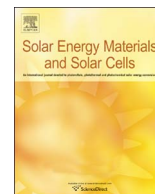




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# Influence of $\text{MgCl}_2$ content on corrosion behavior of GH1140 in molten $\text{NaCl-MgCl}_2$ as thermal storage medium

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## ABSTRACT

As a thermal energy storage medium (TESM) at moderate-high temperature of concentrating solar power (CSP), the molten  $\text{NaCl-MgCl}_2$  has sharp corrosive action on a metal container. The influence of  $\text{MgCl}_2$  content on a metal corrosion behavior is not clear. The corrosion behavior of a Fe based alloy (GH1140) in molten  $\text{NaCl-MgCl}_2$  (at 1123 K) with different content of  $\text{MgCl}_2$  (wt% : 0.0 , 48.9 , 61.0 , 93.6) were studied by the submergence corrosion experience. Results show that: after corrosion for 5 h, there is a negative correlation between the weight loss of samples and the content of  $\text{MgCl}_2$ . In the molten salt without  $\text{MgCl}_2$ , the sample was corroded according to the mechanism of “dissolution as anode- oxidizing- peeling off of oxide film”. After adding a little  $\text{MgCl}_2$  in the molten salt, an unprotected  $\text{MgO}$  shell was formed on the sample surface. The samples weight decreased and obeyed a line law. The elements of Fe and Cr deplete in the corrosion layer. Corrosion mechanism is “dissolution as anode- oxidizing- reduction- chlorination”. When the content of  $\text{MgCl}_2$  is very high in the molten salt, partial pressure of  $\text{Cl}_2$  increases. The corrosion mechanism is similar to what in the molten salt with a little  $\text{MgCl}_2$ , but the chlorination reaction is more severe.

## 1. Introduction

As a thermal energy storage medium (TESM), molten chloride not only has advantages of stable performance, large latent heat of fusion, but also has relative high molten point, which can meet the requirement of solar energy storage by phase change at moderate-high temperature [1]. Because of the above advantages, the molten chloride and fluoride salt have been chosen as two kinds of candidate materials of cooling medium in nuclear reactor by Oak Ridge National Laboratory [2,3]. Compared with other kinds of chloride, the molten eutectic  $\text{NaCl-MgCl}_2$  ( $\text{MgCl}_2$ : 52 wt%) not only has the advantages of other chloride, but also has larger latent heat (430 kJ/kg) [4]. But the molten chloride has sharp corrosive action on a metal container [5–7]. In addition, when under construction in air, moisture will be introduced by a container wall and the  $\text{MgCl}_2$  which is highly hygroscopic. Then an  $\text{MgCl}_2 \cdot (\text{H}_2\text{O})_6$  is formed. After heating, the  $\text{MgCl}_2 \cdot (\text{H}_2\text{O})_6$  is decomposed into HCl and  $\text{MgO}$ , not  $\text{MgCl}_2$ . Consequently, the content of  $\text{MgCl}_2$  may be changed in the mixture molten salt. In addition, the effect of  $\text{MgCl}_2 \cdot (\text{H}_2\text{O})_6$  on the corrosion behavior of a metal can't be excluded, too.

The corrosion behavior about a molten salt on alloys of Fe based [8], Ni based [9] and Co based [10] have been studied by many

scholars. But the research contents were mainly about the oxysalt film of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaCl}$ ,  $\text{Na}_2\text{VO}_3$  and  $\text{NaCl}$ , and so on. The corrosion mechanism is mainly the alkaline dissolution, except for the sulfide in salt with  $\text{Na}_2\text{SO}_4$ . The oxide film ( $\text{MO}$ ,  $\text{M} = \text{Fe}, \text{Cr}, \text{Ni} \dots$ ) on a sample surface is dissolute by the  $\text{Na}_2\text{O}$  which is broken down products of the oxysalt at high temperature. Then the  $\text{MO}^{2-}$  or  $\text{MCl}$  forms and transfers to the gas/salt interface where with high oxygen partial pressure and are oxidized to a porous oxide [10]. In addition, a  $\text{Cl}_2$  forms after the  $\text{MCl}$  is oxidized. The  $\text{Cl}_2$  will through the oxide film and reacts with the metal sample. A  $\text{MCl}$  forms again. The above process is repeated. That is called activation- oxidation mechanism or oxidation- chlorination mechanism [8,11,12]. C. C. Tsaur et. al. considered that a  $\text{NaCl}$  is primary cause of corrosion. Consequently, corrosion behavior of molten chloride film, which without oxysalt, on the metal of pure Cr, Fe-Cr were studied. A metal oxide film reacts with molten  $\text{NaCl}$  or  $\text{KCl}$ . Then the protective oxide film is destroyed.  $\text{Cl}_2$  and a film of  $\text{Na}_2\text{CrO}_4$  or  $\text{K}_2\text{CrO}_4$  form. The  $\text{Cl}_2$  through the oxide film and reacts with the metal sample as said above. A liquid material with low melting point forms when the chromate of alkali metal reacts with  $\text{NaCl}$ . The liquid material through the oxide film by capillary action and promote corrosion process [11,13–15]. The above researches aimed at

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the hot corrosion about a oxysalt or chloride film. There is enough oxygen which is decomposition products of oxysalt, or dissolved from air. But the corrosion medium of this paper is molten NaCl-MgCl<sub>2</sub>. Oxysalt is void in the mixture salt. In order to simulate working condition of the TESM and construction, A metal sample was submerged in the molten salt completely in air. Although moisture and impurity oxygen in the molten salt can't be excluded, but compare with the oxysalt or molten salt film, the oxygen partial pressure level is low. So, compare with other researches, the corrosion environment is different in this paper. Next, the content of an alkali metal chloride has strong influence on the corrosion resistance of metal in the molten salt [7]. GH1140 is a super-alloy of Fe-Ni-Cr based, which is strengthened by the elements of Mo and W. The alloy is usually used to a combustor or the parts of it in a gas turbine engine [16]. Consequently, based on the work conditions of NaCl-MgCl<sub>2</sub> as TESM, the influence of MgCl<sub>2</sub> content on GH1140 in the molten NaCl-MgCl<sub>2</sub> were studied. The corrosion mechanisms were discussed, too.

## 2. Experiment

Based on electrolytic pure (purity > 99.9%) metal of Fe, Ni, Cr, Mo, W, Al and Ti, GH1140 casting was made in a vacuum mid-frequency induction furnace (Type: SP-25TC). Nominal composition as follows (wt %): Ni: 37.5%, Cr: 21.5%, Mo: 2.25%, W: 1.6%, Al: 0.4%, Ti: 0.9, Fe: Bal. [16]. The samples were cut into a cube with the dimension of 10 mm × 10 mm × 3 mm by a electrical spark linear incising machine tool under water cooling condition. Those cube samples were heated to 1873 K (heating rate 5 K/min) and heat preservation for 10 min, then cooled to room temperature in a furnace. There is carbide (M<sub>x</sub>C) along a grain boundary on substrate of austenite (γ phase). The micro-structure image is shown in Fig. 1, which was filmed by an scanning electron microscopes (SEM, ZEISS MERLIN Compact) with the parts of energy-dispersive spectrometer (EDS). M<sub>x</sub>C are mainly TiC and a certain amount of W<sub>2</sub>C or Mo<sub>2</sub>C. All samples were polished with 600#, 1200# and 2500# metallographic sandpaper successively. Then cleared and dried.

The mixtures NaCl-MgCl<sub>2</sub> were made by anhydrous NaCl and MgCl<sub>2</sub>. Before mixing, NaCl (Purity ≥ 99.5 wt%. Registered trademark: “Shuangshuang”, provider: Shuangshuang Co., Ltd. in Yantai city) was dried in a drying oven (DHG-9140A, Shanghai Jinghong Laboratorial Apparatus Co., Ltd.) at 393 K for 48 h. The purity of the anhydrous MgCl<sub>2</sub> (Aladdin, provider: Sinopharm Chemical Reagent Beijing Co., Ltd.) is greater than 99 wt%. The mixture salts in four corundum crucibles were mixed in a glove-box. The four mixture salts with MgCl<sub>2</sub> mass fraction is 0.0% (1#), 48.9% (2#), 61.0% (3#) and 93.6% (4#), respectively. Then the four corundum crucibles were put in a muffle furnace and heated in air. In order to weaken absorption moisture by

the mixture salt during fusion process, the muffle furnace had been heated to 1123 K with heating rate was 5 K/min before the mixture salt were put in it. Details about the muffle furnace: type: SX2-8-13, Supplier: Xinxin Instruments Equipment Co., Ltd. After the mixture salt melted, every corundum crucible was put in four samples. And assuring all samples were below the molten salt upper surface. Photographs of the setup, sample and molten NaCl-MgCl<sub>2</sub> were shown in Fig. 2(a) and (b). Before those samples were put in the molten salt, all samples were measured surface area by a vernier caliper with accuracy 0.02 mm (Hengliang-530-150, Supplier: Shanghai Hengliang measuring tool Co., Ltd.) and weighted by a electronic analytical balance with accuracy 0.1 mg (SOPTOP-FA2004, Shanghai Sunny Hengping Scientific Instrument Co., Ltd.).

After corrosion for 5 h, the four corundum crucibles were taken out from the muffle furnace. When cooling to room temperature, the sample which were used to corrosion test continuously later were ultrasonic cleared in distilled water and ethanol at same conditions (for example, cleaning time in distilled water and ethanol, temperature, ultrasonic intensity and so on). Then dried by cool air and weighted by electronic analytical balance (SOPTOP-FA2004). After that, the samples were put in fresh melted salt again. The second corrosion test begins. The above processes were repeated seven times. After the last corrosion test, those samples didn't ultrasonic cleared in a distilled water and ethanol. Different handing methods were used for different detection needs. Those samples which were used to observe surface topography by a scanning electron microscope (SEM, ZEISS MERLIN Compact and JSM-6610LV) were prepared by the submerged-water method. In detail about the submerged-water method, the sample with residual salt on surface was submerged in distilled water quietly at room temperature. After the residual salt dissolved thoroughly, they were moved in alcohol carefully and immersed for one minute, then take out from the alcohol and dried with cold air. The sample which was used to analyze cross section topography was avoided ultrasonic cleaning, but made by the dry grinding method. The dry grinding method is that the sample cross section was polished without water-based polishing agent to avoid the loss of water-soluble corrosion products. Surface morphology and the distribution of elements on cross section were analyzed by SEM with parts of energy-dispersive spectrometer (EDS). The residual salt and corrosion products on sample surface were detected by Rigaku D/max-2500/PC X-ray diffractometer (XRD) with a Cu K $\alpha$  radiation source ( $\lambda=0.1541$  nm). Tube voltage and current was 40 kV and 200 mA, respectively.

### 2.1. Experiments results

After corroded for the first 5 h in the molten salt of 1#, 2#, 3# and 4# and then prepared by the submerged-water method (without ultrasonic cleaning), the sample surface topography and EDS results are shown in Fig. 3(a), (b), (c) and (d), respectively. As shown in Fig. 3(a), there is a cracked shell which is mainly O, Cr, and a little Fe on sample surface after corroded in 1# salt. The shell is mainly Cr<sub>2</sub>O<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub> after detected by XRD. But there is a poor adhesion power between the shell and the sample matrix. So, an experimenter needs to be very careful when preparing the corroded samples. Intergranular corrosion is found on metal surface where under the shell. After corroded in 2# salt, the sample surface is loose. The shell which is shown in Fig. 3(b) can't be found clearly on the sample surface (Fig. 3(b)). As shown in Fig. 3(c), after corroded in 3# molten salt, the sample surface is covered by a lot of granular matter. The mainly composition is MgO. There are corrosion holes under the granular matter. A relatively complete MgO shell forms on the sample surface after corroded in 4# molten salt. The sample substrate with a lot of corrosion holes is exposed after the shell flaking off, too.

In addition, after corroded for the first 5 h, all samples in each kinds of salt were ultrasonic cleared in distilled water and ethanol for 10 min and 5 min, respectively. A weight change unit area is shown in Fig. 4.

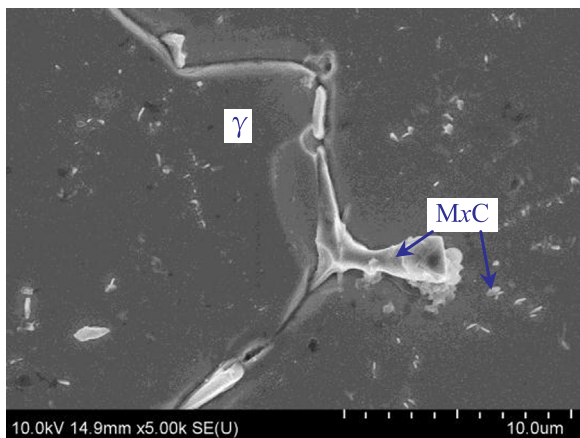


Fig. 1. SEM micro-structure image of GH1140.

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