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ARTICLE

Corrosion Behavior and Mechanism of Fe-14Cr-Mn Alloy in Molten Eutectic NaCl-$MgCl_2$ at Different Temperatures

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Abstract: Operating temperature waves around the melting temperature of molten eutectic NaCl-$MgCl_2$ which is thermal storage media at medium-high temperature. But the corrosion behavior of the molten salt on metal at different temperatures is not clear. In the present paper, the corrosion behavior and mechanism of the molten salt on Fe-14Cr-Mn alloy were studied by an immersion salt corrosion method at 718, 768 and 818 K. Results show that corrosion rate increases lightly with the increase of corrosion temperature. Corrosion kinetics characteristics obey the linear law (slope $k \approx -4.806\times10^{-4}$). At the early stage of corrosion, there are lots of vacuoles, while a large number of pit holes are formed after corroding for 80 h. Corrosion products are mainly Fe, Fe-Cr and MgO. Corrosion mechanism is as follows: absorbed oxygen on molten salt surface and oxygen atom that is introduced in the form of moisture-absorbed $MgCl_2$ are as depolarizing agents. Chlorides of Cr and Mn are got when oxide of Cr and Mn react with Cl^-. The chlorides of Cr and Mn with water, e.g. $CrCl_3\cdot 6(H_2O)$ and $MnCl_2\cdot n(H_2O)$ that have low melting point would escape from corrosion system. In addition, there is a salt crust that is composed of $MgCl_2\cdot(H_2O)_6$, NaCl and MgO on molten salt upper surface, while NaCl coexists with $NaMgCl_3$ inside mixture salt.

Key words: molten salt; corrosion; steel; chlorination; thermal storage

Molten salt phase change thermal storage is one of the principal means in solving the solar energy intermittence of solar energy photo-thermal utilization field. Molten chlorate is the most appropriate thermal storage media for its stable physicochemical property, low cost and so on. Molten chlorate has also been selected as cooling medium of next generation nuclear plant by the Oak ridge national laboratory[1-3]. Physicochemical properties have been compared in more than 50 kinds of mixed chlorate used as thermal storage media. It is found that eutectic NaCl-$MgCl_2$ has good application prospect in drying food and pasture field, solar thermal power plant field and so on, for its higher latent heat per unit mass (430 J/g) and suitable melting point (445 ℃)[4]. However, molten NaCl-$MgCl_2$ has strong corrosive action on metals, and it requires material with good thermal shock resistance since the temperature fluctuates near the salt melting point in work state[5-7]. Therefore, the study about the effect of temperature on corrosion behavior of metals in molten eutectic NaCl-$MgCl_2$ is significant to practical applications.

There are a lot of studies about metal corrosion behavior in molten chlorate salt. Mohanty et al[8] added NaCl to molten Na_2SO_4. The average mass loss rate of Fe-25.5wt%Cr-13.0wt%Ni alloy after corrosion in the mixed molten salt is 100 times larger than that in Na_2SO_4. The effect of NaCl added to molten sulfate at 850 ℃ on $Cr1_3Ni_5Si_2$ corrosion behavior was studied by Yuan et al[9]. The hot corrosion behavior of NiCoCrAlYSiB

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coating in molten Na_2SO_4-K_2SO_4 and Na_2SO_4-NaCl at 900 ℃ was studied by Lu et al[10]. The above results proved that NaCl accelerates hot corrosion process. What's more, average mass loss rate increases with the increase of Cr content in alloy. And the kinetics curves obey the linear law. Major reasons are as follows: Cr_2O_3 film is destroyed not only for volatile $CrCl_3$ formed by Cr and Cl^- in molten chlorate, but also its higher solubility than other oxides (for example Fe_3O_4, NiO) at the same oxygen partial pressure in molten chlorate[11-14]. The corrosion behavior of Ti-48Al-8Cr-2Ag coating which was produced by magnetron-sputter deposition in 900 ℃ molten Na_2SO_4-NaCl was studied by Xi et al[15]. Results showed that lots of nano crystal grain boundaries as diffusion channels of Al which decreased corrosion rate decreased for thick Al_2O_3 film were formed on the sample surfaces[15]. Corrosion behaviors of pure iron, pure chromium and Fe-Cr materials with aluminum/silicon addition were investigated at 650 ℃ in air accompanied with gaseous or solid KCl salt[16]. It was found that alloy elements Al and Si contributed to the formation of Al-Cr oxidation film at the initial stage. A protective inner layer of silica on the matrix surface formed to suppress the rapid growth of iron oxide. However, K_2CrO_4 was got by the reaction of KCl and $Cr_{23}C_6$ with oxygen joining in, which accelerated corrosion reaction[16]. Corrosion studies were performed on uncoated high density graphite and plasma sprayed partially stabilized zirconium (PSZ) coated graphite, which was high density graphite with NiCrAlY bond coat in molten LiCl–KCl eutectic salt at 600 ℃ for periods of 250, 1000 and 2000 h under inert argon atmosphere by Sure et al[17]. Graphite was corroded because atoms of molten salt replaced graphite atoms on its surface. The corrosion resistance of high density graphite with PSZ coating increased obviously. However, the coating chipped and peel off from matrix, which was due to the differences of thermal expansion between the coating and matrix[17]. The above studies indicated that molten chlorate salt had serious corrosion effects on metal and nonmetal. However, the effects of corrosion temperature on metal corrosion behavior in molten chlorate salt are seldom studied. Consequently, the present paper took eutectic NaCl-$MgCl_2$ (46.4~53.6 wt%) as corrosion media, which is solar energy thermal storage media at medium-high temperature and analyzed the effects of corrosion temperature on Fe based alloy corrosion behavior by an immersion salt corrosion method. The corrosion mechanism was also discussed.

1 Experiment

The measured composition of the Fe-Cr-Mn board which was bought from Lanzhou Zhuxin Stainless Steel Co. LTD is as follows (wt%): Cr 14.41, Mn 10.93, Ni 0.858, and the rest is Fe. The board was cut into 10 mm×10 mm×3 mm samples by an electrical spark line cutting machine in triplicate, and the samples were ground with silicon carbide paper of 600 grit, 1200 grit, and 2000 grit in sequence, then polished with 1 μm diamond powder, ultrasonic cleaned in acetone, and finally dried. Afterwards, the surface area and the mass of each sample was measured. Analytically pure NaCl and $MgCl_2$ were mixed together in definite proportion after NaCl was dried. Then the mixed salt was stored in three corundum crucibles. The three crucibles were heated in three muffle furnaces at temperature of 718, 768 and 818 K, respectively. After the mixed salt melting, three parallel samples were put into one crucible. After being corroded for 10 h, these samples were taken out from muffle furnaces and air-cooled. NaCl in the three crucibles were collected, and then composition was analyzed by XRD. According to GB/T 16545-1996, these samples were cleaned for 30 min by ultrasonic wave in deionizer water and alcohol, separately. After being dried, these samples were weighed by electronic balance (0.1 mg) and measured with vernier caliper. Then, the average mass loss rate and the corrosion kinetics curves were made. Finally, the above processes were repeated, and the second corrosion experiment started. The sample used for surface topography observation were not cleaned by ultrasonic wave.

The above experiment processes were repeated 8 times (total corrosion time was 80 h), and the last corrosion experiment did not need cleaning process. Average mass change rate and corrosion kinetics curves were calculated and drawn based on the first seven circulation experiment results. The sample surface was cleaned with a wood draw knife before X-ray diffraction (XRD) analysis. Then the composition of corrosion products was detected. At last, sample cross section was polished by SiC sand paper and cloth successively without water and other polishers. The morphology of corrosion layer were observed by SEM and the cross section element distribution was analyzed by energy dispersive spectrometer (EDS).

2 Results and Discussion

2.1 Average mass loss rate and corrosion kinetics characteristic

Average mass change rate at different temperatures after corroding for the first 70 h in molten NaCl-$MgCl_2$ is shown in Fig.1a. It indicates that the mass of all samples at different temperatures decreases. The mass loss rate per 10 h $V \approx 0.0048$, 0.0048 and 0.0054 mg/mm^2 at T=718, 768 and 818 K. The mass loss rate per 10 h V=0.0054 mg/mm^2 at T=818 K, which increases by 12.5% compared with that at 718 K (0.0048 mg/mm^2). However, the values of mass loss rate (V) per 10 h are the same at 718 and 768

K; it's probably because the values of mass loss rate are similar at the similar temperature. What's more, date errors are inevitable during experiments. Consequently, mass loss rate increases slightly with corrosion temperature increasing.

Fig.1b is corrosion kinetic curves of samples at different temperatures. It is found that average mass of all samples decreases at the three temperatures. The value of slope is similar which is about -4.806×10^{-6}. The results agree with conclusion of average mass change rate got from Fig.1a.

2.2 Morphology of sample surface and cross section

Fig.2 is SEM images of surface morphology for the samples corroded in molten NaCl-$MgCl_2$ at 818 K for 10 and 80 h. After corrosion for 10 h, there are lots of vacuoles, while a large number of pit holes are formed after being corroded for 80 h.

After being polished without water and other polisher, the SEM images and EDS element distribution of the cross section of the samples are shown in Fig.3. Fig.3a, 3b and 3c show cross section morphologies of samples corroded for 80 h at 718, 768 and 818 K, respectively. It is found that porous corrosion layer forms on the sample surface. The thickness of corrosion layer is about 20 μm. The contents of Na, Mg and Cl increase obviously on the cross section near sample surface, which are possibly NaCl, $MgCl_2$ and $NaMgCl_3$ based on XRD results in Fig.4. Particularly in corrosion cavitations, Na, Mg and Cl increase very obviously. It is indicated that molten salt penetrates into corrosion layer during the corrosion process. The contents of Cr and Mn decrease obviously while Ni isn't on the cross section near sample surface.

2.3 Corrosion products and residual salt

XRD patterns of corrosion products on samples surface at the three temperatures are shown in Fig.4. It is found that there are mainly NaCl, Fe, Fe-Cr and MgO on sample surface. MgO/FeO which contains 91% MgO forms after part of Mg atoms are replaced by Fe atoms. Similarly, $(Mg_{0.4}Ni_{0.6})O$ forms when 60% of Mg atoms are replaced by Ni atoms. Fig.5 is XRD patterns of residual salt after corrosion which mainly contains Na_2MgCl_4, $NaMgCl_3$, NaCl and trace amounts of Na_2MnCl_4.

2.4 Other results

There is a salt crust on the top of crucible after mixed salt of NaCl-$MgCl_2$ melting. The morphology of the broken salt crust cooled to room temperature is shown in Fig.6. XRD pattern of the salt crust is shown in Fig.7, which mainly contains MgO, NaCl and a little $MgCl_2\,(H_2O)_6$.

2.5 Discussion

All the samples are corroded badly in the similar degree in

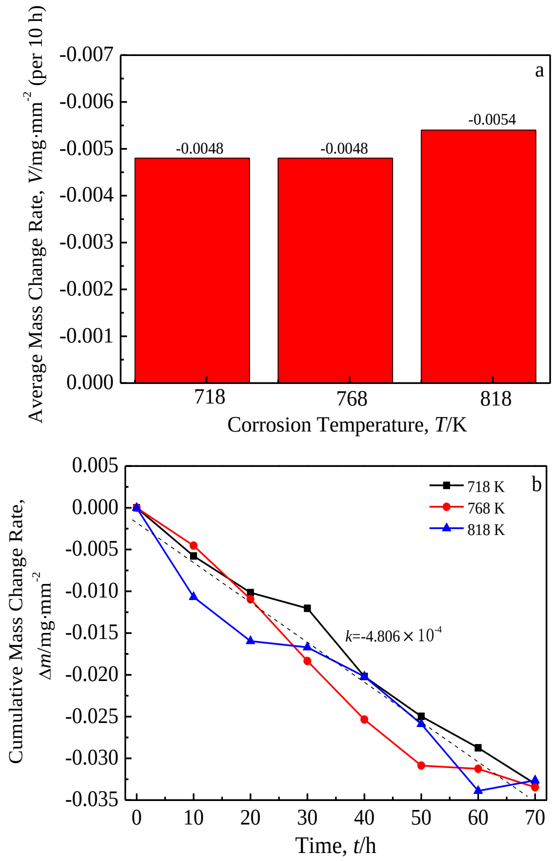

Fig.1 Average mass change rate (a) and corrosion kinetics curves (b) of samples at 718, 768 and 818 K

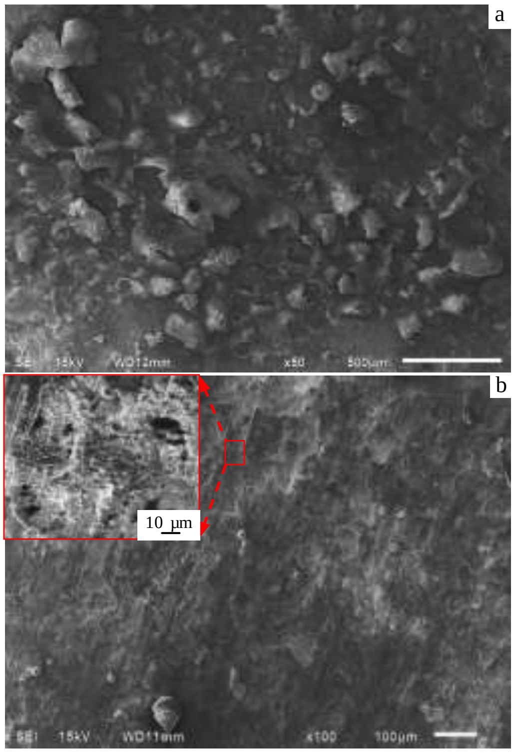

Fig.2 SEM images of sample surface after being corroded for different time at 818 K: (a) 10 h and (b) 80 h

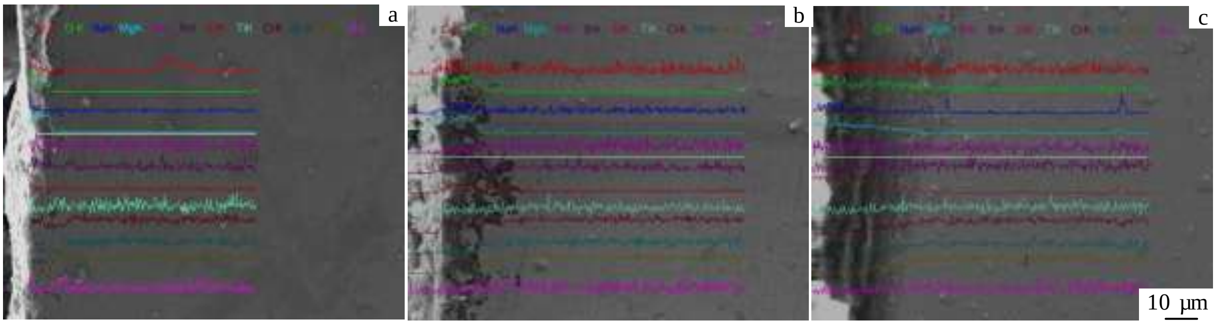

Fig.3 SEM images and EDS elements distribution on cross section after corrosion for 80 h at different temperatures: (a) 718 K, (b) 768 K, and (c) 818 K

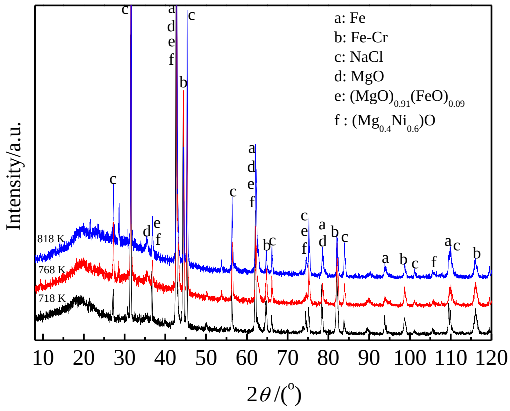

Fig.4 XRD patterns of corrosion products on sample surface at three temperatures

Fig.6 Morphology of the broken salt crust

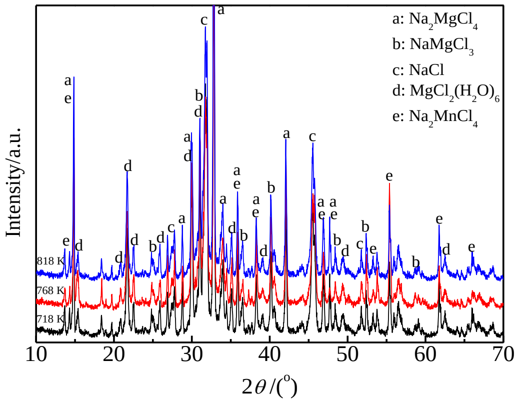

Fig.5 XRD patterns of residual salt after corrosion

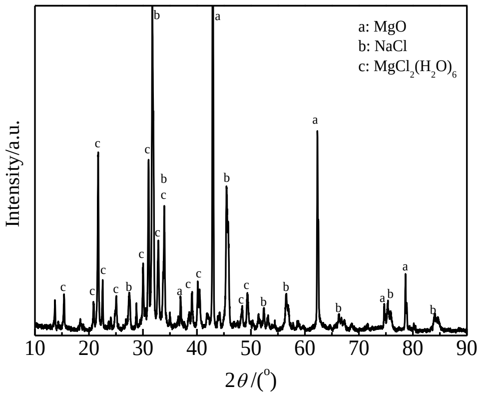

Fig.7 XRD pattern of the salt crust

molten sodium chloride-magnesium chloride ($NaCl-MgCl_2$) at 718, 768 and 818 K. Corrosion kinetics characteristics obey the linear law, which indicates that there is no protective film formed on sample surface. The conclusions can be proved by the SEM images that are shown in Fig.2 and Fig.3. Bubbles form on sample surface at the initial corrosion stage. However, the bubbles break and peel off badly. As corrosion goes on, lots of corrosion holes form on sample surface, making structure near sample surface loose.

The contents of chromium (Cr) and manganese (Mn) on loose corrosion layer decrease obviously. From XRD results of Fig.5, it is found that sodium manganese chloride (Na_2MnCl_4) forms when sodion (Na^+) and chloridion (Cl^-) unite with alloy element manganese (Mn) in molten sodium chloride-magnesium chloride (NaCl-$MgCl_2$). However, the compound of chromium (Cr) is not found clearly, for which molten sodium chloride-magnesium chloride (NaCl-$MgCl_2$) is strong electrolyte. There are a lot of micro-batteries of electrochemical non-uniformity on alloy surface. Consequently, electrochemical corrosion process must be excited[18]. Anodic reaction will occur when n elements are lost from alloy element M:

$$M \rightarrow M^{n+} + ne^- \quad (1)$$

During the corrosion process, the crucible containing molten salt was put in high temperature air. Although the solubility of oxygen in air is very low in molten salt, upper surface of molten sodium chloride-magnesium chloride (NaCl-$MgCl_2$) contacts with high temperature air. When oxygen molecules collide with molten salt surface, they will be absorbed in molten salt surface. Then the oxygen molecules break up into adsorbed oxygen[19]:

$$O_2 \rightarrow 2O \quad (2)$$

When adsorbed oxygen diffuses to alloy surface in molten salt, it will capture two elements, and change into chemisorptions oxygen:

$$O + 2e^- \rightarrow O^{2-} \quad (3)$$

It can't be excluded that oxygen ion is introduced in the form of water (H_2O) when magnesium chloride ($MgCl_2$) absorbs moisture as following description. Corrosion micro-cell forms when reaction (1) and (3) play the role of anodic reaction and cathodes reaction, respectively. After getting oxygen ion (O^{2-}), the following reaction takes place:

$$2M^{n+} + nO^{2-} \rightarrow M_2O_n \quad (4)$$

Fig.4 shows that magnesium oxide (MgO) exists on sample surface for it is steady in molten sodium chloride-magnesium chloride (NaCl-$MgCl_2$). While for M_2O_n is unstable in molten sodium chloride-magnesium chloride (NaCl-$MgCl_2$), it will react with chlorine (Cl_2) as follows. Volatile MCl_n forms and escapes from corrosion system[8]:

$$2M_2O_n + 2nCl_2 \rightarrow 4MCl_n(g) + nO_2(g) \quad (5)$$

Chlorine (Cl_2) is a reaction product of hydrogen chloride (HCl) and oxygen (O_2). The hydrogen chloride (HCl) is a decomposition product of magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) after heating. As described in the previous section, a certain amount of magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) and a part of magnesium oxide (MgO) are found in residual salt at the three temperatures after corroding, for magnesium chloride ($MgCl_2$) is extremely hygroscopic. Moisture absorption takes place not only during the process of preparing mixed salt, but also during sodium chloride-magnesium chloride (NaCl-$MgCl_2$) melting, and then magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) forms. Once magnesium chloride ($MgCl_2$) absorbs moisture, it can't be regained by simple heating as the experiment in this paper. When heating temperature is higher than 671 K, magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) breaks down into magnesium oxide (MgO), hydrogen chloride (HCl) and water (H_2O):

$$MgCl_2 \cdot 6H_2O \rightarrow MgO + 2HCl(g) + 5H_2O \quad (6)$$

The Gibbs free energies of the chemical reaction (6) are –27.095, –55.128 and –84.029 kJ at 718, 768 and 818 K, respectively. Therefore, there are magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) that have not been broken down and magnesium oxide (MgO) as described in corrosion residual salt above. And salt crust which mainly contains magnesium oxide (MgO) and magnesium chloride with water ($MgCl_2 \cdot (H_2O)_6$) forms on the upper surface of melting salt. That is shown in Fig.6 and Fig.7.

Chemical reaction takes place between hydrogen chloride (HCl) and oxygen (O_2) dissolved in molten salt:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O \quad (7)$$

Chlorine (Cl_2) may react with metal directly, and react outside with M_2O_n as the chemical reaction (5):

$$2M + nCl_2(g) \rightarrow 2MCl_n \quad (8)$$

Firstly, it is found from the relationship graph of temperature and standard free energy formation (T-ΔG_0) that standard free energy formation (ΔG_0) of oxide of chromium (Cr) and manganese (Mn) is more negative than oxide of iron (Fe) and nickel (Ni). Consequently, the chromic oxide (Cr_2O_3) and manganese oxide (MnO) are more easily formed than oxide of iron (Fe) and nickel (Ni)[19]. Secondly, chromic oxide (Cr_2O_3) dissolves in molten chloride salt more easily than oxide of iron (Fe) and nickel (Ni). Therefore, chromic oxide (Cr_2O_3) will be dissolved preferentially, which destroys oxide layer[13]. Thirdly, in reference to the standard electrode potential value, the value of chromium (Cr) (–0.913 V) is smaller than that of iron (Fe) (–0.44 V) as well as nickel (Ni) (–0.25 V). In reaction (1), chromium (Cr) and manganese (Mn) will replace M and be corroded preferentially. Then reactions (5) and (8) take place successively. Chloride with water forms after the reaction products of chromic chloride ($CrCl_3$) and $MnCl_2$ absorb moisture. The chloride which has a low boiling point will escape from the corrosion system. Consequently, the chromium (Cr) impoverishment is found in all samples after being corroded at the three temperatures, which is shown in Fig.3. A sketch of above corrosion mechanism is shown as Fig.8.

It is found from Fig.4 that there are lots of iron (Fe) and iron-chromium (Fe-Cr) without the oxide of iron (Fe) and chromium (Cr) on the sample surface. Except for dissolving of the oxide of chromium (Cr) and manganese (Mn) in

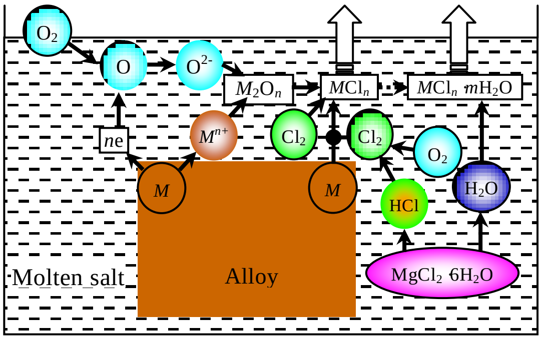

Fig.8 Sketch of corrosion mechanism

molten chloride salt and the reaction of (5) and (8), the partial pressure of oxygen is low in the molten salt. Only a few magnesium (Mg) atoms are replaced by iron (Fe) and nickel (Ni). Mixture of magnesium oxide/ferrous oxide (MgO/FeO) which contains 91% magnesium oxide (MgO) forms, and nickel-magnesium oxide ($(Mg_{0.4}Ni_{0.6})O$) in which 60% magnesium (Mg) atoms are replaced by Ni forms too.

Magnesium chloride with water ($MgCl_2\cdot(H_2O)_6$), magnesium oxide (MgO) and hydrogen chloride (HCl) form after magnesium chloride ($MgCl_2$) absorbing moisture and being heated, which decreases the content of magnesium chloride ($MgCl_2$) in eutectic sodium chloride-magnesium chloride (NaCl-$MgCl_2$). The mixed salt composition point will move to the left in phase-stability diagram of sodium chloride-magnesium chloride (NaCl-$MgCl_2$) (Fig.9)[20]. After the composition point moving to the left of 'A', sodium chloride (NaCl) will be found in solid mixed salt. Thus, sodium chloride (NaCl) is found in residual salt and salt crust.

Because the contact area between the mixed salt upper surface and air is large, and huge areas of magnesium chloride ($MgCl_2$) have absorbed moisture before sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) melting (temperature higher than 718 K) in the form of eutectic, there are only sodium chloride (NaCl), magnesium oxide (MgO) and magnesium chloride with water ($MgCl_2\cdot(H_2O)_6$) decomposition in salt crust. However, before temperature rises to 718 K, a part of magnesium chloride ($MgCl_2$) absorbs moisture inside mixed salt while mixed salt that has not absorbed moisture will melt in the form of eutectic. The phenomenon that sodium chloride (NaCl) coexists with sodium magnesium chloride ($NaMgCl_3$) is found in corrosion residual salt.

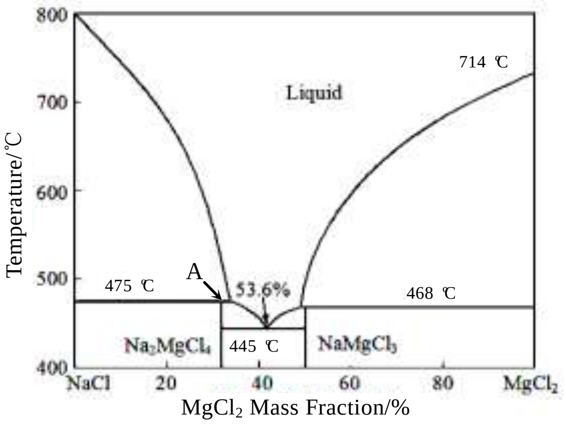

Fig.9 Phase-stability diagram of NaCl-$MgCl_2$[20]

3 Conclusions

1) Corrosion rate of Fe-14Cr-Mn in molten eutectic NaCl-$MgCl_2$ increases slightly with the increase of corrosion temperature. Mass loss rate per 10 h is –0.0048 ~ –0.0054 mg/mm^2 at between 718 and 818 K. The kinetics curves of them obey the linear law.

2) Corrosion mechanism is electrochemical corrosion. Alloy elements are anode. Oxygen atoms participate in cathodic reaction in molten salt. The oxygen atoms come from air and water (H_2O) which are absorbed by magnesium chloride ($MgCl_2$). Metal oxide forms firstly. Afterwards, volatile metal chloride forms with the action of chlorine (Cl_2), and then escapes from the corrosion system. Chromium (Cr) and manganese (Mn) are the main causes of the corrosion.

3) Oxygen partial pressure is relatively low in the molten salt. It can't form lots of metal oxides which contain alloy elements of iron (Fe) and chromium (Cr).

4) The composition point of the mixture salt shifts to left after magnesium chloride ($MgCl_2$) absorb moisture. Magnesium chloride with water ($MgCl_2\cdot(H_2O)_6$), sodium chloride (NaCl) and magnesium oxide (MgO) form on the upper surface of molten salt. However, inside mixture salt which has not absorbed moisture would melt when the temperature rises to melting point. The phenomenon of sodium chloride (NaCl) coexisting with sodium magnesium chloride ($NaMgCl_3$) is found in corrosion residual salt.

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Fe-14Cr-Mn合金在不同温度熔融共晶NaCl-$MgCl_2$中腐蚀行为及机理研究

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摘　要：熔融共晶NaCl-$MgCl_2$作为太阳能中高温相变储热介质，运行状态下其温度常在熔点附近波动。但不同温度下该熔融盐对金属容器材料腐蚀行为不清楚。以Fe-14Cr-Mn合金为例，采用浸盐法研究了718、768和818 K共晶熔融NaCl-$MgCl_2$对该合金的腐蚀行为，探讨了腐蚀机理。结果表明：腐蚀速率随温度增加略微增加，3种温度下试样腐蚀动力学曲线服从线性规律（斜率$k\approx-4.806\times10^{-4}$）。腐蚀初期，试样表面形成泡状腐蚀产物，腐蚀80 h后形成腐蚀坑洞，主要是Fe、Fe-Cr和MgO，也检测到含微量Fe和Ni的Mg-Fe-Ni的氧化物。腐蚀机理主要是$MgCl_2$吸潮后以H_2O形式引入的氧原子和溶解在熔融盐中的微量氧作为阴极去极化剂，合金元素Cr和Mn与Cl^-反应生成氯化物，氯化物吸附水分子，形成具有低熔点的含水氯化物（如$CrCl_3$ 6(H_2O) 和$MnCl_2$ n(H_2O)）逃逸腐蚀体系。另外，在熔盐表面形成了由$MgCl_2$ (H_2O)$_6$，NaCl和MgO组成的盐壳，而在熔融盐内部，NaCl与$NaMgCl_3$共存。本研究为研发耐熔融NaCl-$MgCl_2$腐蚀的新合金奠定了基础。

关键词：熔融盐；腐蚀；钢；氯化；储热

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