

Hot corrosion behavior of commercial alloys in thermal energy storage material of molten $\text{MgCl}_2/\text{KCl}/\text{NaCl}$ under inert atmosphere



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ABSTRACT

Hot corrosion behavior of three commercial alloys (stainless steel SS 310, Incoloy 800 H, Hastelloy C-276) in molten $\text{MgCl}_2/\text{NaCl}/\text{KCl}$ (60/20/20 mol%) under inert atmosphere was investigated by immersion tests at 700 °C for 500 h. SS 310 exhibited the highest corrosion rate, while Hastelloy C-276 showed the best corrosion resistance. All the studied alloys could not meet the requirements for commercial application (i.e., corrosion rate < 10 $\mu\text{m}/\text{year}$ for 30 year's lifetime). Microstructural analysis on the exposed alloy specimens using SEM, EDX and XRD shows that Cr was dissolved preferentially than Fe and Ni to form a corrosion layer with a porous structure during the corrosion. Moreover, the corrosion products (e.g., MgO, MgCr_2O_4 , etc.) precipitated on the surface of the exposed specimens, as well as in the pores of the Cr-depleted corrosion layer. For SS 310 containing 2 wt% Si, Si was also dissolved and corrosion products containing Si were observed in the pores of the corrosion layer. Based on these findings, an impurity-driven corrosion mechanism is proposed to describe the hot corrosion behavior of the studied alloys in molten $\text{MgCl}_2/\text{NaCl}/\text{KCl}$ under inert atmosphere, which could assist the development of corrosion mitigation technologies in future work.

1. Introduction

Concentrated solar power (CSP) technology is emerging as one important technology in the future renewable energy system. It is reported that global installed CSP-capacity has increased nearly fifteen-fold from 2005 to 2015 (up to 4.8 Gigawatts) and grew at an average rate of 50% per year from 2010 to 2015 [1]. In CSP plants, storage of the heat from sunlight in thermal energy storage (TES) materials such as molten salts allows them to generate dispatchable power during the absence of sunlight and adds value of such power plants [2]. In commercial CSP plants, a non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate, commonly known as Solar Salt, is typically utilized as the TES material. The properties of commonly considered solar salts are listed in Table 1.

For power tower systems, it is desirable to raise the maximum operation temperature in order to increase the power block efficiency. This leads to reduced level of electricity costs. At present, two-tank molten salt storage is the only commercially available concept for CSP plants with a large thermal storage requirement [6]. This TES system can further be divided into the direct and indirect types. In a direct

system, the salts work both as heat transfer fluid (HTF) and the storage medium, while in an indirect storage system, the thermal storage is decoupled from the HTF loop by the heat exchanger.

Table 2 gives detailed parameters about these direct and indirect two-tank molten salt TES systems with Solar Salt. Both systems have similar thermal capacities, but the tower system has much lower molten salt inventory. This is due to the fact that the thermal storage capacity of a molten salt is proportional to the temperature difference between the hot and cold tank. In other words, the large temperature difference between the cold and hot tank leads to a small sized TES system.

Since Solar Salt, listed in Table 1, decomposes at the temperatures around 550 °C, the temperature difference and the upper operation temperature of the TES system is limited [3]. In order to improve the power tower system performance, work on improving the stability of Solar Salt at high temperature has been done in our research group [7].

The current paper presents a new type of molten salts - molten chloride salts. Compared with the commercial molten nitrate salts used in CSP, this type of salts not only has high thermal stability (stable at above 800 °C) and relatively high heat capacity, but also a lower cost (Table 1). These advantages allow to operate them at temperature

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Table 1
Properties of commonly used molten salts as TES materials in CSP.

Molten salts Composition (wt%)	Melting point (°C)	Stability limit (°C)	Heat capacity (kJ kg ⁻¹ K ⁻¹)	Cost (\$/kg)
Solar Salt NaNO ₃ /KNO ₃ (60/40)	240 [3]	530–565 [3]	1.55 (500 °C) [3]	0.5–1 [3]
Hitec NaNO ₃ /KNO ₃ /NaNO ₂ (7/53/40)	142 [4]	535 [4]	1.56 (300 °C) [4]	0.7–1.1 [4]
ZnNaK chlorides ZnCl ₂ /NaCl/KCl (68.6/7.5/23.9)	204 [4]	850 [4]	0.81(300–600 °C) [4]	0.5–1 [4]
MgNaK chlorides MgCl ₂ /NaCl/KCl (68.2/14.0/17.8)	380 [2]	> 800 [5]	~1.0 (500–800 °C) [5]	< 0.5 ^a

^a Price of MgNaK chlorides is estimated with the approximate large-scale prices for all chloride salts.

Table 2
Commercial two-tank systems with Solar Salt [6].

	Direct storage	Indirect storage
CSP type	Power tower	Parabolic trough
System name	Gemasolar	Andasol 1
Thermal capacity	~ 1000 MWh	1010 MWh
Inventory	8500 tones	28500 tones
Cold tank temperature	290 °C	292 °C
Hot tank temperature	~565 °C	386 °C
Temperature difference	~275 °C	94 °C

above 600 °C, which means higher efficiency of thermal to electrical energy conversion [8]. Moreover, a larger temperature difference might lead to a small sized and cost effective TES system.

However, the application of molten chlorides at high temperatures causes additional challenges, particularly increased corrosiveness of metallic containers and structural materials [8–10]. Table 3 summarizes the corrosion rates (CR) of commercial Fe-Ni-Cr alloys in various molten salts under different conditions. It shows that even under inert atmosphere the super corrosion resistance Ni-based superalloys like Hastelloys C-22 and C-276, which are more expensive compare with SS 304, cannot meet in molten chlorides (e.g., ZnCl₂/KCl/NaCl at 800 °C) the requirements of corrosion resistance in commercial applications (CR < 10 μm/year for 30 year's lifetime). Gomez-Vidal and Tirawat [12] reported the severe corrosion (corrosion rates > 2000 μm/year) of selected alloys (SS 347, SS 310, In 800 H and In 625) in NaCl/LiCl (34.42/65.58 wt%) at 650 °C under nitrogen atmosphere. When the molten MgCl₂/NaCl/CaCl₂ is swept with the air, the Ni-based superalloys (e.g. Inconel 625, Hastelloys X and B-3) exhibit severe corrosion, even at 600 °C (CR > 100 μm/year) [11]. Immersion tests of Vignarooban et al. [9] show that the anaerobic CR value of Ha C-276 in

Table 3
Corrosion of Fe-Ni-Cr-based alloys in commonly used molten salts as TES materials.

Molten salts	Alloys	Ni (wt%)	T (°C)	Corrosion rate (μm/year)
Solar Salt	SS 316	10–14	600	15.9 ^a [4]
	Ha 230	47–56	600	47 ^a [4]
Hitec	SS 321	9–12	570	2 ^a [4]
	SS 304	8–11	400	> 15 ^b [9]
ZnNaK chlorides ZnCl ₂ /NaCl/KCl (68.6/7.5/23.9 wt%)	Ha C-22	~56	400	~ 8 ^b [9]
	Ha C-22	~ 56	800	~ 12 ^b [9]
	Ha C-276	~ 57	500	~ 80 ^a [9]
	Ha C-276	~ 57	400	~ 3 ^b [9]
	Ha C-276	~ 57	800	~ 5 ^b [9]
	IN 625	~62	600	121 ^a [11]
MgNaCa chlorides MgCl ₂ /NaCl/CaCl ₂ (14.95/53.43/31.61 mol%)	Ha X	~47	600	153 ^a [11]
	Ha B-3	~65	600	145 ^a [11]
	IN 625	~62	650	2800 ^b [12]
NaLi chlorides NaCl/LiCl (34.42/65.58 wt%)	SS 347	9–12	650	7490 ^b [12]
	SS 310	~20.5	650	6420 ^b [12]
	In 800 H	30–35	650	5940 ^b [12]
	IN 625	~62	650	2800 ^b [12]

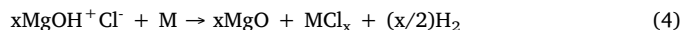
SS: Stainless steel; Ha: Hastelloy; IN: Inconel; In: Incoloy.

^a In air.

^b In inert atmosphere.

ZnCl₂/NaCl/KCl is only 5 μm/year at 800 °C, whereas it reaches to 80 μm/year even at 500 °C in presence of air.

Besides the operating temperature and atmosphere, it is well accepted that impurities in molten chlorides have significant effect on corrosion rates of the alloys [2,13,14]. The impurities mainly come from the water and the oxygen existing in the chloride salts and/or the atmosphere above the salts [8]. Water in the chloride salts (e.g., strong hydrophilic chloride - MgCl₂), probably from hydrated phases and/or in the atmosphere, hydrolyzes following reactions (1) and (2) and produce corrosive impurities MgOHCl and HCl [15]. The hydrochloric acid reacts with the metallic containers and structural materials according to reaction (3), while oxygen containing species existing in the molten chloride salts (e.g. MgOH⁺Cl⁻, dissolved oxygen) corrode the containers and structural materials by oxidizing the alloying components as shown in the reactions (4) and (5) [11].



M: alloying element, e.g., Cr.

Research efforts have been made to understand the corrosion mechanism of Fe-Ni-Cr-based alloys in molten chloride salts, e.g., MgCl₂/CaCl₂/NaCl [11] and MgCl₂/NaCl [16], but only under air conditions. As shown in Fig. 1, the combined effect of dissolution, oxidation and chlorination was considered in the corrosion mechanism of alloys in molten chlorides [11,16]. During the exposure, oxygen and water in air were continually dissolved in the molten chlorides and reacted with the molten chlorides to form corrosive HCl and Cl₂. These corrosive impurities can accelerate the corrosion of alloys, particularly the Cr element in the alloys, which has a strong electromotive force (EMF) in molten chlorides [17,18] and is very reactive to O₂, HCl and Cl₂ [11,16]. In this system, CrCl₄, MgCr₂O₄ and CrO₂Cl₂ are considered to be the main corrosion products.

Table 3 clearly shows the difficulty to control the corrosion rates of Fe-Ni-Cr-based alloys, exposed to molten chlorides under air atmosphere, below 10 μm/year (≥ 600 °C), due to the effect of O₂ and H₂O. Compared to air atmosphere, the alloys have much lower corrosion rates when exposed to the molten chlorides under inert atmosphere [9]. Besides, Ni-based alloys show better corrosion resistance than Fe-based steels. However, the prices of the materials also typically increase as Ni amount increases. However, there is still a lack of reliable data and research on the corrosion rates and mechanism of commercial Fe-Ni-Cr-based alloys in molten chlorides under inert atmosphere. Therefore, in order to realize the application of molten chlorides at high temperatures, it is important for corrosion mitigation, to study the corrosion behavior of commercial Fe-Ni-Cr-based alloys exposed to molten chlorides under inert atmosphere.

In this work, three commercial Fe-Ni-Cr-based alloys (SS 310, Incoloy 800 H, Hastelloy C-276) are selected. Since the prices of MgNaK chlorides are lower than ZnNaK chlorides, immersion tests were performed in molten MgCl₂/NaCl/KCl (60/20/20 mol%) under argon

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