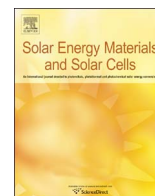




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Corrosion resistance of alumina-forming alloys against molten chlorides for energy production. I: Pre-oxidation treatment and isothermal corrosion tests

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ABSTRACT

Advanced components in next-generation concentrating solar power (CSP) applications will require advanced heat-transfer fluids and thermal-storage materials that work from about 550 °C to at least 720 °C, for integration with advanced power-conversion systems. To reach the cost target, less-expensive salts such as molten chlorides have been identified as high-temperature fluid candidates. High-strength alloys need to be identified and their mechanical and chemical degradation must be minimized to be used in CSP applications. Approaches for corrosion mitigation need to be investigated and optimized to drive down corrosion rates to acceptable levels—in the order of tens of micrometers per year—for achieving a long system lifetime of at least 30 years. Surface passivation is a good corrosion mitigation approach because the alloy could then be exposed to both the liquid and the vapor phases of the salt mixture. In this investigation, we pre-oxidized the alumina-forming alloys Inconel 702, Haynes 224, and Kanthal APMT at different temperatures, dwelling times, and atmospheres to produce the passivation by forming protective oxides at the surface. The pretreated alloys were later corroded in molten MgCl₂ – 64.41 wt% KCl at 700 °C in a flowing Ar atmosphere. We performed electrochemical techniques such as open-circuit potential followed by a potentiodynamic polarization sweep and conventional long-term weight-change tests to down-select the best-performing alloy and pre-oxidation conditions. The best corrosion results were obtained for In702 pre-oxidized in zero air at 1050 °C for 4 h. Metallographic characterization of the pre-oxidized alloys and of the corroded surfaces showed that the formation of dense and uniform alumina scale during the pre-oxidation appears to protect the alloy from attack by molten chloride.

1. Introduction

Molten chlorides are being considered as heat-transfer fluids (HTFs) and thermal energy storage (TES) candidates for advanced high-temperature thermal applications because of their high decomposition temperatures and good thermal properties. Advanced concentrating solar power (CSP) plants are considering the use of these molten salts [1]. This technology requires the use of high-temperature HTFs in the range of 550–800 °C. In the nuclear energy sector, LiCl-containing salts were considered as coolants and TES media. Chloride molten salts were explored earlier for nuclear applications but because of major drawbacks including the more corrosive characteristics of chloride systems relative to fluoride systems, they were not considered for further nuclear applications [2,3]. For CSP, NaCl, KCl, MgCl₂, and/or ZnCl₂ mixtures could be used as the HTF in solar receivers and/or as

sensible- or latent-TES material. Structural materials are needed for constructing high-temperature thermal components, e.g., heat exchangers, piping, and storage vessels, but molten chlorides are usually corrosive to typical alloys.

The type of corrosion typical of chromia-forming alloys in molten chlorides when a small amount of oxygen is allowed in the system has been reported to be localized, such as intergranular and pitting corrosion [4,5]. Groll et al. [4] evaluated the corrosion behavior of steel containers in latent-TES molten eutectic KCl–LiCl from 310 °C to 420 °C in air and argon with a long-term weight-loss technique up to 4032 h of immersion time. The effect of water and other impurities in the salt was studied. Pitting corrosion patterns were detected and additions of 2 wt% H₂O caused a severe increase in corrosion in these environments. Mechanical failure of components due to localized corrosion (pitting or intergranular) is catastrophic because the failure

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Nomenclature

CSP	concentrating solar power
HTF	heat transfer fluid
TES	thermal energy storage
Al-FA	alumina-forming alloy

is usually quick and unexpected. Uniform corrosion, in which the surface gradually degrades, is preferred because it is easy to control. It has been observed that Cr is commonly depleted near the degradation zone. The corrosion mechanism proposed elsewhere is that CrCl_3 formed at the bottom of the pits or degraded grain boundaries, and it rapidly diffused toward the alloy surface. At the fluid/alloy interface, dissolved oxygen is higher in content than at the bottom of the pits. Because of the higher oxygen potential, CrCl_3 is oxidized to non-protective and non-adherent Cr_2O_3 , and chlorine is liberated so that the degradation process continues by forming more CrCl_3 [6]. Chromium can cause deterioration of the corrosion resistance in chloride molten salts exposed to oxidizing atmospheres by forming chromates and chromium chlorides that are oxidants and can increase corrosion [7].

Creep-resistant, alumina-forming austenitic (AFA) stainless steels have been successfully developed at Oak Ridge National Laboratory (ORNL), which targeted the high-temperature applications in the range of ~ 600 – 900 °C through the guidance of computational thermodynamics. To date, various AFA grades have been developed that include the alloys with higher-temperature oxidation resistances up to 950 °C, low-Ni-containing inexpensive materials, or high creep strength comparable or superior to advanced austenitic stainless steels or Ni-based alloys. Good creep resistance in AFAs is achieved by precipitating multiple types of second phases [8].

Other iron-and nickel-based alumina-forming alloys (Al-FAs) such as Inconel 702 (In702), Haynes 224 (HR224), and Kanthal APMT are considered for high-temperature thermal applications because of their ability to form protective oxide layers on the surface. These alloys exhibit good high-temperature oxidation resistance by forming a protective Al_2O_3 scale with excellent chemical and thermal stability. The formation of protective alumina scales at elevated temperatures offers oxidation resistance that is superior to that of chromia-forming conventional stainless steels. Protective alumina scales have been shown to be a more effective barrier to the inward penetration of aggressive components such as chlorine and chloride molten salts [9]. Chromia-forming alloys have been shown to not be corrosion resistant in chloride molten salt environments [10]. Alumina grows at a slower rate than chromia, is more stable thermodynamically with oxygen, and affords a significantly higher degree of protection in the presence of many aggressive oxidizing species. Brady et al. [11] prepared and tested several Al-FAs in aggressive sulfidation–oxidation environments of $\text{Ar}-20\%\text{H}_2-20\%\text{H}_2\text{O}-5\%\text{H}_2\text{S}$ at 650 °C. The $\text{Fe}-25\text{Ni}-4\text{Al}-2.5\text{Nb}-0.2\text{C}$ (wt%) alloy showed the lower corrosion rate of 596 $\mu\text{m}/\text{year}$. This alloy was identified as of interest for future scale-up activities.

The molten salt corrosion behavior of Fe–Cr, Fe–Al, and Ni–Al

Table 1

Candidate alumina-forming alloys chemical composition and mechanical properties. UTS: ultimate tensile strength; YS: yield strength.

Alloy	Composition, wt%					Mechanical properties, MPa			
	Ni	Cr	Al	Fe	Other	UTS (T, °C)		2% _{offset} YS (T, °C)	
Haynes 224	46.4	20.5	3.2	27.6	0.2Mo, 0.3Mn, 0.3Si, 0.4Ti, 0.4Co	575 (650)	499 (760)	398 (650)	420 (760)
Kanthal APMT	–	21	5	~ 70	3Mo	420 (600)	120 ^a (800)	–	–
Inconel 702	~ 75	14 – 17	2.75 – 3.75	2	0.2Mo, 0.7Mn, 0.7Ti	620 (650)	550 (760)	550 (650)	482 (760)

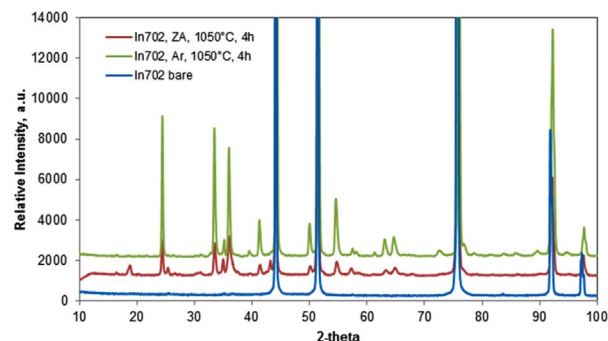
Note: Alloys were selected based on similar UTS and YS values to those of other high-strength alloys. These alloys are usually Ni-superalloys, Incoloy 800H, and high-stainless steel.

^a No data are available at 760 °C for comparison with the other alloys. The maximum CSP operating temperature is expected to be around 730 °C.

Table 2

Test matrix for pre-oxidation conditions.

Atmosphere	Alloy	Conditions: T (°C), t (h)			
		1	2	3	4
Zero Air (80%N ₂ , 20%O ₂)	HR224	1050, 4	950, 8	950, 20	
	APMT	1050, 8	950, 8	950, 20	
	In702	1050, 4	1050, 8	950, 8	950, 20
Pure Ar (99.9999%)	HR224	1050, 4	950, 8	950, 20	
	APMT	1050, 8	950, 8	950, 20	
	In702	1050, 4	1050, 8	950, 8	950, 20



Sample	Ref. Code	Compound Name	Chemical Formula
In702 bare	00-033-0945	austenitic steel	$\text{Ni}_{2.9}\text{Cr}_{0.7}\text{Fe}_{0.36}$
	03-065-5559	Chromium Nickel	$\text{Cr}_{1.12}\text{Ni}_{2.88}$
In702, ZA, 1050°C, 4h	00-035-1112	Chromium Iron Oxide	$\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$
	00-051-1394	Corundum - Aluminum Chromium Oxide	$\alpha\text{-(Al}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$
	01-085-1828	Hercynite	Al_2FeO_4
In702, Ar, 1050°C, 4h	01-084-0311	Iron Oxide	Fe_2O_3
	00-046-1212	Corundum	$\alpha\text{-Al}_2\text{O}_3$

Fig. 1. XRD patterns and identified phases of In702 bare and oxidized in zero air (ZA) and argon (Ar).

alloys was investigated with a surface deposit of NaCl – KCl melt in air at 670 °C. Fe–Al alloys improved their corrosion resistance with increasing Al content. Chromium exhibited a detrimental effect on corrosion of Fe–Cr alloys under the same conditions. The best corrosion resistance was observed in Ni–Al alloys, in which Ni remained relatively stable in the chloride system [7].

Hellstrom et al. tested the corrosion behavior of pre-oxidized FeCrAl alloy (Kanthal APMT) in 5% O_2 with 40% H_2O plus 300 ppm of SO_2 at 600 °C in the presence or absence of KCl. They found that KCl strongly accelerated the corrosion of the alloy by forming soluble K_2CrO_4 and gaseous HCl, depleting Cr and triggering the formation of a fast-growing iron-rich scale. Adding SO_2 suppressed corrosion due to the conversion of corrosive KCl to stable K_2SO_4 . They reported that the corrosion rate was significantly lower than that of chromia-forming alloys. Pre-oxidation decreased the corrosion rate even further, making Kanthal APMT a promising candidate material for combustion plant components, particularly from a corrosion point of view [12].

The protective behavior of alumina scales is attributed to the formation of stable $\alpha\text{-Al}_2\text{O}_3$ phase. Several metastable Al_2O_3 poly-

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