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ARTICLE

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, Al_2O_3 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. Al_2O_3 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 KNO_3-60%$NaNO_3$, 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 Na_2SO_4. 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 Na_2SO_4. The effect of NaCl added in molten sulfate at 850 °C on $Cr1_3Ni_5Si_2$ corrosion behavior was studied by L. Yuan et al[4]. The hot corrosion behavior of NiCoCrAlYSiB coating in molten Na_2SO_4-K_2SO_4 and Na_2SO_4-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: Cr_2O_3 film is destroyed by volatile $CrCl_3$ formed by Cr and Cl^- in molten chlorate, and the solubility is higher than that of other oxides (for example Fe_3O_4, 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 Na_2SO_4-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-*X*Fe alloy in 850 °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 °C for 2 h. The crucibles with dried NaCl were placed in a box muffle furnace and heated to 850 °C with heating velocity of 5 °C/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 °C. After being corroded for 10 h, these samples were taken

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.
3#	10.0	10.0	Bal.

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,