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 MgCl_2 – 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.

Keywords – molten salts; corrosion; chlorides; alumina-forming alloys; alumina; oxidation

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°C to 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 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 CrCl₃ 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, CrCl₃ is oxidized to non-protective and non-adherent Cr₂O₃, and chlorine is liberated so that the degradation process continues by forming more CrCl₃ [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°C–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 $596\text{ }\mu\text{m}/\text{year}$. 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 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].

Hellstroom et al. tested the corrosion behavior of pre-oxidized FeCrAl alloy (Kanthal APMT) in $5\%\text{O}_2$ with $40\%\text{H}_2\text{O}$ 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 polymorphs such as γ and θ phases tend to form in oxidizing environments at temperatures lower than $1,150^\circ\text{C}$. $\alpha\text{-Al}_2\text{O}_3$ typically forms at longer oxidation times and/or higher temperatures. Metastable γ - and $\theta\text{-Al}_2\text{O}_3$ scales contain lattice defects, so they provide no significant protection to further oxidation of the alloys compared with $\alpha\text{-Al}_2\text{O}_3$ scale [13,14]. The transformation from these metastable phases to $\alpha\text{-Al}_2\text{O}_3$ can lead to crack formation caused by volume changes ($\sim 13\%$) [15]. Li and Spiegel determined that a dense alumina surface layer was particularly stable in the presence of KCl vapor [9]. To selectively control the formation of protective $\alpha\text{-Al}_2\text{O}_3$

at lower temperatures, low oxygen partial pressures (pO_2) can be used. Dense and smooth α - Al_2O_3 scales are formed rapidly by treatment at $1050^\circ C$ under low pO_2 , where both aluminum and chromium in the Al-FAs are oxidized and other elements such as iron and nickel are not. Thermodynamic calculations predicted that only α -(Al,Cr) $_2O_3$ will be produced during the pre-oxidation of CoNiCrAlY under a low oxygen partial pressure (pO_2 below 10^{-9} Pa) at $1050^\circ C$ for 4 h [15,16]. Pre-oxidation results showed the formation of a dense α - Al_2O_3 scale with large grains. By contrast, under a higher pO_2 (above 10^{-9} Pa), all the components in the alloy were oxidized and formed a non-protective mixed-oxide scale including metastable θ - Al_2O_3 [13,15,16]. It has been reported that adding chromium or iron to Al-FAs accelerates the transformation from metastable polymorphs to α - Al_2O_3 [17–20].

Kanthal APMT is a FeCrAlMo alloy optimized for continuous service up to $1250^\circ C$. This alloy exhibits an attractive combination of resistance to oxidation and corrosion and good mechanical properties at elevated temperatures. This is due to the oxide-dispersion-strengthened (ODS) microstructure obtained from rapid solidification powder metallurgy. Jönsson et al. determined that the adherent alumina layer formed during service provided excellent resistance to corrosion attacks in most industrial atmospheres and gave great advantages compared to chromia-forming high-temperature Ni-based alloys in terms of maximum operating temperature and life. The high creep resistance allows for design of moderately loaded components up to the maximum recommended continuous operation temperature of $1250^\circ C$ [21].

Weight-loss corrosion techniques are very accurate but are time-intensive. To obtain corrosion rates, more than 500 h of immersion time is usually required [5]. The use of electrochemical techniques allows continuous corrosion evaluation, as well as the determination of instantaneous corrosion rates, corrosion mechanisms, and process-controlling steps after only a few hours of testing. These techniques have been employed for a better understanding of the fundamentals behind the corrosion mechanisms for molten-salt electrolytes [6,22–26]. Potentiodynamic polarization sweep (PPS) is commonly employed to determine the corrosion rate of materials. Before polarizing the sample by applying the cathodic and anodic over-potentials, the system must establish the open-circuit potential (OCP), which is the equilibrium potential for the undisturbed system.

The PPS diagrams, which plot the applied potential versus log-scale of measured current density, are used to determine the corrosion current (I_{corr}) that is found at the interception of the extrapolated linear or Tafel portions of the cathodic and anodic curves (usually found in the linear portions between -250 mV and $+250$ mV relative to the OCP or corrosion potential (E_{corr}) of the sample) [5, 6, 10, 25, 26].

The corrosion rate is calculated using the Stern-Geary equation through Faraday's Law as follows [27]:

$$CR = \frac{I_{corr} \cdot K \cdot EW}{\rho A}, \quad (1)$$

where CR is the corrosion rate ($\mu\text{m}/\text{yr}$), K is a constant equal to $3,272 \times 10^3$ [$\mu\text{m}/(\text{A} \cdot \text{cm} \cdot \text{yr})$], EW is the equivalent weight of the alloy ($\text{g}/\text{equivalent}$), ρ is the alloy density (g/cm^3), and A is the exposed surface area (cm^2).

The equivalent weight for alloys is calculated as follows:

$$EW = NEQ^{-1} \quad (2)$$

$$NEQ = \sum \left(\frac{f_i \cdot n_i}{MW_i} \right), \quad (3)$$

where NEQ is the number of equivalent, f_i is the weight fraction, n_i is the number of electrons being transferred, and MW_i is the atomic weight.

Morks et al. [28] determined the protective nature of plasma-sprayed alumina-coated mild steel in aqueous chloride corrosive environments at room temperature by employing OCP, PPS, and electrochemical impedance spectroscopy (EIS). They found that alumina-coating reduced the corrosion rate of the steel from $3,110 \mu\text{m}/\text{yr}$ (bare) to $240 \mu\text{m}/\text{yr}$ (coated).

In this work, the National Renewable Energy Laboratory (NREL) evaluated the corrosion resistance behavior of Al-FAs (In702, HR224, and APMT) pre-oxidized in argon and zero air (ZA) and corroded in molten 35.59 wt.% MgCl_2 – 64.41 wt.% KCl ($T_m = 423^\circ\text{C}$) at 700°C in a flowing Ar (99.9999%) atmosphere. The conventional weight-change technique up to 500 h and electrochemical techniques were employed.

2. Material and methods

2.1 Preparation of salt mixture

The eutectic MgCl_2 – KCl was prepared using single components with a purity greater than 99 wt% acquired from Alfa Aesar. Because MgCl_2 is highly hygroscopic, the salts were kept in a vacuum furnace at 120°C for at least 48 h before mixing. The dried salts were weighed and mixed to the proper ratio in 125-g batches in a glove box under dry nitrogen. The salts were then placed in a boron nitride crucible because this material previously was shown to be stable in chloride molten-salt systems. The salt mixture was placed in the vacuum furnace at 120°C for at least 24 h prior to the pre-melting and purification process.

The following purification process was used during pre-melting of the salt: 1) purge 100 sccm of Ar through salt while holding at 100°C for 5 h; 2) raise the temperature to 200°C for 2 h; 3) raise to 300°C for 2 h; 4) raise to 400°C and hold until Ar purge tube can be removed; 5) because MgCl_2 melts at $\sim 714^\circ\text{C}$, increase temperature to 800°C and hold it for 1 h to guarantee good mixing. The BN crucible also was shown to not be wetted by the chlorides, so removal of the salt after solidification was much easier. To

avoid moisture absorption after cooling, the pre-melted and solidified salt was stored at 120°C in the vacuum furnace until needed for testing.

2.2 Alloy preparation and pre-oxidation

Table 1 shows the nominal composition of Al-FAs tested. Samples of 12 × 25 × 3 (mm) were used for electrochemical tests while 12 × 12 × 3 (mm) was used for weight-change long-term tests. The samples required for electrochemical corrosion tests were progressively polished using up to a 1200-grit SiC abrasive paper, cleaned with deionized water, and dried with acetone and compressed air. Polishing is required before electrochemical corrosion tests to control the amount of flat surface area exposed to the corroding fluid that is used to normalize the corrosion current density of the samples.

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} (T, °C)	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* (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)

*: 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.

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.

The test matrix of pre-oxidation conditions is shown in Table 2. Down-selection of the best pre-oxidation conditions per alloy was performed based on corrosion rates obtained from PPS tests. These pre-oxidation conditions were used to study in detail the formation of a protective scale. The rate of protective scale formation was evaluated for best pre-oxidation condition (temperature, atmosphere) per alloy that gave the lower corrosion rate. Each alloy was subjected to pre-oxidation for certain periods of time.

2.3 Corrosion evaluations

2.3.1 Electrochemical techniques

PPS and OCP were used to determine the Tafel slopes and corrosion rates of Al-FAs after 4 h of immersion in molten MgCl₂ – 64.41 wt.%KCl at 700°C in flowing Ar (99.9999%). The data handling used to calculate these values is reported elsewhere [10]. To form the required protective alumina layer oxide at the surface of the alloys, they were pre-oxidized following conditions from Table 2. The electrochemical cell experimental set-up used in this work is given elsewhere [10, 29]. A crucible electrical

resistance furnace was used to contain the cell made of 316L. The electrochemical cell contains a quartz liner and an off-gas treatment to trap the chloride by-products. A three-electrode arrangement was used with the working electrode (WE) as the sample, the pseudo reference electrode (RE) made from 0.5-mm-diameter platinum wire, and the counter electrode (CE) made from platinum mesh. The required stability time of 45 min for the pseudo-Pt RE in the chloride molten salt was determined in a previous work [10]. The electrochemical tests were performed using a potentiostat (AUTOLAB–PGSTAT302N).

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

For the PPS experiments, the WE's potential (E) was continuously recorded starting immediately after its salt immersion until $dE/dt \leq 100 \mu\text{V/s}$ was obtained, and thus, OCP was established. The PPS test was conducted immediately after by applying cathodic (–) and anodic (+) external potentials from –0.35 V to +0.6 V around the OCP or corrosion potential at 0.001 V steps and 0.001 V/s. More than five coupons per test were performed under the same conditions to evaluate the reproducibility of the results. Some results were discarded based on PPS curve behavior. The corrosion current density, j_{corr} , was calculated from the intersection of the extrapolated straight sections of the cathodic and anodic Tafel slopes within an interval of 120 mV with respect to E_{corr} .

2.3.2 Weight-change long-term tests

A controlled atmosphere tube furnace was used for the weight gain/loss tests. Down-selection of the best pre-oxidation conditions per alloy was previously determined from PPS and OCP tests. Two replicates per sample were placed in quartz crucibles (10 cm³ of volume) with about 10 g of purified, pre-melted and solidified salt. The tests were performed at 700°C in flowing Ar during 175, 325, and 505 h. After each period of time, the samples were removed from the salt and cleaned using ASTM G1-03. Mass change was recorded and thickness loss was calculated.

2.4 Characterization of the alloys and salts

The samples were metallographically characterized before and after pre-oxidation and after corrosion tests with X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) with energy-dispersive X-ray spectrometry (EDX). Salt

specimens from the purified salt and those being removed from progressive long-term immersion stages were dissolved in an acidic medium. The solutions were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) to determine chemical composition.

3. Results and discussion

3.1 Oxidation of Al-FAs to form protective oxide layers

XRD was used to identify the phases formed after oxidation of HR224, In702, and APMT in ZA and Ar. Figures 1 – 3 show the XRD patterns and the identified crystalline phases. Using X'PertHighScore Plus software, the patterns resolved the corundum α -aluminacrystalline structure. In some cases, Cr(0.052 – 0.1 molar fraction) substituted Al atoms into the corundum structure forming the aluminum chromium oxide. Single or combined oxides containing Fe, Ni, and/or Cr were identified. Since these oxides are much less protective than alumina, it is expected that the zone containing them will corrode first. If a uniform and dense internal layer of protective alumina is formed underneath these oxides, it is hypothesized that the corrosion will be delayed and thus corrosion could be controlled by the presence of a protective alumina layer.

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).

Sample	Ref. Code	Compound Name	Chemical Formula
HR224 bare	00-047-1405	Iron Nickel	$\text{Fe}_{0.64}\text{Ni}_{0.36}$
	00-003-1209	Iron Nickel	Fe Ni
HR224, ZA, 1050°C, 4h	01-074-2081	Nickel Iron Oxide	$\text{Ni Fe}_2\text{O}_4$
	01-075-0782	Corundum	$\alpha\text{-Al}_2\text{O}_3$
	01-084-0311	Hematite	Fe_2O_3
	01-082-1484	Chromium Oxide	Cr_2O_3
	01-089-3855	Iron Chromate	$\text{Fe Cr}_2\text{O}_4$
HR224, Ar, 950°C, 8h	00-049-1657	Aluminum Iron Oxide	$\text{Al}_3\text{Fe}_5\text{O}_{12}$
	00-051-1394	Corundum - Aluminum Chromium Oxide	$\alpha\text{-(Al}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$

Fig.2. XRD patterns and identified phases of HR224 bare and oxidized in zero air (ZA) and argon (Ar).

XRD is a qualitative analysis in which the presence of crystalline phases is resolved. To determine the relative proportion and the morphology of the oxides, cross-section metallography was performed. FESEM analyses were used to determine the surface cross-section microstructure. EDS mapping analyses were performed to determine the distribution of elements such as C (from the encapsulation), O, Fe, Ni, Cr, and Al. This was used to help determine the best conditions to produce uniform layers of protective alumina and determine the growth pattern of this oxide.

Figures 4 – 6 show the FESEM micrographs and EDS elemental maps of Al-FA with the best-performing pre-oxidation conditions determined during this investigation based on preliminary potentiodynamic polarization sweep (PPS) electrochemical corrosion tests. In all the cases, chromia (Cr_2O_3) appears as the top layer with alumina (pure or with Cr substitution) as the internal layer. Alumina grows in In702 as a dispersed phase surrounded by an enriched Ni matrix (Figs. 4a and 4b). HR224 produces powdery/granular alumina phases (Figs. 5a and 5b). $(\text{Al}, \text{Cr})_x\text{O}_y$ oxides are mixed with high concentrations of Cr (Fig. 5a). It appears that the alumina layers formed in Kanthal-APMT (Figs. 6a and 6b) are denser and more uniform than in the other Al-FAs. In all cases, alumina layers are only a few micrometers thick.

Sample	Ref. Code	Compound Name	Chemical Formula
Substrate	01-085-1410	Iron	Fe
	00-045-0982	Aluminum Iron	Al _{0.4} Fe _{0.6}
APMT, ZA, 1050°C, 4h	01-089-0599	Hematite	Fe ₂ O ₃
	01-071-0958	Corundum - Aluminum Chromium Oxide	(Al _{0.948} Cr _{0.052}) ₂ O ₃
APMT, Ar, 950°C, 8h	01-089-0596	Hematite	Fe ₂ O ₃
	00-051-1394	Corundum - Aluminum Chromium Oxide	(Al _{0.9} Cr _{0.1}) ₂ O ₃

Fig.3. XRD patterns and identified phases of Kanthal APMT oxidized in zero air (ZA) and argon (Ar).

Fig. 4.Down-selected pre-oxidized In702. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 1050°C, 4 h), (b) (Ar, 1050°C, 4 h).

Fig. 5. Down-selected pre-oxidized HR224. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 1050°C, 4 h), (b) (Ar, 950°C, 8 h).

Fig. 6. Down-selected pre-oxidized APMT. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 950°C, 8 h), (b) (Ar, 950°C, 8 h).

The thickness of aluminum oxide layers was measured and averaged using the FESEM/EDS micrographs and maps as a function of oxidation time up to 25 h. Figure 7 shows the averaged alumina thickness with trend lines as a function of time for each

oxidized Al-FA. Oxidation of In702 in ZA, HR224 in Ar, and APMT in ZA follow the parabolic rate law: ($x^2 = 2k_p \cdot t$), where x : oxide film thickness; t : time, and k_p : diffusion rate constant (directly proportional to diffusivity of ionic species that is the rate controlling step). The parabolic rate law is typical for protective oxides. The other oxidation for In702 in Ar, HR224 in ZA, and APMT in Ar follow a linear rate law which is an empirical relationship that is applicable to the formation and build-up of a non-protective oxide layer [30].

Fig. 7. Alumina scale thickness of pre-oxidized Al-FAs as a function of time: (a) In702 (b) HR224, and (c) APMT.

Oxidation of In702 in ZA produced two distinct alumina zones, with a denser layer formed on top of an internal dispersed phase (Fig. 7a). The dispersed alumina phase formed in In702 (ZA) is thicker than the dense layer. Because the alumina resolved in XRD is the crystalline polymorphic α -corundum phase, which is the most protective structure because it has less crystalline defects, it is hypothesized that the denser alumina layer could protect the alloy from corrosion in molten chlorides. Alumina layers in HR224 are thicker than in APMT alloys (see Figs. 7b and 7c). Aluminum oxides in HR224 are granular and are mixed with Cr and/or Fe (see Figs. 5a and 5b). This could be the reason why they are thicker than in APMT alloys. Only dense and uniform alumina layers are present in APMT; but they are the thinnest among the Al-FA alloys.

Figure 8 shows the mass and thickness loss of the pre-oxidized alloys exposed to molten-salt corrosion as a function of immersion time. The maximum thickness loss of $\sim 14 \mu\text{m}$ was obtained for HR224 (ZA and Ar) after 505 h of exposure. The minimum of $3 \mu\text{m}$ was obtained for In702 (ZA) for 505 h of corrosion time.

Fig. 8. Mass (a) and thickness losses (b) of down-selected pre-oxidized Al-FAs with time during long-term corrosion test in molten eutectic $\text{MgCl}_2 - 64.41 \text{ wt\% KCl}$ at 700°C in Ar. Corroded samples were chemically and mechanically cleaned following standard ASTM G1-03.

From the long-term corrosion tests in flowing Ar, it can be seen that HR224 is the worst alloy with the lowest corrosion resistance against molten chlorides. As reported above, its oxides were mixed granular Al, Cr, and Fe oxides—hence, high mass loss on exposure to chlorides because they are less stable in these environments. The best-performing alloy is In702 pre-oxidized in ZA at 1050°C during 4 h. This alloy showed denser top alumina layers with dispersed internal alumina zones. This alumina morphology and configuration might have helped bridge the mismatch in coefficient of thermal expansion between the dense top layer and the underlying metallic alloy. This could decrease the rate of spallation (corroborated by lower mass loss in Fig. 8). If the top layer is dense and uniform enough, it could stop ingress of corrosive media toward

the alloy matrix. These hypotheses should be confirmed with further evaluations. None of the Al-FAs reached the expected asymptotic (very small changes with time) corrosion behavior. The pseudo-constant behavior represents the expected passivation of the alloys from the protective behavior of alumina layers.

Some samples were corroded during 1000 h for XRD analyzes of corrosion products. These samples were removed from the salt, rinsed in DI water and analyzed in XRD. The XRD patterns (shown in Fig. 9) were analyzed using X'PertHighScore Plus software. Identified crystalline phases are shown in Fig. 9.

Fig. 9. XRD patterns with identified phases of (a) In702(Ar) and (b) HR224(Ar) after 1000 h immersion in molten eutectic MgCl_2 – 64.41 wt% KCl at 700°C in Ar.

Al-FA samples corroded during 505 h were metallographic characterized to determine distribution of corrosion products across the surface. For this, they were removed from the salt, rinsed in DI water, and encapsulated in bakelite for cross-section analysis. FESEM/EDS micrographs of pre-oxidized and corroded Al-FAs are shown in Figs. 10 – 12. Under isothermal conditions, it appears that alumina scales are stable. It is interesting to see that the oxide scales grew during exposure to molten chlorides, which implies that oxygen permeation occurred into the tube-furnace system used. Thicker alumina layers were obtained for corroded In702 (Ar and ZA) (Fig. 10). Thicknesses were about 50 μm and 25 μm , for In702(Ar) and In702(ZA), respectively. The other alloys presented thinner alumina layers after corrosion. In702 (Fig. 10) and APMT (Fig. 12) showed uniform corrosion, but it appears that HR224 (Fig. 11) has some cracks at the surfaces that could initiate localized corrosion in the future. To determine any change in the corrosion mechanism, longer periods of exposure time will be required.

Fig. 12. FESEM micrographs (left) and FESEM/EDS maps (right) of APMT pre-oxidized and molten chloride corroded at 700°C during 505 h in Ar atmosphere: (a) ZA, 950°C, 8 h, and (b) Ar, 950°C, 8 h.

The oxidation atmosphere (ZA or Ar) plays an important role in the formation of dense and uniform layers of protective oxides against corrosion in molten chloride. It was noticed that alumina layers formed in Ar atmospheres were in some cases denser but they were in general too thin. Also the low partial pressure of oxygen in Ar atmospheres did not stop the formation of other Fe-containing oxides. By using ZA atmospheres to pre-oxidize Al-FAs, it is expected that the process will be commercially feasible and cost-effective because regular air can be used instead of controlled inert atmospheres.

The salts collected after each exposure time were analyzed using XRD. Figure 13 shows the XRD patterns and the identified crystalline phases. Aluminum oxides were identified as well as oxides containing Ti, Mo, Ca, Cr and/or Fe. Other chlorides such as MoCl_3 and CrCl_3 were resolved. CaFeO_4 is present in salts from alloys HR224 and AMPT. It is interesting that MgO was resolved as part of the crystalline phases contained in most of the salts after corrosion. Mg only comes from the MgCl_2 of the molten salt, which means that this salt reacts with dissolved oxygen from the environment to form periclase MgO at high temperatures.

Fig. 13. XRD patterns of salt samples taken after corrosion tests and crystalline phases resolved.

(a) HR224(ZA), (b) HR224(Ar), (c) APMT(ZA), (d) APMT(Ar), and (e) In702(ZA)

- 1 Chemical composition of the salt samples was performed using ICP-MS. Acid
- 2 digestion was employed to completely dissolve the sample and have all the elements in
- 3 solution. The composition of salts (see Fig. 14) shows that elements such as Al, Cr, Ni,
- 4 Fe, Ti, and Mo were dissolved from the alloys into the molten salts during corrosion. Ca
- 5 is an impurity from the salt and Si is mostly coming from the alloy and the quartz
- 6 crucible. The highest concentrations were observed for Cr and Fe. From these data, it

- 1 can be concluded that the worst alloys are HR224(ZA) and AMPT(ZA). In general, the
 2 best-performing alloy is In702 (ZA, 1050°C, 4 h).

3 **Fig. 14.** ICP-MS analyses showing concentration (in ppm) of dissolved elements in molten
 4 chloride after corrosion at different immersion times.

The literature states that formation of metastable alumina polymorphs can lead to crack formation when transforming into stable α -Al₂O₃ phase [13, 14]. To avoid cracking formation due to this solid-solid transformation, protective α -Al₂O₃ was produced at the surface of Al-FAs at 1050°C in ZA atmospheres. This pre-oxidation treatment already established the presence of the protective layer; so it is believed that if during corrosion this layer spalls off in the salt, the oxygen compounds dissolved into the chloride system will probably allow the reformation of α -Al₂O₃, even at low temperatures because of the presence of α -Al₂O₃ at the surface that will serve as nucleants of new crystals.

To allow the reformation of alumina certain amount of dissolved oxygen must be present in the molten salt. To maintain a certain level of oxygen-dissolved compounds in the salt, it is recommended to evaluate the effect of oxygen-containing gases bubbled into the molten salt. This evaluation should focus on corrosion mitigation of Al-FAs by determining if the regeneration of protective α -Al₂O₃ is feasible. To stabilize the alumina layers during corrosion in molten salts, it is suggested to use an atmosphere with a higher oxidation potential, which could move the alloy's potential to a passivation region in which the aluminum oxide at the surface could remain stable and protective.

4 Conclusions

Long-term weight-change corrosion tests up to 505 h and electrochemical techniques were employed to study the corrosion of alumina-forming alloys (Al-FAs) in molten chlorides in flowing Ar atmospheres. Corrosion tests showed that the best-performing alloy resulted in In702 pre-oxidized in ZA at 1050°C during 4 h due to the presence of more stable alumina layers. XRD, ICP-MS, and FESEM/EDS of Al-FAs demonstrated that high Ni content might decrease the corrosion of alloys in molten chlorides. From ICP-MS analysis, Cr and Fe are highly corroded from the alloys into the molten salts, followed by Al, Ni, and then Mo.

XRD patterns resolved the formation of several oxides as corrosion products, which confirms that a certain amount of oxygen permeated during the corrosion tests. It is believed that this amount of permeated oxygen, dissolved into the molten chloride, was not enough to stabilize and reform alumina layers.

To determine if alumina scales can re-heal and be stable, future testing will be performed under thermal cycling in an oxygen-containing atmosphere. These conditions are found in CSP applications and the stability of the protective oxides must be verified.

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Nomenclature

CSP concentrating solar power

- 1 HTF heat transfer fluid
- 2 TES thermal energy storage
- 3 Al-FA alumina-forming alloy

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8

1 **Tables' captions**

2 **Table 1.**Candidate alumina-forming alloys chemical composition and mechanical
3 properties. UTS: ultimate tensile strength; YS: yield strength.

4 **Table 2.**Test matrix for pre-oxidation conditions.

5

1 **Table 1.**

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* (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)

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

4 *Note:* Alloys were selected based on similar UTS and YS values to those of other high-strength alloys. These alloys
5 are usually Ni-superalloys, Incoloy 800H, and high-stainless steel.
6

1 **Table 2.**

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

2

Figure captions

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

Fig. 2. XRD patterns and identified phases of HR224 bare and oxidized in zero air (ZA) and argon (Ar).

Fig. 3. XRD patterns and identified phases of Kanthal APMT oxidized in zero air (ZA) and argon (Ar).

Fig. 4. Down-selected pre-oxidized In702. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 1050°C, 4 h), (b) (Ar, 1050°C, 4 h).

Fig. 5. Down-selected pre-oxidized HR224. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 1050°C, 4 h), (b) (Ar, 950°C, 8 h).

Fig. 6. Down-selected pre-oxidized APMT. Left: FESEM-BSE micrograph, right: EDS maps: (a) (ZA, 950°C, 8 h), (b) (Ar, 950°C, 8 h).

Fig. 7. Alumina scale thickness of pre-oxidized Al-FAs as a function of time: (a) In702 (b) HR224, and (c) APMT.

Fig. 8. Mass (a) and thickness losses (b) of down-selected pre-oxidized Al-FAs with time during long-term corrosion test in molten eutectic $\text{MgCl}_2 - 64.41 \text{ wt\% KCl}$ at 700°C in Ar. Corroded samples were chemically and mechanically cleaned following standard ASTM G1-03.

Fig. 9. XRD patterns with identified phases of (a) In702(Ar) and (b) HR224(Ar) after 1000 h immersion in molten eutectic $\text{MgCl}_2 - 64.41 \text{ wt\% KCl}$ at 700°C in Ar.

Fig. 10. FESEM micrographs (left) and FESEM/EDS maps (right) of In702 pre-oxidized and molten chloride corroded at 700°C during 505 h in Ar atmosphere: (a) ZA, 1050°C, 4 h, and (b) Ar, 1050°C, 4 h.

Fig. 11. FESEM micrographs (left) and FESEM/EDS maps (right) of HR224 pre-oxidized and molten chloride corroded at 700°C during 505 h in Ar atmosphere: (a) ZA, 1050°C, 4 h, and (b) Ar, 950°C, 8 h.

Fig. 12. FESEM micrographs (left) and FESEM/EDS maps (right) of APMT pre-oxidized and molten chloride corroded at 700°C during 505 h in Ar atmosphere: (a) ZA, 950°C, 8 h, and (b) Ar, 950°C, 8 h.

Fig. 13. XRD patterns of salt samples taken after corrosion tests and crystalline phases resolved. (a) HR224(ZA), (b) HR224(Ar), (c) APMT(ZA), (d) APMT(Ar), and (e) In702(ZA).

Fig. 14. ICP-MS analyses showing concentration (in ppm) of dissolved elements in molten chloride after corrosion at different immersion times.

1 **Fig. 1.**

2

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	$\alpha\text{-Al}_2\text{O}_3$

1 **Fig. 2.**

2

Sample	Ref. Code	Compound Name	Chemical Formula
HR224 bare	00-047-1405	Iron Nickel	$\text{Fe}_{0.64}\text{Ni}_{0.36}$
	00-003-1209	Iron Nickel	Fe Ni
HR224, ZA, 1050°C, 4h	01-074-2081	Nickel Iron Oxide	$\text{Ni Fe}_2\text{O}_4$
	01-075-0782	Corundum	$\alpha\text{-Al}_2\text{O}_3$
	01-084-0311	Hematite	Fe_2O_3
	01-082-1484	Chromium Oxide	Cr_2O_3
	01-089-3855	Iron Chromate	$\text{Fe Cr}_2\text{O}_4$
HR224, Ar, 950°C, 8h	00-049-1657	Aluminum Iron Oxide	$\text{Al}_3\text{Fe}_5\text{O}_{12}$
	00-051-1394	Corundum - Aluminum Chromium Oxide	$\alpha\text{-(Al}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$

3

1 **Fig. 3.**

2

Sample	Ref. Code	Compound Name	Chemical Formula
Substrate	01-085-1410	Iron	Fe
	00-045-0982	Aluminum Iron	Al _{0.4} Fe _{0.6}
APMT, ZA, 1050°C, 4h	01-089-0599	Hematite	Fe ₂ O ₃
	01-071-0958	Corundum - Aluminum Chromium Oxide	(Al _{0.948} Cr _{0.052}) ₂ O ₃
APMT, Ar, 950°C, 8h	01-089-0596	Hematite	Fe ₂ O ₃
	00-051-1394	Corundum - Aluminum Chromium Oxide	(Al _{0.9} Cr _{0.1}) ₂ O ₃

3

4

1 **Fig. 4.**

1 **Fig. 5.**

1 **Fig. 6.**

1 Fig. 7.

1 Fig. 8.

2

3

1 **Fig. 9.**

2

3

1 **Fig. 10.**

2

3

1 Fig. 11.

(a)

(b)

2

3

1 **Fig. 12.**

2

3

1 Fig. 13.

(a)

(b)

(c)

(d)

(e)

2

3

1 Fig. 14.