Corrosion behavior of NO6600 alloy in molten chloride salts

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Abstract. In this paper, the corrosion behavior of Ni-based N06600 alloy in molten salts NaCl-53.63wt%MgCl$_2$ at 773.15K was studied by gravimetric methods. The cross section characteristics, the elements distribution features and corrosion products of the samples after corrosion were analyzed by SEM, XRD and EDS. The results showed that the corrosion kinetics curve of NO6600 alloy for 84 h obeyed the linear law, and the corrosion rate is 732.268 μ m /y. After corroding for 84 h , loose and porous structures were observed on the sample surface .The cross section morphology showed that there were a large pores in the top of the sample, and corrosion layer depths of the sample was about 30 μm .The corrosion mechanisms of this alloy are the loss of Fe and Cr.

1. Introduction

At present, thermal efficiency of concentrated solar power is between 30 and 40% [1]. Higher operating temperatures increase efficiency of the concentrating solar power plants. However, the marked degradation of nitrate salts which starts above 873.15K does not allow to increase the hot storage temperature further[1-2]. Molten chloride salts are candidates for CSP applications because of their high decomposition temperatures and good thermal properties, especially NaCl-53.63wt%MgCl$_2$ mixed salts whose latent heat value is up to 430J/g, and become the most potential energy storage molten salt [3].However, molten chlorides are usually corrosive to salt storage equipment, so it is meaningful to study the corrosion behavior of alloys in molten Chloride salts at high temperature [4].

There are a lot of studies about metal corrosion behavior in molten Chloride salts. Liubo et al. [5] studied the corrosion behavior of In625, HX and HB-3 in molten NaCl-CaCl$_2$-MgCl$_2$ at 873.15K. It was pointed out that the Ni and Mo in the Ni-based alloys showed higher stability. After comparing the corrosion behavior of the alloy with different Cr content, Manohar S. Sohal [6] concluded that the increment of Cr increased the corrosion rate of alloys. However, Vignarooban et al. [7] studied the corrosion behavior of HastelloyC-276, C-22 and Hastelloy N in molten NaCl-KCl-ZnCl at 523.15K and 773.15K. The results showed that C-276 and C-22 alloy with higher Cr content than Hastelloy N had a better corrosion resistance.

In summary, Ni showed higher stability in chloride salts while the corrosion behavior of Cr in molten salt is still not clear now. So we chose the NO6600 alloy and used gravimetric method to study the corrosion mechanism of Cr in molten NaCl-53.63wt%MgCl$_2$ at 773.15K, in order to provide the theoretical basis for optimizing the CSP structure materials.

2. Experiment

The nominal chemical composition of NO6600 alloy which was purchased from Shanghai Special Alloy Co. LTD is as follows(wt.%): Cr14.0~17.0, Fe 6.0~10.0, C≤0.15, Cu≤0.5, Si≤0.5, Mn≤1.0, S≤0.015 and the rest is Ni. The alloy was cut into small samples with 15mm x15mm x 5mm by wire cutting machine, Then ground with SiC paper of 600#, 1500# and 2000#, followed polishing, ultrasonic cleaning in alcohol, and finally dried by cold air. The quality and size of the samples were measured by analytical balance and vernier caliper, respectively. After that, analytical pure $MgCl_2$ and NaCl were mixed in eight crucibles and stored in muffle furnace. When the corrosion experiment started, the muffle furnace was heated to 773.15K with a rate of 5K/min. After the salt melting, three samples were put into every crucible, and the No.1 to No.6 crucibles were removed every 12 h, and then No.7and No.8 crucibles were removed after being corroded for 84 h. When the samples were taken out of the muffle furnace, they were cooled to room temperature together with the molten salt to avoid oxidation. These samples were treated with the standard method described in ASTM G1-03[8]. All characterization methods have been described in details in [9]. The formulas for calculating the mass loss and corrosion rate of the alloy are as follows [10-11]:

$$\frac{\Delta m}{S_0} = \frac{m_i - m_f}{S_0} \tag{1}$$

$$CR(\mu m/y) = (365).10000[\Delta m/(\rho.S.T)] \tag{2}$$

Where m_i is the initial mass of the sample (g) , m_f is the mass of this sample at time T (g), and S_0 is the initial area (cm^2), Δm is the weight loss (g), ρ is density(g cm^{-3}),S is the total immersed area (cm 2),T is the immersion duration in days(d).

3. Results and discussion

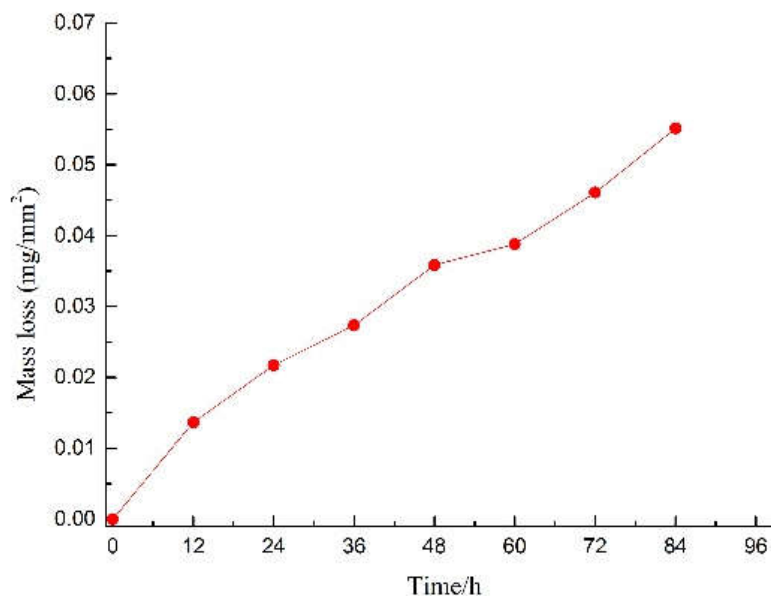### 3.1. Experimental results

Fig. 1 Corrosion kinetics curve of No6600 in NaCl-53.63wt%$MgCl_2$ at 773.15K

The mass loss for No6600 alloy in molten NaCl-53.63wt%MgCl$_2$ at 773.15K is shown in Fig. (1). The corrosion kinetics curve of sample obeyed the linear law. The corrosion rate of the sample was calculated to be 732.268 μm/y by formula (2).

The XRD patterns of corrosion products on the surfaces of samples after corrosion for 0,84 h are shown in Fig.2.It can be seen that Cr$_{0.19}$Fe$_{0.7}$Ni$_{0.11}$, [Fe, Ni] are dectectd on the surface of sample before corrosion, .but after corrosion for 84 h , Ni$_{2.9}$Cr$_{0.7}$Fe$_{0.36}$, Ni, NiO, MgO are decteced.
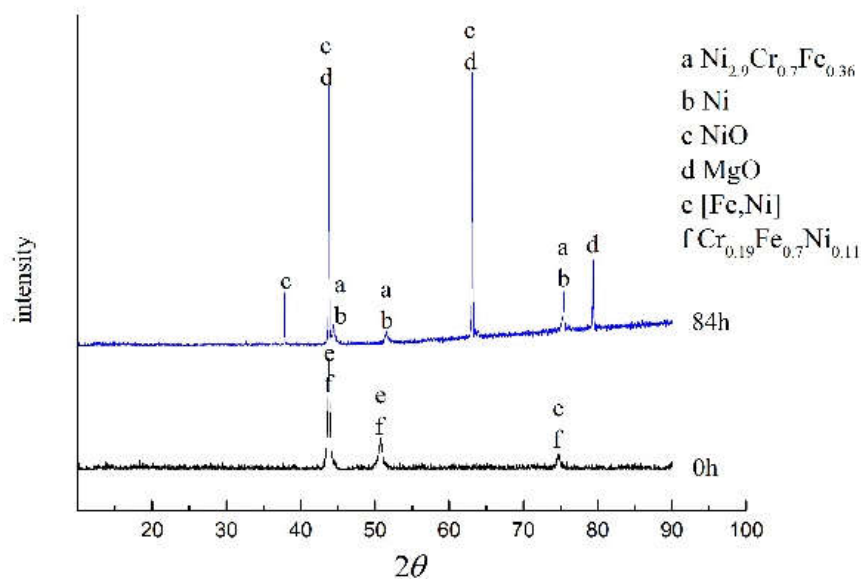

Fig. 2 XRD patterns of corrosion products on the surface of sample

The surface morphologies of sample after being corroded for 84 h in molten NaCl-53.63wt%MgCl$_2$ at 773.15K is shown in Fig. 3 (a). It can be seen from Fig, 3 (a) that there were many particles on the surface of the sample, and the alloy was seriously corroded. Combined with the results of Fig.2 and Fig. 3 (b), MgO and NiO were covered in region A, in which particles are mainly MgO, and the region B is mainly the matrix.
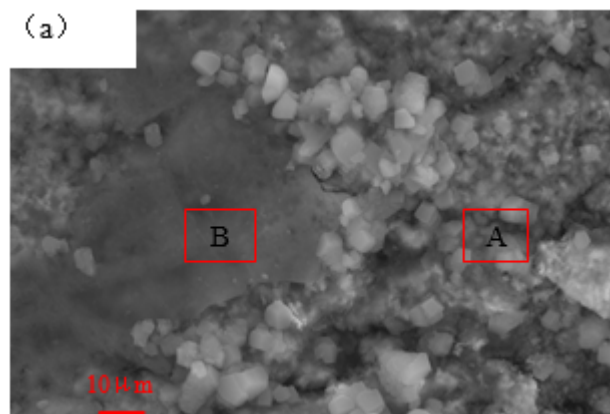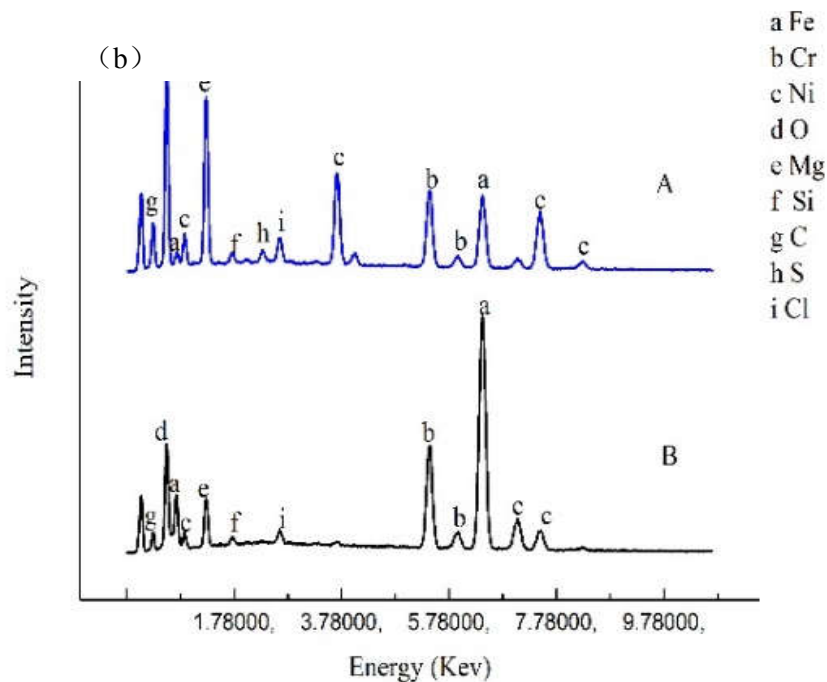
Fig. 3 SEM images (a) and EDS (b) of the sample surface after corroded for 84 h

After being cleaned with alcohol, SEM and EDS element distribution on cross section after corrosion for 84 h in molten NaCl-53.63wt%MgCl$_2$ at 773.15K is shown in Fig.4. It was found that there were many channels on cross-section surface .The thickness of corrosion layer was about 30 μm. Near sample surface, the content of Fe and Ni decreased, while Mg and O increased, and there were a higher Cr content in corrosion layer.
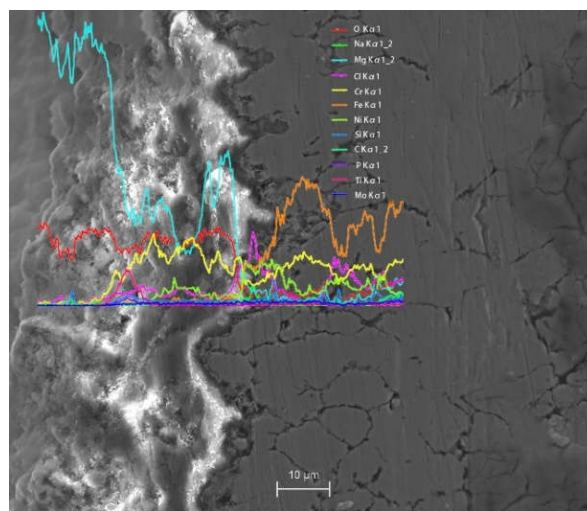

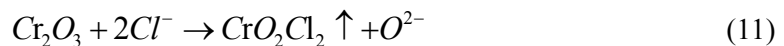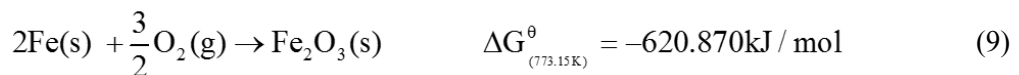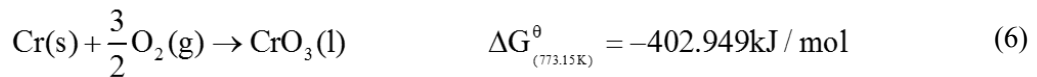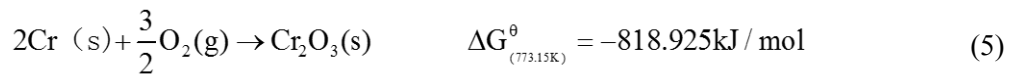**Fig. 4** SEM image and EDS element distribution on cross section after corrosion for 84 h

3.2. Discussion
It is reported that oxygen and water vapor can accelerate the corrosion rate of alloys in the molten salts [12]. O$_2$ (g) and H$_2$O (g) react with Cl$^-$ to form Cl$_2$ and HCl. H$_2$O (g) can react with MgCl$_2$ in the molten salts to form MgO. So MgO is detected on the surface of specimens.

$$4Cl^- + O_2(g) \rightarrow 2O^{2-} + 2Cl_2(g) \qquad (3)$$

$$H_2O(g) + 2Cl^- \rightarrow O^{2-} + 2HCl(g) \qquad (4)$$
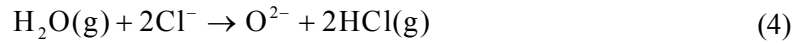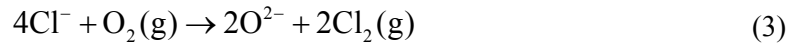
When the samples are immersed in molten salt, the oxygen dissolving in molten salt will react with Fe, Cr, Ni in alloy, and produce metal oxides. In order to judge reaction tendency, the Gibbs free energy of the following reactions are calculated [13].Comparing the value of free energy of every reactions, it can be inferred that Cr was preferentially oxidized, following by Fe and Ni. It may explain the form of NiO. On the other hand, the boiling point of CrO_3 are 523. 15K [13], which means it can easily escape from the system as gas at the test temperature. So CrO_3 was not detected on the surface of specimens.
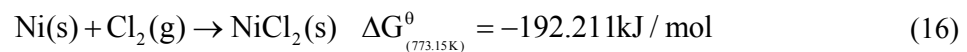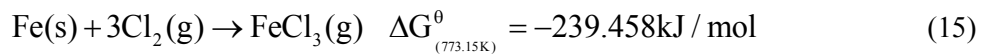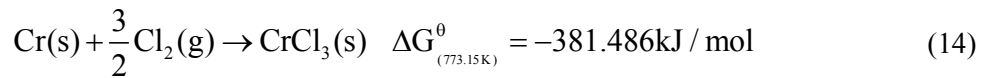
In addition, Cr_2O_3 was not deceted because it has a higher solubility than Fe and Ni oxides, and it will react more readily with chloride salt [14-15].

$$2Cr\ (s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s) \qquad \Delta G^\theta_{(773.15K)} = -818.925 kJ/mol \qquad (5)$$

$$Cr(s) + \frac{3}{2}O_2(g) \rightarrow CrO_3(l) \qquad \Delta G^\theta_{(773.15K)} = -402.949 kJ/mol \qquad (6)$$

$$2Fe(s) + \frac{1}{2}O_2(g) \rightarrow FeO(s) \qquad \Delta G^\theta_{(773.15K)} = -221.049 kJ/mol \qquad (7)$$

$$3FeO(s) + \frac{1}{2}O_2(g) \rightarrow Fe_3O_4(s) \qquad \Delta G^\theta_{(773.15K)} = -865.469 kJ/mol \qquad (8)$$

$$2Fe(s) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta G^\theta_{(773.15K)} = -620.870 kJ/mol \qquad (9)$$

$$Ni(s) + \frac{1}{2}O_2(g) \rightarrow NiO(s) \qquad \Delta G^\theta_{(773.15K)} = -167.822 kJ/mol \qquad (10)$$

$$Cr_2O_3 + 2Cl^- \rightarrow CrO_2Cl_2 \uparrow + O^{2-} \qquad (11)$$

However, MxOy is unstable in molten salts, it will react with Cl_2 as follow reactions, then Volatile MxCly will form and escape from system [16].It is why Fe and Cr oxides were not detected on the surface of specimens.

$$2M_xO_y + yCl_2 \rightarrow 2M_xCl_y + yO_2 \qquad (12)$$

$$Cr_2O_3 + 2Cl^- \rightarrow CrO_2Cl_2 \uparrow + O^{2-} \qquad (13)$$
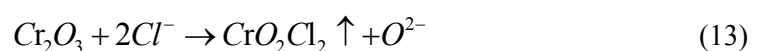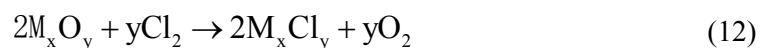
It was also reported that Cl_2 had the ability to permeate through pores and cracks and react with the alloys [17], this takes the following reaction:

$$Cr(s) + \frac{3}{2}Cl_2(g) \rightarrow CrCl_3(s) \quad \Delta G^{\theta}_{(773.15K)} = -381.486 kJ/mol \tag{14}$$

$$Fe(s) + 3Cl_2(g) \rightarrow FeCl_3(g) \quad \Delta G^{\theta}_{(773.15K)} = -239.458 kJ/mol \tag{15}$$

$$Ni(s) + Cl_2(g) \rightarrow NiCl_2(s) \quad \Delta G^{\theta}_{(773.15K)} = -192.211 kJ/mol \tag{16}$$

The chlorides of Fe, Cr and Ni were not detected on the surface of alloy because these metal chlorides are very volatile at the test temperature [17]. In particular, the boiling point of $FeCl_3$ (g) is just 593.15K, and it is easy to escape from system.

It was reported Cr had a preferential solubility and depleted in the corrosive zone [18]. Many channels in the cross-section were formed for this reason, which accelerates the diffusion of O_2 and Cl_2 to the substrate to improve the corrosion rate of alloy in molten salts.

It can be seen from Fig. 3 (a) and Fig.4 that there is no dense Fe-Cr-Ni oxide film on the sample surface, which indicated that there was no protective film formed during the test process. as Fig,4 showed, the Fe and Cr content sharply decreased while Ni is almost unchanged. So Ni has the better stability than Fe and Cr.

4. Conclusion
(1) The kinetics curve of NO6600 in molten eutectic NaCl-53.63wt%MgCl$_2$ for 84 h obeyed linear law, and the corrosion rate is 732.268 μm/y.

(2) After corroding for 84 h, there were loose and porous structures formed on the surface of sample, and no dense oxide film.

(3) A large number of pores caused by the preferential dissolution of Cr appeared on the cross section of the sample, which provided a channel for the diffusion of O_2 and Cl_2, and accelerated the corrosion rate of the alloy.

(4) The corrosion mechanism is mainly the loss of Cr and Fe, which was caused by the volatilization of CrO_3, CrO_2Cl_2 and $FeCl_3$, while the loss of Ni is mainly caused by the formation of NiO. Ni presents better stability in molten salts.

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