistance and the corrosion resistance against the molten salt is still the essential development direction. Hence, the composite coatings, smart coatings, or functionally gradient coatings are the new development trends of coatings to deal with the complex and harsh service environment. The common composite coatings, including the $LaPO_4$/yttria stabilization zirconia (YSZ)/NiCoCrAlY[63], $Sm_2SrAl_2O_7$/NiCrAlY[64], and YSZ/Al_2O_3[14]-dispersed NiCrAlY coatings, can effectively improve the hot corrosion resistance of the components. The smart coatings or the functionally gradient coatings still lack the deep investigations in terms of hot corrosion, which shows a good application prospect in the gas turbine industry.

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高温防护涂层的熔盐热腐蚀研究进展

李小亚[1,2,3]，邹俭鹏[1]，石　倩[2,3]，代明江[2,3]，林松盛[2,3]，唐　鹏[2,3]，苏一凡[2,3]

(1. 中南大学 粉末冶金国家重点实验室，湖南 长沙 410083)

(2. 广东省科学院新材料研究所 现代材料表面工程技术国家工程实验室，广东 广州 510651)

(3. 广东省现代表面工程技术重点实验室，广东 广州 510651)

摘　要：高温热腐蚀是热元件主要失效形式之一，Na_2SO_4和NaCl熔盐会加速高温下的热腐蚀，甚至导致灾难性事故发生。本文就Na_2SO_4和/或NaCl熔盐引起的热腐蚀进行了讨论，其中Na_2SO_4是主要的腐蚀反应物，详细介绍了2种典型的热腐蚀行为和性能特点。重点介绍了几种热腐蚀模型和机理，以及Na_2SO_4、NaCl、Na_2SO_4+NaCl熔盐的反应公式和腐蚀机理。根据目前的研究状况来看，制备防护涂层是缓解热腐蚀的最佳途径，总结了近年来*M*CrAlY涂层、NiAl涂层、热障涂层和新型涂层的发展情况，并探讨了进一步提高涂层耐腐蚀性能的方法。最后，展望了防护涂层的未来发展方向。

关键词：热腐蚀；熔盐；高温防护涂层

作者简介：李小亚，女，1991年生，博士，中南大学粉末冶金国家重点实验室，湖南 长沙 410083，电话：0731-88876630，E-mail：li_xiaoyazjh@163.com