Effect of Alloy Element Al on the Corrosion Behavior of Ni-10wt%Fe Based Alloy in Molten NaCl

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Abstract: NaCl and its mixed salt have many advantages as a medium of solar energy phase change thermal storage at moderate and high temperature. But molten chloride has sharp corrosive action on metal thermal storage vessel. The corrosion behavior of three kinds of Ni-10 wt% Fe based alloy (1#, 2# and 3#) in 850 °C molten NaCl was studied. The content of Al in 1#, 2# and 3# sample was 0.0 wt%, 5.0 wt% and 10.0 wt%, respectively. The components of NaCl after corroding and corrosion products on samples surface were analyzed. Elements change trend and corrosion characteristics on cross section of the three samples were contrasted. Corrosion mechanisms were discussed finally. Results show that the kinetics curves of the three kinds of sample obey a liner rule. The average mass loss rate declines when Al is added in the sample. The rate of 2# and 3# is only 12% and 20% of that of 1#, respectively. There are two reasons for the value reduction: firstly, Al will be oxidized prior to oxidization of Fe or Ni, and the atomic mass of Al is small; secondly, Al₂O₃ is very stable at high temperature as corrosion products. However, when the content of Al is very high (for example 10 wt% in here) in Ni-10 wt% Fe based alloy, Al oxidized on sample surface provides a convenient condition for Al atom transmission from sample inside to surface. Al₂O₃ film becomes thick and exfoliates easily. The exfoliation increases the average mass loss rate in turn.

Key words: corrosion; molten salt; NaCl; Al

Nitrate, such as KNO₃-60%NaNO₃, which with low fusion point is widely used as a heat-transfer and thermal storage medium in the field of tower and parabolic trough solar thermal power. But for dish solar thermal power generation with very high heat-collecting temperature, NaCl and its mixed salt will be used as a thermal storage medium^[1,2], since NaCl and its mixed salt have relatively high melting point, well stability of physical-chemistry and high phase change latent heat. Molten salt is a strong electrolyte, which has sharp corrosive action on metal thermal storage vessel.

B. P. Mohanty et al^[3] added NaCl in molten Na₂SO₄. The average corrosion mass loss rate of Fe-25.5wt%Cr-13.0wt% Ni alloy in the mixed molten salt is 100 times larger than in Na₂SO₄. The effect of NaCl added in molten sulfate at 850 °C on Cr₁₃Ni₃Si₂ corrosion behavior was studied by L. Yuan et

al^[4]. The hot corrosion behavior of NiCoCrAlYSiB coating in molten Na₂SO₄-K₂SO₄ and Na₂SO₄-NaCl at 900 °C was studied by Xuyang Lu et al^[5]. The above results show that NaCl will accelerate the hot corrosion process. What's more, the average mass loss rate increases with the increase of Cr content in alloy. And the kinetics curves obey a liner rule^[6,7]. The major reasons is as follows: Cr₂O₃ film is destroyed by volatile CrCl₃ formed by Cr and Cl⁻ in molten chlorate, and the solubility is higher than that of other oxides (for example Fe₃O₄, and NiO) at the same oxygen partial pressure in molten chlorate^[6,8-10]. The corrosion behavior of Ti-48Al- 8Cr-2Ag coating which was produced by magnetron-sputter deposition in 900 °C molten Na₂SO₄-NaCl was studied by Yanjun Xi et al^[11]. Results show that a lot of nano crystal grain boundaries act as diffusion channels of Al. So, the corrosion rate decreases

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for thick Al_2O_3 film formed on the sample surface^[11]. The corrosion behavior of aluminizing Ni based superalloy M247 in molten Na_2SO_4 -25%NaCl was studied by J. H. Cho. NiAl forms between aluminizing film and substrate, which inhibits flaking off of Al_2O_3 from the sample substrate and enhances the sample corrosion resistance^[12]. The effects of 5 wt%Al on the corrosion behavior of Fe-Cr alloy under the condition of KCl molten salt film was studied by Y. S. Li et al^[13]. Results show that corrosion resistance was enhanced by adding Al.

In conclusion, NaCl plays a key role in molten Na_2SO_4 -NaCl. Cr is the major cause of alloy corrosion in molten chlorate. The content of Al in alloy of Ref. [11-14] is relatively high. Experiment results show that Al play an important role in enhancing alloy corrosion resistance. But the concrete effect of Al content on corrosion behavior is not clear. So, the effect of Al content on the corrosion behavior of Ni-10wt%Fe based alloy (without Cr) in pure molten NaCl was studied in the present paper. And the corrosion mechanism was discussed.

1 Experiment

Three kinds of alloys were made by a medium-frequency induction furnace. The mass of each sample was 500 g, which made of pure Ni, Fe and/ or Al. The composition of the three kinds of alloys is shown in Table 1. The ingots were cut into the dimension of 10 mm×10 mm×5 mm by an electrical spark line cutting machine in triplicate. The samples were ground with a series of 400#, 600#, 1000# silicon carbide paper in sequence, polished with 1 μm diamond powder and ultrasonic cleaned in acetone for 10 min and then dried. Finally, each kind of sample was measured (surface area), weighed and recorded. Except for the former reasons about choosing Ni-10wt%Fe based alloy as experiment samples. The two other reasons is as follows: firstly, Ni is very stable, which can dissolve many kinds of alloy elements and doesn't produce bad phase. Secondly, it is found from former corrosion experiment results of Ni-XFe alloy in 850 $^{\circ}\text{C}$ molten NaCl that the corrosion rate of Ni-10wt%Fe is the highest. So, the effect of Al content on corrosion behavior of this alloy (Ni-10wt%Fe) may be more significant than other kinds of alloy.

Analytically pure NaCl was placed in three 50 mL alumina crucibles and dried in a drying oven at 500 $^{\circ}\text{C}$ for 2 h. The crucibles with dried NaCl were placed in a box muffle furnace and heated to 850 $^{\circ}\text{C}$ with heating velocity of 5 $^{\circ}\text{C}/\text{min}$. Finally, samples were immersed completely in the molten NaCl correspondingly (three parallel samples were prepared for each kind of alloy). Corrosion experiments started at 850 $^{\circ}\text{C}$. After being corroded for 10 h, these samples were

3#	10.0	10.0	Bal.
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out from the muffle furnace and air-cooled. After the corrosion experiment, NaCl in three crucibles were collected. Then phase composition was analyzed by XRD. According to GB/T 16545-1996, these samples were cleaned by ultrasonic wave in deionized water and alcohol for 30 min. After drying, these samples were weighed and measured with electronic balance (0.1 mg) and vernier caliper. Then, the average mass loss rate and the corrosion kinetics curves were made. Finally, the above process was repeated, and the second corrosion experiment started.

The above experiment process was repeated for 8 times (corrosion time was 80 h). The cleaning process was abandoned after the last corrosion experiment. Instead, these sample surfaces were cleared with a wood draw knife before the XRD phase analysis. Then the composition of corrosion products was detected. At last, sample cross sectional was polished by SiC sand paper and cloth successively. The morphology of corrosion layer and the cross sectional element distribution were observed and analyzed by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS), respectively. So, the average mass loss rate and the corrosion kinetics curves were calculated and drawn based on the seven previous experiment results.

2 Results

Average mass loss rate of the three kinds of sample after corroding for 70 h is shown in Fig.1. It shows that the relationship of the three kinds of samples is 1#>3#>2#. The average mass loss rate decreases sharply after adding Al in the sample. When adding 5 wt%Al, the mass loss rate value is only 12% of that without Al. When adding 10 wt% of Al, the value is 20% of that without Al, which is slightly higher than that of adding 5 wt%.

Corrosion kinetics curves of the three kinds of sample for 70 h obey a liner law, which are shown in Fig.2. The fitting line slope is k_i ('i' is sample number). The relationship of the three kinds of sample is $k_1 > k_3 > k_2$. The lager the k_i , the higher the corrosion rate, which agree with the result of Fig.1.

Fig.3a shows XRD patterns of NaCl which corrodes the three kinds of sample for 10 h. It is found from the figure that there is nothing, such as chlorine and oxides of Fe, Ni and Al,

Table 1 Composition of three kinds of alloy samples (wt%)

Sample No.	Fe	Al	Ni
1#	10.0	0.0	Bal.
2#	10.0	5.0	Bal.

Fig.1 Average mass loss rate of three kinds of samples

Fig.2 Corrosion kinetics curves of three kinds of sample

Fig.3 XRD patterns of corrosion residual salt after corrosion for 10 h (a) and corrosion products on three kinds of sample surface after corrosion for 80 h (b)

except NaCl. Fig.3b shows XRD patterns of corrosion products on the three kinds of sample surface after corroding for 80 h. It is found from the figure that: firstly, NaCl exists on the surface of all samples, which is residual salt after clearing by a scraping method with a wood draw knife at the last corrosion experiment. Although the three kinds of sample were cleared by one with the same method, it is found from XRD pattern in Fig.3b that the NaCl intensity of 2# and 3# is higher than that of 1#. This shows that residual NaCl on the surface of 2# and 3# samples is more than that of 1#. Secondly, a few oxides of Fe and Ni (Fe_3O_4 and NiFe_2O_4) are detected on the surface of 1#. The oxides don't be detected on the surface of

2# and 3#, but Al_2O_3 is found on their surface obviously.

Fig.4a, 4b and 4c shows SEM images of cross section of 1#, 2# and 3# samples after being corroded in molten NaCl at 850 °C for 80 h, respectively. It is found from Fig.4a that the section of 1# is smooth. There are a lot of corrosion holes near surface. The thicknesses of those hole layers are different. The relatively thick layer and thin layer is about 60 and 25 μm , respectively. It is found that corrosion holes form near surface of 2# sample from Fig.4b, too. Those filamentous corrosion holes extend from sample surface to inside. Compared with 1#, the number of corrosion holes is little; the thickness of corrosion holes layers is thin. SEM images of cross section of 3# in Fig.4c shows that wormlike or nearly spherical biggish corrosion holes form near the sample surface in 60 μm . What's more, the sample surface is covered by a layer of material with poor electrical conductivity. It is speculated from XRD pattern of Fig.3b that most of these compounds are Al_2O_3 and NaCl.

Fig.5a and Fig.5b show EDS elements line distribution on cross section of sample 2# and 3# after corroding in molten NaCl at 850 °C for 80 h, respectively. It is found that: firstly, the Al content of 2# and 3# decreases obviously near sample surface. Secondly, the Fe content of 2# sample near surface decreases obviously, too. But the Fe content of 3# nearly remains constant. Thirdly, for 2# and 3#, the content of elements O, Na, Cl and Al in corrosion holes are higher than that on sample inside. It indicates that molten NaCl permeates into sample inside through corrosion holes. In addition, Al_2O_3 is formed.

3 Discussion

Oxides will be formed when Fe and Ni react with microscale oxygen which is dissolved in molten NaCl for Fe-Ni alloy. Because the Gibbs free energy of Fe oxide is more negative than Ni at 850 °C, Fe will be oxidized preferentially. A

Fig.4 SEM images of cross section of 1# (a), 2# (b), and 3# (c) after

being corroded in molten NaCl at 850 °C for 80 h

Fig.5 EDS elements line distribution on cross section of sample 2# (a) and 3# (b) after corroding at 850 °C for 80 h

following reaction will occur in molten NaCl^[15]:

Based on the active-oxidation theory, the product of Cl_2 bleeds into oxide film/metal interface and reacts with metal (M), chloride produce as follows:

The phenomenon of volatilization is obvious when vapor pressure of a material is higher than 10 Pa at certain temperature. The temperature is called T_4 temperature of the material. The temperature of T_4 is low for common chloride. For example, FeCl_3 is 167 °C, FeCl_2 is 536 °C, and NiCl_2 is 607 °C. The molten point of FeCl_3 -25 at% NaCl is only 156 °C^[16]. All of those temperatures are lower than the experiment temperature. So, corrosion products may volatilize as gaseous state. As a result, although the three kinds of sample are corroded severely, Fig.3a shows that compounds of Fe or Ni don't be detected in residual NaCl after corroding.

Metal oxides on the surface of the three kinds of sample in Fig.3b not only form by the reaction between oxygen which is dissolved in molten NaCl and metal atoms on the surface of sample, but also chloride which is produced in reaction (2) will be oxidized when it diffuses to molten salt/sample interface where oxygen part pressure is relatively high. The reaction is as follows^[17]:

Metal oxide deposits on sample surface and provides material condition for reaction (1).

It is found that Fe_3O_4 and NiFe_2O_4 form on the surface of 1#. These oxides have stable structure of spinel. Al_2O_3 which is very stable at high temperature forms on the surface of 2# and 3#, too. All of those metallic oxides have a protective effect for sample. However, molten NaCl has a good fluidity. It penetrates into the interface of oxide/metal through the oxide film on the sample surface. The molten NaCl plays a role of

mass transfer carrier in chemical reaction (1) ~ (3), which makes these reaction occur continuously. As a result, corrosion kinetics curves of the three kinds of sample obey the liner law. That is shown in Fig. 2.

The average mass loss rate of 1# is much higher than that of 2# and 3#. But it is found that the corrosion layer thickness of 1# is not thicker than that of 2# and 3# from Fig.4. That is because: firstly, volatile MCl is produced near oxide layer/metal layer from chemical reaction (2). Gap forms between corrosion layer and metal after MCl volatilizing. So, the adhesion ability of oxide layer declines. The oxide layer exfoliates easily. The crack is obvious in Fig.4c. Secondly, when the samples are taken out from 850 °C molten NaCl and cooled to room temperature, the plasticity of corrosion layer decreases after molten salt penetrating in the corrosion layer. Thirdly, the corrosion layer will craze for pressure stress during cooling and peel off when residual salt is cleared. The process is shown as Fig.6a, 6b and 6c. So, average mass loss rate of 1# is higher than that of 2# and 3#, but it is shown in Fig.4 that the corrosion layer thickness of 1# is not thicker than that of 2# and 3#.

The average mass loss rate of 2# and 3# is much lower than that of 1#. This is because: firstly, from thermodynamics perspective, the Gibbs free energy of oxidation reaction of Al is less (more negative) than Fe and Ni. Element Al will react with trace oxygen which is dissolved in molten NaCl and produce Al_2O_3 . Even if Fe or Ni has oxidized, the oxide will be reduced by Al and produces Al_2O_3 . Al will volatilize in the form of AlCl_3 during the active-oxidation reaction process. The process cannot be ruled out. But Al_2O_3 has a protective effect on the sample, because it has good stability at high temperature and strong adhesive. The Al_2O_3 film inhibits the mass transfer process and decreases corrosion rate. In addition, the NaCl diffraction peak intensity of 2# and 3# is high

relatively in Fig.3b. That's because the adhesive of Al_2O_3 is strong. The amount of adhesive NaCl is large after clearing.

Fig.6 Schematic diagram of corrosion layer peel off on 1# sample surface in molten salt at 850 °C (a), cooled to room temperature (b), and after clearing residual salt (c)

Secondly, it is found that the consumed mass of Al is only 42.9% of Fe when consume 1 mol oxygen, by comparing two chemical reactions in Table 2. The atomic mass of Ni is larger than that of Fe. When consumed 1 mol oxygen and parts of Fe are replaced by Ni in iron oxide (for example NiFe_2O_4 in this paper), the total atom mass of Fe and Ni in oxygen will be larger than that of Al, because the oxygen that dissolved in molten NaCl is little. So, the sample average mass loss rate decreases when Al is oxidized prior to Fe or/and Ni. Combined the above two reasons, the average mass loss rate of the sample with Al (2# and 3#) is small.

Compared 2# with 3#, the average mass loss rate of 2# is relatively small. That is because the radius of Al atom is larger about 15% than that of Fe and Ni (Al: 1.43 nm, Fe: 1.24 nm, Ni: 1.25 nm). The diffusion of Al is difficult by the interstitial diffusion mechanism. In alloy of Ni-10 wt%Fe with Al, a point defect of Al will form on the sample surface when Al escape from alloy lattice in the form of Al_2O_3 or AlCl_3 by oxidation or active-oxidation reaction way. The original compressive stress between atoms relaxes. Since the amount of Al in 2# is low, there are Fe or Ni atoms primarily around the point defect. Distance between the point defect and the nearest Al atom is far. So, the diffuse rate of Al is slow by transposition or vacancy mechanism. The Gibbs free energy of Fe oxidation reaction is less (more negative) than that of Ni. Consequently, Fe will take part in the chemical reaction and volatilize in the form of chloride when insufficient Al loses reaction chance. The schematic diagram is shown as Fig.7a. Active-oxidation reaction of Fe occurs. Fe will volatilize in the form of chloride after molten NaCl penetrating into Al_2O_3 film. It decreases the content of Al and Fe near sample surface. The thickness of Al_2O_3 film is thin, which is shown as Fig.5a.

For 3# sample, because the content of Al is high, Al atom

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Fig.7 Schematic diagram of atom diffusion of 2# sample (a) and 3# sample (b) (○Ni ○Fe ●Al)

diffuses to the point defect easily in the way of transposition or vacancy mechanism. The vacancy produced after the second Al atom diffusing away provides facilities for the third Al atom diffusing. Oxidizing and active-oxidation reaction of Al will occur continuously when the above process occur in cycles. In the process, an abundant supply of Al deprives Fe of reaction opportunity. So, the content of Fe near sample surface does not change obviously. The final content change result of Fe and Al is shown as Fig.5b. The schematic diagram is shown as Fig.7b. A pretty thick and stable Al_2O_3 film forms on sample surface after much Al is oxidized. Al_2O_3 film which likes oxide film of Fe and Ni will craze and peel off with the action of thermal stress. What's more, because the thickness of Al_2O_3 film is thick, the film is more likely to peel off for high thermal stress. Once the film peels off, the sample surface is uncovered. And corrosion rate increases. Consequently, the average mass loss rate of 3# is higher than that of 2#.

After a lot of Al atoms diffusing from inside to surface of 3# sample, many wormlike or nearly spherical biggish corrosion holes form in macroscopic view. But for 2# sample, corrosion occurs firstly from grain boundary where atoms

Table 2 Comparison of metal consumption in different oxidizing reactions

Chemical reaction	Oxygen consumption/mol	Metal consumption/g
$4/3\text{Al} + \text{O}_2 = 2/3\text{Al}_2\text{O}_3$	1	36

arrange chaos and have high energy. Then corrosion holes expand to sample inside. So, the characteristic of filaments intergranular corrosion is shown in Fig.4b. Whether the corrosion holes are wormlike, nearly spherical or filamentous, these corrosion holes are transmission channels for molten salt penetrating into sample inside. So, it is found that NaCl content is high inside corrosion holes from Fig.5a and Fig.5b. In addition, it is found that producing volatile MCl needs Cl_2 from the chemical reaction (2). But Cl_2 is produced with the participation of oxygen in reaction (1). The content of oxygen that dissolves in molten NaCl is less. The rest of oxygen is much less after thronging corrosion holes and reacting with Al (produce relatively stable Al_2O_3). The chemical reaction (1) can't occur. So, the content of Al in corrosion holes of 2# and 3# sample is high, which is shown as Fig.5.

4 Conclusions

1) Corrosion resistance of Ni-10wt%Fe based alloy in 850 °C molten NaCl increases by adding 5 wt% Al or 10 wt% Al. The average mass loss rate of the two kinds of sample is 12% and 20% of that of the sample of absence Al, respectively. But the three kinds of sample are corroded severely and obey the linear corrosion law.

2) The corrosion mechanism of the three kinds of sample is active-oxidation reaction. The reasons for corrosion rate decrease of the sample containing Al are that, Al has small atomic mass to replace Fe and Ni atoms is oxidized. During the corrosion process, the mass transfer process is suppressed by much stable Al_2O_3 film at high temperature after Al oxidizing.

3) Compared with the sample that contains 5 wt% Al, for the sample with 10 wt%Al, the transfer of Al from sample inside to surface becomes easy, which results in the thickness of Al_2O_3 film increase. The film exfoliates easily with the

action of thermal stress. So, the corrosion rate increases.

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合金元素 Al 对 Ni-10%Fe 基合金在熔融 NaCl 中腐蚀行为的影响

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摘 要: NaCl 及其混合盐作为太阳能中高温相变储热介质有许多优点, 但熔融氯化盐对金属储热容器材料具有强烈腐蚀性。研究了 Al 添加量(质量分数)分别为 0%、5%和 10%的 3 种 Ni-10%Fe 基合金(分别为 1#、2#和 3#)在 850 °C 熔融 NaCl 中的腐蚀行为, 分析了试样表面腐蚀产物和腐蚀残盐成分, 对比了试样横截面腐蚀特征和元素变化趋势, 探讨了腐蚀机制。结果表明, 3 种试样的腐蚀动力学曲线均满足线性腐蚀规律; 添加 Al 的试样平均质量损失率大幅降低, 2#和 3#试样腐蚀速率分别为 1#试样的 12%和 20%。原子量较小的 Al 优先于 Fe、Ni 被氧化和生成高温稳定性好的 Al_2O_3 , 是腐蚀速率降低的两个主要原因。但 Al 含量较高(如 10%)时, 内部的 Al 原子向试样表面扩散较为容易, 氧化膜较厚, 且易于脱落, 又导致腐蚀速率增大。

关键词: 腐蚀; 熔融盐; NaCl; Al

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