Corrosion Behavior of 45 Steel in Molten Nitrate Salts with 3wt% Impurities at 773.15K

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Abstract. In this paper, the corrosion behavior of 45 steel in molten HitecXL salt (1# salt) and HitecXL salt with 3wt%MgCl2 (2# salt) at 773.15K is studied by gravimetric methods. The cross section characteristics, the elements distribution features and corrosion products of the samples after corrosion are analyzed by SEM, XRD and EDS. The results show that the corrosion kinetics curves of 45 steel for 84 h in 1# and 2# salt all obey the linear law. The cross section morphology show that the corrosion layer depths of the samples are about 10μm and 25μm, respectively. Cl- react with O2 dissolved in the molten salts to form Cl2.then, Cl2 can react with Fe or the oxides of Fe to form FeCl3, which make 45 steel have bigger corrosion rate in 1# salt. The corrosion mechanisms of 45 steel in two kinds of salt are the loss of Fe.

1. Introduction

Nowadays, renewable energy and its practical application have been increasingly studied. The concentrated solar power(CSP) is one of the most interesting cleaning energy alternative. An important component of a thermal-energy storage (TES) system is the choice of heat transfer fluids (HTF) in the solar plant [1-2]. At present, high quality solar salts (60wt%NaNO3-40wt%KNO3) is used as storage medium in commercial facilities [3]. Fernández et al [1] pointed out that the HitecXL salt (48wt%Ca(NO3)2-45wt%KNO3-7wt%NaNO3) is less corrosive compared to the commonly used solar salt.

Current CSP plants installations are designed with huge TES systems with thousands of molten salts tons. So molten salt inventory cost is a very important item in the in the overall TES cost of a CSP plant, which is in the range of 23-48wt% of the total energy cost depending on installed storage capacity [4-5]. F. Javier Ruiz-Cabañas [3] pointed out that the use of salts with higher impurity levels would reduce the cost of molten salts inventory and the investment cost of the storage systems, but the impurities such as chlorides, sulfates, carbonates, and nitrates, would improve the corrosive effect of solar salts over metallic materials. It was reported that chlorides increase molten salts aggressiveness over carbons steels and low alloyed steels due to the formation of chlorine [6]. A.G. Fernández [7] pointed out that the presence of both oxygen and chlorine increases the corrosive capacity of these salts. Medrano et al. [8] noticed that the presence of magnesium impurities in solar salt (60wt%NaNO3-40wt%KNO3), which add complexity to the melting process in commercial salts.
The effect of Cl- and Mg2+ on the corrosion behavior of nitrate salts containment materials has been reported in few references, but the mechanism is still under debate. In this work, the corrosion behavior of 45 steel in the clean molten HitecXL and HitecXL with Cl- and Mg2+ is studied by gravimetric and metallographic methods. The mechanisms of corrosion are discussed.

2. Experiment

The nominal chemical composition of 45 steel which is purchased from Shanghai Special Alloy Co. LTD is as follows (wt.%): C 0.42~0.50, Si 0.17~0.37, Mn 0.50~0.80, Cr ≤0.25, Ni ≤0.30, Cu ≤0.25 and the rest is Fe. The alloy is cut into small samples with 15mm x 15mm 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 are measured by analytical balance and vernier caliper, respectively.

After that, analytical pure KNO3, NaNO3 and Ca(NO3)2 (1# salt: HitecXL salt) are mixed in eight crucibles and stored in 1# muffle furnace; analytical pure KNO3, NaNO3, Ca(NO3)2 and MgCl2 (2# salt: 97wt% HitecXL salt-3wt%MgCl2) are mixed in eight crucibles and stored in 2# muffle furnace. When the corrosion experiment started, the two muffle furnaces are heated to 773.15K with a rate of 5K/min. After the salt melting, three samples are put into every crucible in 1# and 2# muffle furnace, and the No.1 to No.6 crucibles are removed every 12 h, and then No.7 and No.8 crucibles are removed after being corroded for 84 h. When the samples are taken out of the muffle furnace, they are cooled to room temperature together with the molten salt to avoid oxidation. These samples are treated with the standard method described in ASTM G1-03[9]. All characterization methods have been described in detail [10]. The formulas for calculating the mass loss [7, 11]:

\[
\frac{\Delta m}{S_0} = \frac{m_i - m_f}{S_0}
\]

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 (cm²).

3. Results and discussion

3.1. Experimental results

The mass loss for 45 steel in 1# and 2# molten salts at 773.15K is shown in Fig.1. The corrosion kinetics curve of samples all obey the linear law.

![Figure 1. Corrosion kinetics curves of S45 in 1# and 2# molten salt at 773.15K](image-url)
The XRD patterns of corrosion products on the surface of samples in 1# and 2# molten salts after corrosion for 84 h are shown in Fig.2. It can be seen that Fe, Fe3O4 are detected on the surface of sample in 1# molten salt, and Fe3O4, Fe2O3, MgO and MgFe2O4 are detected on the surface of sample in 2# molten salt.

**Figure 2.** XRD patterns of corrosion products on the surface of samples in 1# and 2# molten salt

The surface morphologies of samples after being corroded for 84 h in 1# and 2# molten salt at 773.15K are shown in Fig.3 (a) and (b). It can be seen from Fig.3 (a) that there are a large amount of particles on the surface of the sample, and the substrate is slightly corroded. Combined with the results of Fig.2 and Table 1, Fe3O4 and Fe are covered on the sample surface. It is found from Fig.3 (b) that there are many holes on the surface of the sample, and 45 steel is seriously corroded in 2# salt. Combined with the results of Fig.2 and Table 1, the main components of the sample surface are Fe2O3, Fe3O4, MgO and MgFe2O4.

**Figure 3.** SEM images and EDS of the sample surface after corroded for 84 h. (a): sample in 1# salt; (b) sample in 2# salt

| Region | Fe  | O   | Ca  | Mg  | Mn  | Mo  | Si  | C    |
|--------|-----|-----|-----|-----|-----|-----|-----|------|
| 1      | 78.14 | 19.57 | 0.79 | 0.00 | 0.00 | 0.00 | 0.22 | 1.28 |
| 2      | 21.96 | 50.28 | 16.10 | 0.00 | 0.00 | 0.00 | 0.00 | 11.65|
| 3      | 67.25 | 24.86 | 0.98 | 0.00 | 0.00 | 3.30 | 0.24 | 2.93 |
| 4      | 51.91 | 26.07 | 0.60 | 18.72 | 0.25 | 0.00 | 0.00 | 2.45 |
| 5      | 2.07  | 43.16 | 5.47 | 40.90 | 0.00 | 0.00 | 0.00 | 8.40 |
| 6      | 14.17 | 46.84 | 22.06 | 6.00 | 0.00 | 0.00 | 0.00 | 10.93|

**Table 1.** Surface EDS analysis of 45 steel specimens after 84 h immersion (wt %).
After being cleaned with alcohol, SEM and EDS element distribution on cross section after corrosion for 84 h in molten is shown in Fig.4. According to Fig.4 (a), the thickness of corrosion layer is 10 μm. Near the substrate, the content of Fe decrease, while the content of Ca, O and K increase. According to Fig.4 (b), the thickness of corrosion layer is 25 μm. Near the substrate, the content of Fe decrease but has higher content in Oxide layer, while the content of Mg, Cl, O and Ca increase in corrosion layer.

![Figure 4. SEM image and EDS element distribution on cross section after corrosion for 84 h.](a): sample in 1# salt; (b) sample in 2# salt.)

3.2. Discussion

The aggressiveness of nitrate baths could be enhanced by the formation of peroxide and superoxide ions in the medium by the following chemistry [12–14]:

\[
\text{NO}_3^- + 2e^- \leftrightarrow \text{NO}_2^- + \text{O}^{2-}
\]  

(2)

In addition, the presence of O\textsubscript{2} will also accelerate the corrosion rate of alloys by the following chemistry.

\[
\text{O}_2 + 4e^- \leftrightarrow 2\text{O}^{2-}
\]  

(3)

3.2.1. Discussion on the Corrosion Mechanism of 45 steel immersed in 1# Salt. It is found from Fig. 2 that Fe\textsubscript{3}O\textsubscript{4} is detected on the surface of the sample immersed in the 1# salt because the following reactions (4-6) occur.

\[
\text{Fe} + \text{O}^{2-} - 2e^- \rightarrow \text{FeO}
\]  

(4)

\[
3\text{Fe} + 4\text{O}^{2-} - 2e^- \rightarrow \text{Fe}_3\text{O}_4
\]  

(5)

\[
2\text{Fe}_3\text{O}_4 + 9\text{O}^{2-} - 2e^- \rightarrow 3\text{Fe}_2\text{O}_3
\]  

(6)

According to the kinetics curve of the sample in Fig.1, the slope of the kinetic curve does not change, which indicate that the products on the sample are not protective. It is found from Fig.4 (a) that the corrosion mechanism of 45 steel in1# salt is the loss of Fe.

3.2.2. Discussion on Corrosion Mechanism of 45 Steel immersed in 2# Salt. When 45 steel is immersed in 2# salt, the (4-6) reactions will occur. In addition, Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, MgO and MgFe\textsubscript{2}O\textsubscript{4}
are detected on the surface of the substrate due to the presence of water vapor by the following chemistries [15].

\[
\text{MgCl}_2(s) + \text{H}_2\text{O}(g) \rightarrow \text{MgO}(s) + 2\text{HCl}(g)
\] (7)

\[
\text{MgO}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow \text{MgFe}_2\text{O}_4(s)
\] (8)

It has been reported that MgFe\textsubscript{2}O\textsubscript{4} covered uniformly on the surface of the sample can effectively relieve the corrosion rate of alloy in nitrate salt [2], but the corrosion rate of sample immersed in 2\# salt is the higher than the sample immersed in the 1\# salt. The main reasons are as follows.

It is reported that O\textsubscript{2} and H\textsubscript{2}O immersed in the molten salt can accelerate the corrosion rate of the alloys [15]. The reactions are as follows:

\[
4\text{Cl}^- + \text{O}_2(g) \rightarrow 2\text{O}^{2-} + 2\text{Cl}_2(g)
\] (9)

\[
\text{H}_2\text{O}(g) + 2\text{Cl}^- \rightarrow \text{O}^{2-} + 2\text{HCl}(g)
\] (10)

It was also reported that Cl\textsubscript{2} had the ability to permeate through pores and cracks, and react with the alloys [16].

\[
\text{Fe}(s) + 3\text{Cl}_2(g) \rightarrow \text{FeCl}_3(g)
\] (11)

\[
2\text{Fe}_3\text{O}_4(s) + 9\text{Cl}_2(g) \rightarrow 6\text{FeCl}_3(g) + 4\text{O}_2(g)
\] (12)

\[
2\text{Fe}_2\text{O}_3(s) + 6\text{Cl}_2(g) \rightarrow 4\text{FeCl}_3(g) + 3\text{O}_2(g)
\] (13)

In particular, the boiling point of FeCl\textsubscript{3} (g) is just 593.15K [17], so FeCl\textsubscript{3} is easy to escape from system to accelerate the corrosion rate of 45 steel. When MgFe\textsubscript{2}O\textsubscript{4} is not uniformly covered on the sample surface, and Cl\textsubscript{2} can react with the substrate to cause mass loss. In addition, Cl\textsubscript{2} can react with iron oxides to produce volatile FeCl\textsubscript{3} to accelerate the corrosion rate of sample. The reaction of Cl\textsubscript{2} with the Fe or iron oxides make oxides peel off from matrix, which accelerates the corrosion rate of 45 steel.

4. Conclusion

(1) The kinetics curves of 45 steel in two kinds of salt for 84 h all obey linear law.
(2) The corrosion mechanisms of 45 steel in two kinds of salt are mainly the loss of Fe.
(3) The corrosion rate of 45 steel immersed in 2\# salt is higher than that immersed in the 2\# salt. Cl\textsuperscript{-} react with O\textsubscript{2} dissolved in molten salt to form the Cl\textsubscript{2}, which can react with Fe or iron oxides to form FeCl\textsubscript{3} to accelerate the corrosion rate of 45 steel in molten salt.
(4) 45 steel cannot be used as structural materials in HitecXL salts with 3wt% MgCl\textsubscript{2}.

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