Corrosion evaluation of alloys and MCrAlX coatings in molten carbonates for thermal solar applications

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Abstract

Stainless steels (SS) 310, 321, 347, Incoloy 800H (In800H), alumina-forming austenitic (AFA-OC6), Ni superalloy Inconel 625 (IN625), and MCrAlX (M: Ni, and/or Co; X: Y, Hf, Si, and/or Ta) coatings were corroded in molten carbonates in N₂ and bone-dry CO₂ atmospheres. Electrochemical tests in molten eutectics K₂CO₃–Na₂CO₃ and Na₂CO₃–K₂CO₃–Li₂CO₃ at temperatures higher than 600°C were evaluated using an open-circuit potential followed by a potentiodynamic polarization sweep to determine the corrosion rates. Because the best-performing alloys at 750°C were In800H followed by SS310, these two alloys were selected as the substrate material for the MCrAlX coatings. The coatings were able to mitigate corrosion in molten carbonates environments. The corrosion of substrates SS310 and In800H was reduced from ~2,500 µm/year to 34 µm/year when coated with high-velocity oxyfuel (HVOF) NiCoCrAlHfSiY and pre-oxidized (air, 900°C, 24 h, 0.5°C/min) before molten carbonate exposure at 700°C in bone-dry CO₂ atmosphere. Metallographic characterization of the corroded surfaces showed that the formation of a uniform alumina scale during the pre-oxidation seems to protect the alloy from the molten carbonate attack.

Keywords – molten salts; corrosion; carbonates; coating; alumina; oxidation.

1. Introduction

Advanced components in next-generation concentrating solar power (CSP) applications will require advanced heat transfer fluids (HTF) and thermal-storage materials, working from about 550°C to at least 720°C, for integration with advanced power-conversion systems. In particular, the supercritical CO₂ (sCO₂) Brayton power cycle has received much attention. Promising direct-sCO₂ receivers are under development [1], yet they are of little value without viable thermal energy storage (TES) designs. For a viable full-plant system, sCO₂ receivers require TES systems that will operate with the sCO₂ HTF [2].

Carbonate-based TES systems, tailored to work with sCO₂ HTF, can play an essential role in the development and deployment of the sCO₂ power cycle for CSP. Eutectics Na₂CO₃–K₂CO₃–Li₂CO₃ and K₂CO₃–Na₂CO₃ could be used as HTF and latent TES, respectively. These mixtures have attractive cost and excellent thermophysical properties and thermal stability to at least 850°C [3]. It has been reported that by using a

CO₂ atmosphere, the maximum temperature can be increased up to at least 1,000°C [4].

Current state-of-the-art molten salts used in CSP plants up to 565°C are nitrate/nitrite (oxyanion) mixtures such as solar salt. Increasing the temperature limit will increase the efficiency of the power generation. But this increment requires a detailed understanding of materials corrosion behavior, in addition to the thermal stability properties of salt. Iron-based stainless steels, specifically 321SS and 347SS, have been tested by immersion in the binary nitrate solar salt at temperatures of 400, 500, 600, and 680°C, with air sparging. Samples were tested up to 3000 h to acquire data on time-varying weight gain. Detailed characterization of samples exposed to 680°C exhibited an excessive rate of corrosion, with metal loss in both alloys. Corrosion rates at temperatures of 600°C and below had metal losses of less than 20 µm/year. An increase of 80°C (600 to 680°C) has a 30–40-fold increase in corrosion rate. At 680°C, 321SS corroded at 460 µm/year, and 347SS corroded at 447 µm/year [5].

By their nature, oxyanions such as nitrates and carbonates, have high heat capacities that are beneficial in both sensible and latent TES systems. The degrees of freedom of polyatomic oxyanions lead to higher specific heats than halides and most other salts systems. Carbonates, in general, have higher heat capacities (~2 J/g·K) compared with current state-of-the-art nitrate salts (~1.5 J/g·K) used in commercial CSP plants. Carbonate salts also exhibit high densities, which translates to greater energy density ($\rho \cdot C_p$) and smaller required tank volumes. In addition, carbonate salts are inherently compatible with CO₂. Any salt-to-sCO₂ heat exchanger may eventually develop leaks, allowing the high-pressure CO₂ to contact the salt. In a carbonate salt system, this would lead to no detrimental reactions and would be easily identified by an increase in the CO₂ cover-gas pressure.

The cost of the non-media components (e.g., tanks, heat exchangers) in the current 2-tank sensible TES systems that employ solar salt account for about \$10 to 15/kWh_{th} [6]. Accounting for the smaller (200 K vs 270 K) ΔT of the carbonate/sCO₂ system and the greater $\rho \cdot C_p$ of carbonates, the required tank volume will decrease by about 20%. This indicates that a sensible-TES system will cost in the range of \$18 to \$22/kWh_{th} assuming similar alloy costs. The impact on levelized cost of energy (LCOE) was calculated using the System Advisor Model (SAM) developed by the National Renewable Energy Laboratory (NREL) [7] for all system metrics set at their U.S. Department of Energy (DOE) SunShot targets [8] with the exception of the thermal storage cost at \$25/kWh_{th} rather than \$15/kWh_{th}. SAM reported that the overall LCOE increases from the SunShot target of 6.0¢/kWh to only 6.4¢/kWh. Less-expensive salts such as molten chlorides have been identified as candidate high-temperature fluids for CSP applications. Oxyanions—in particular, carbonate systems—are less corrosive than chloride systems [9–11]. Blended carbonate/chloride systems are also reported to

be less corrosive than pure chlorides [11]. High-strength alloys need to be identified and their mechanical and chemical degradation must be minimized for their use in CSP applications. Corrosion mitigation approaches need to be investigated and optimized to drive corrosion rates down to acceptable levels in the order of tens of micrometers per year for achieving a long system lifetime of at least 30 years.

One limitation that chloride molten salts have is that intergranular corrosion is the identified degradation mechanism when oxygen is allowed in the system [12]. Mechanical failure of components due to localized corrosion (pitting or intergranular) is catastrophic since the failure is usually quick and unexpected. Degradation in carbonate molten salts is typically a uniform corrosion type [13], in which the surface gradually degrades. This type of corrosion is preferred because it is easy to control.

To protect turbine blades from molten salt attack, MCrAlX (M: Ni, and/or Co; X: Y, Hf, Si, and/or Ta) coatings have been used for several decades. Research in turbine-blade technology has reported that these coatings rely on the formation of dense and adherent alumina layers to provide high-temperature corrosion resistance against molten salts [14,15]. Because the oxidation of aluminum is self-limiting, high to medium concentrations of chromium are required to help in the formation of thicker protective α -alumina films [16,17]. The formation temperature of α -Al₂O₃ can decrease from 1,200°C to 900°C in alloys containing Cr [18]. Cr₂O₃ forms at the outset of oxidation, and it immediately acts as a nucleus for α -Al₂O₃ from the oxidation of Al atoms at the interface of Cr₂O₃/alloy. Cai et al. determined that a pre-oxidation treatment on Fe–Al alloys air heated for 10 h at 900°C formed a dense and continuous alumina scale [19].

Standard molten carbonate fuel cells operate at 650°C and employ corrosive molten eutectic Li₂CO₃–K₂CO₃. The wet seal of separator plates has been coated with Al-containing coatings to control their corrosion in the molten carbonate. Commercially available atmospheric plasma spray (APS) and high-velocity oxyfuel (HVOF) deposition techniques have been evaluated for this purpose. FeCrAl, and NiAl, as well as a quasi-crystalline alloy AlCoFeCr, were deposited on AISI 310 foils. The coatings were then tested by immersion in a 62 mol.% Li₂CO₃–38 mol.% K₂CO₃ molten carbonate eutectic mixture at 700°C in air by electrochemical impedance spectroscopy (EIS) [20]. On exposure to the molten carbonate mixture, Ni and Fe aluminide coatings developed a LiAlO₂ protective layer [21]. The quasi-crystalline AlCoFeCr as well as FeCrAl exhibited excellent behavior against the molten carbonate. In particular, FeCrAl deposited by HVOF remained unchanged after 1000 h of exposure [20].

Weight-loss corrosion techniques are very accurate but time-intensive. To obtain corrosion rates, more than 500 h of immersion time is usually required [22]. Corrosion in molten salts has been evaluated using electrochemical techniques such as open-circuit potential (OCP) followed by potentiodynamic polarization sweep (PPS) [18] because they can determine instantaneous corrosion rates, process-controlling steps, and the

corrosion mechanisms after a few hours of sample immersion. An electrical potential (E) is established when metallic materials are immersed in ionic molten salts. The OCP is set when this potential reaches the equilibrium under no external applied potential. Because this equilibrium is dynamic, the steady state is determined when the potentials reach a certain stability that is usually for $dE/dt \leq 100\mu\text{V/s}$ [23–26].

After the equilibrium is established, the sample is anodically ($E > \text{OCP}$) and cathodically ($E < \text{OCP}$) polarized. Figure 1 shows a PPS plot of applied potential as a function of current density (I) in mA/cm^2 . The metallic area exposed to the molten salt is used to calculate I . The intersection between the cathodic and anodic Tafel slopes, usually found in the linear portions between -250 mV and $+250\text{ mV}$ relative to the OCP or corrosion potential (E_{corr}) [26], defines the corrosion current density (I_{corr}), which is used to calculate the corrosion rate (CR), in $\mu\text{m/year}$, using the Stern-Geary equation through Faraday's law [23–26]:

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

where K is a constant equal to $3,272 [\mu\text{m}/(\text{A} \cdot \text{cm} \cdot \text{year})]$, EW is the equivalent weight of the alloy (g/mole-e), and ρ is the alloy density (g/cm^3).

The equivalent weight for multicomponent alloys is calculated as follow:

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

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

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.

Fig. 1. Potentiodynamic polarization sweep plot used to calculate the corrosion current density (I_{corr}) using the intersection of Tafel slopes [26].

The current investigation studied the corrosion of conventional alloys in molten carbonate environments and the ability of thermal-sprayed MCrAlX coatings (M: Ni, and/or Co; X: Y, Hf, Si, and/or Ta) to mitigate their corrosion. Electrochemical techniques (OCP followed by PPS) were employed to determine instant corrosion rates after 4 h of sample immersion.

2. Materials and methods

2.1 Preparation of salt mixture

The eutectic salt mixtures (in wt.%) $46.2\text{K}_2\text{CO}_3 - 53.8\text{Na}_2\text{CO}_3$ ($T_e = 709^\circ\text{C}$) and $33.4\text{Na}_2\text{CO}_3 - 34.5\text{K}_2\text{CO}_3 - 32.1\text{Li}_2\text{CO}_3$ ($T_e = 398^\circ\text{C}$) were prepared using ACS-grade anhydrous salts from Alfa Aesar, each with a purity greater than 99 wt.%. The single salts were placed at 120°C in air in a drying oven (DK-42, American Scientific Products) for at least 48 h to ensure low moisture content. The salts were weighed to the proper ratio in 600-g batches and kept in the drying furnace for at least 24 h before complete mixing. To obtain homogeneous eutectic compositions, the salts were mixed in a ball mill with $\frac{1}{4}$ " alumina balls as the mixing media, during 1.5 h. Batches of 125 g were then placed in alumina crucibles, which have shown to be chemically stable in molten carbonates [27], and kept in a vacuum furnace at 120°C for 24 h before pre-melting. To pre-melt the salt mixtures, they were then transferred to a muffle furnace (Vulcan 3-1750). The heating process was the following: i) 300°C for 3 h; ii) heat at $5^\circ\text{C}/\text{min}$ to a temperature of 100°C above the eutectic point (T_e) and keep at that temperature for 1 h. The pre-melted and solidified salt mixtures were stored at 120°C in the vacuum furnace until needed for testing to avoid moisture absorption. Any further purification of the mixture was not used because CSP plants cannot pursue very complicated and expensive mixing and melting procedures of the salts.

2.2 Preparation of alloys and coatings

The bare alloys evaluated for corrosion were: stainless steel (SS) AISI i) 310, ii) 321, and iii) 347; iv) Incoloy 800H (In800H); v) Alumina-forming austenitic (AFA-OC6); and vi) Ni superalloy Inconel (IN) 625. The nominal composition of tested alloys is shown in Table 1. The alloys were machined to 8 mm in diameter and 12 mm in height. After the corrosion results, the two best-performing alloys that showed the lowest corrosion rates were selected as the substrate for coating deposition. The nominal composition of the raw material used for coating deposition is shown in Table 2. Two thermal deposition technologies were employed: HVOF and APS. The difference in composition between raw materials A9 and SPM4 is that Ta is present in A9, and SPM4 contains Hf and Si. It has been reported that hafnium increases adhesion of the oxide layer. Because preliminary corrosion results of the pre-oxidized A9 coating showed promising results, we decided to modify the coatings composition to determine if Hf and Si were able to provide a better coating behavior. Coating SPM4-2667 was selected to be deposited on

In800H to also evaluate the pre-oxidation condition on the integrity of this alloy compared to SS310. The coating's vendor recommended the use of APS to deposit SPM4-2667.

Table 1. Nominal composition of tested bare alloys.

Alloy	Composition [wt.%]							
	Fe	Ni	Cr	C	Mn	Si	Al	other
SS310	~51	20.5	25	0.25	2	1.5		
SS321	~49.8	10.5	18	<0.08	<2	<1		
SS347	~68.5	9.6	17.7	0.05	1.66	0.77		Cu:0.4; Mo:0.4; Co:0.2; Ta:0.021; Nb:0.72
In800H	~46.2	33.2	19.6	0.06	0.8	0.3	0.5	Cu:0.2; Ti: 0.3-0.7
AFA-OC6	~51.9	25	13.8	0.11	1.99	0.13	3.56	Cu:0.5; Mo:0.2; Ti:0.53; W:0.2; Ti:0.05; Nb: 2.5
IN625	5	58	21.5					Mo: 9; Ta: 3.55

AFA-OC6 was provided by Oak Ridge National Laboratory. A commercial version of it may be available from Carpenter Technology Corporation.

Table 2. Nominal composition of commercially available gas atomized raw powders for MCrAlX coatings. Deposition technique (DT): high velocity oxyfuel (HVOF) and atmospheric thermal plasma spray (APS). Substrates are SS310 and In800H.

Coating	DT	T _{Smax} [°C]	Composition [wt.%]					
			Ni	Co	Cr	Al	Y	Other
Amdry 510 (A5)	HVOF	980	66		22	10		2 max.
Amdry 997 (A9)		1050	44.4	22	20.5	8.5	0.6	Ta: 4
Diamalloy 4700 (D4)		850	32	38	21	7.5	0.5	1 max.
Diamalloy 4008NS (D4NS)		800	95			5		
SPM4-2667 (SPM4)	APS	1050	47.6	22	17	12	0.5	Hf: 0.5; Si: 0.4

T_{Smax}: maximum service temperature

Usually, 3 to 5 mm of the cylinders were immersed into the molten salt. Therefore, only the bottom area and about 12 mm of the sides of the cylinders were coated. A coated sample is shown in Fig. 2 as the working electrode (WE). The three-electrode arrangement used to evaluate corrosion is shown. To control the amount of area exposed to corrosion and thus normalize the measured current in the electrochemical tests, bare and coated alloys were progressively polished using SiC abrasive paper up to a 1200 grit, cleaned with deionized water and acetone in ultrasonic baths, and dried with compressed air. Some coatings were pre-oxidized in atmospheric air, before

corrosion exposure, to determine the effect of alumina layers against molten carbonate attack.

The electrical connection required for electrochemical testing was obtained by spot-welding a Ni20Cr wire (0.5-mm diameter) to the top of the specimens. Alumina tubes (3.175-mm diameter) were used for isolating the wire from the molten salt; the union between the tube and the spot-welded area was filled with refractory zirconia-based cement (Fig. 2).

Fig. 2. Three-electrode arrangement (PtCE, pseudo-PtRE, and WE/sample) showing a coated sample.

2.3 Electrochemical corrosion tests

The electrochemical cell experimental setup used in this work is given elsewhere [27]. The electrochemical AISI316L cell (with a quartz liner) was held in a crucible electrical resistance furnace. The three-electrode arrangement (Fig. 2) used is: i) working electrode (WE) as the sample; ii) 0.5-mm-diameter Pt wire as the pseudo reference electrode (pseudo-PtRE), and iii) Pt-gauge spot welded to 0.5-mm-diameter Pt wire for the counter electrode (PtCE). The crucible containing the pre-melted salt was placed in the cell and the three electrodes were aligned. A type-K thermocouple in an alumina well was used near the electrodes to record the test temperature. The electrochemical cell setup was sealed and purged with the carrier gas for about two hours. A total heating process of about 20 h under controlled atmosphere was employed for each test to allow thermal and chemical equilibration of the system with the atmosphere. The off-gas passed through a series of traps to remove hazardous vapors before being vented to local exhaust. After reaching thermal equilibration at the testing temperature (about 1 h), the pseudo-PtRE and the PtCE were immersed into the molten salt and allowed to stabilize for about 60 min. The electrical stability of the couple pseudo-PtRE/PtCE in molten carbonate salts has been reported in previous work to be reached around 45 to 60 min [27]. Then, the WE was immersed and its potential was recorded as a function of time to determine the OCP. The corrosion evaluations were performed using a potentiostat (AUTOLAB-PGSTAT302N).

The OCP was established when $dE/dt \leq 100 \mu\text{V/s}$ was obtained. PPS was conducted immediately after by applying cathodic (–) and anodic (+) polarization from – 0.4 V to +0.4 V around the OCP 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. I_{corr} was determined using the Tafel slopes' intersection and CR was calculated using Eqs. (1) to (3).

2.4 Sample characterization

After the electrochemical corrosion data were obtained, the electrodes were raised above the molten salt and the furnace was turned off to cool. The WE was removed and metallographically prepared for characterization. Top surface and cross-section analyses were performed using an environmental scanning electron microscope (ESEM). Chemical analysis of the samples was performed using energy-dispersive X-ray spectrometry (EDX). Further oxalic acid electroetching, described in standard ASTM B162 [28], was used to reveal the substrate's microstructure. This was performed to determine if chromium carbide precipitation occurred, which could represent a condition of the austenitic stainless-steel sensitization.

3. Results and discussion

3.1 Corrosion tests

PPS curves of the alloys in molten $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ (Na,K– CO_3) at 750°C in N_2 atmosphere are shown in Fig. 3a. The alloys appear to be exhibiting active corrosion in which the specimen is degrading across all applied potentials. Passivation, which occurs when the alloy forms a protective oxide film and the current (usually lower than I_{corr}) remains stable during a large potential region, is most likely absent from the samples.

AFA-OC6 is an alumina-forming alloy with 3.56 wt.% Al and should be able to form alumina layers during corrosion, so it was allowed to corrode at higher anodic overpotentials (to +0.6 V) to determine if passivation occurs. Its PPS curve is shown in Fig. 3b. The second peak (a drop in current in the anodic branch) that appears at higher positive overpotentials indicates the tendency to form a protective scale. Similar PPS curves were obtained with the MCrAlX coatings.

After using the NOVA 1.10 software for data analysis of the PPS plots, the Tafel slopes and corrosion rates were calculated. Corrosion of alloys is reported in Table 3. The corrosion rates of the alloys in molten Na,K– CO_3 at 750°C increased in the following order: In800H < SS310 < AFA-OC6 < SS347 < IN625 < SS321. The corrosion resistance of the iron-based alloys is probably proportionate to the alloys' nickel composition: the higher the nickel content, the higher the corrosion resistance and the lower the corrosion rate. The most corrosion-resistant alloy was In800H (corrosion rate

of $1,080 \pm 40$ $\mu\text{m}/\text{year}$), which has the highest nickel content of 33 wt.% among the tested steels. The worst-performing alloy was SS321 (lowest nickel content of 9 wt.%) with a corrosion rate of $4,640 \pm 38$ $\mu\text{m}/\text{year}$. Spiegel et al. also observed a high corrosion rate in low-alloy steels in molten $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ [29]. It is interesting that nickel superalloy IN625 has a higher corrosion rate than the steel alloys in the molten Na-K carbonate. IN625 has a very low amount of iron and the highest amount of nickel (> 58 wt.%) of all the tested alloys. It seems that the corrosion mechanism of the nickel superalloys is different. Further testing and metallographic characterization are required to study the nature of the corrosion products and to determine the corrosion mechanisms.

Fig. 3. Electrochemical PPS curves for: (a) tested alloys in molten K_2CO_3 – 53.82 wt% Na_2CO_3 at 750°C in N_2 atmosphere vs. pseudo-PtRE, and (b) AFA-OC6 polarized at higher anodic overpotentials.

Table 3. Corrosion rates (CR) of tested alloys in molten K_2CO_3 – 53.82 wt% Na_2CO_3 at 750°C in N_2 atmosphere vs. pseudo-PtRE. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}).

Alloy	E_{corr} , mV	I_{corr} , $\mu\text{A}/\text{cm}^2$	CR _{Alloy} , $\mu\text{m}/\text{year}$
SS310	-334 ± 91	149 ± 7	$1,530 \pm 80$
SS321	-129 ± 30	440 ± 36	$4,640 \pm 380$
SS347	-451 ± 98	224 ± 37	$2,360 \pm 390$
In800H	-449 ± 70	105 ± 3	$1,080 \pm 40$
AFA-OC6	-656 ± 196	173 ± 49	$1,750 \pm 490$
IN625	-330 ± 80	272 ± 62	$2,600 \pm 590$

Using this preliminary corrosion data, In800H and SS310 were selected as the substrate alloys for the coatings deposition. Table 4 and Fig. 4 show the corrosion of substrate alloys and coatings (in as-deposited and pre-oxidized conditions) in eutectic $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 - \text{Li}_2\text{CO}_3$ (Na,K,Li- CO_3). The substrates were corroded at different temperatures in N_2 and bone-dry CO_2 atmospheres to evaluate their effect in corrosion.

Table 4. Corrosion rates (CR) of substrate alloys and coatings (in as-deposited and pre-oxidized conditions) in eutectic $\text{Na}_2\text{CO}_3 - 34.55 \text{ wt}\% \text{ K}_2\text{CO}_3 - 32.14 \text{ wt}\% \text{ Li}_2\text{CO}_3$ ($T_e = 398^\circ\text{C}$) at different temperatures and carrier gases. HVOF: high-velocity oxyfuel; APS: atmospheric thermal plasma spray.

Substrate/ Deposition/Coating	Condition	CR _{alloy} , $\mu\text{m}/\text{year}$
In800H	$\text{N}_2(\text{g})$, 600°C	451 ± 156
	bone dry- $\text{CO}_2(\text{g})$, 650°C	990 ± 82
	bone dry- $\text{CO}_2(\text{g})$, 700°C	$2,577 \pm 273$
SS310	$\text{N}_2(\text{g})$, 600°C	632 ± 20
	bone dry- $\text{CO}_2(\text{g})$, 650°C	589 ± 29
	bone dry- $\text{CO}_2(\text{g})$, 700°C	2,456
SS310 / HVOF / A9: NiCoCrAlTaY	bone dry- $\text{CO}_2(\text{g})$, 700°C	687 ± 152
	bone dry- $\text{CO}_2(\text{g})$, 700°C , Ox: air, 800°C , 24hr, $0.5^\circ\text{C}/\text{min}$	512
SS310 / HVOF / A5: NiCrAl	bone dry- $\text{CO}_2(\text{g})$, 700°C	344 ± 124
SS310 / HVOF / D4: CoNiCrAlY	bone dry- $\text{CO}_2(\text{g})$, 700°C	228 ± 9
	bone dry- $\text{CO}_2(\text{g})$, 700°C , Ox: air, 800°C , 24h, $0.5^\circ\text{C}/\text{min}$	46
In800H / APS / SPM4: NiCoCrAlHfSiY	bone dry- $\text{CO}_2(\text{g})$, 700°C	$1,150 \pm 42$
	bone dry- $\text{CO}_2(\text{g})$, 700°C , Ox: air, 900°C , 24h, $0.5^\circ\text{C}/\text{min}$	34

Degradation of alloys in N_2 and bone-dry CO_2 is similar. No conclusion can be provided for the effect of the atmosphere. Further corrosion evaluation of the coatings was performed using CO_2 as the carrier gas because it is known that this atmosphere could increase the stability of molten carbonates [4]. Similar corrosion rates ($\sim 600 \mu\text{m}/\text{year}$) for SS310 are obtained in the temperature range of 600°C to 650°C . The corrosion of In800H doubled when the temperature increased from 600°C to 650°C from $451 \pm 156 \mu\text{m}/\text{year}$ to $990 \pm 82 \mu\text{m}/\text{year}$, respectively. At 700°C a dramatic increase in the corrosion rate occurred. In800H corroded at $2,577 \mu\text{m}/\text{year}$ and SS310 at $2,456 \mu\text{m}/\text{year}$. Because CSP plants require a lifetime of 30 years or more, corrosion mitigation approaches must be determined to obtain corrosion rates in the order of tens of micrometers per year. The corrosion rates obtained in bare alloys shows that understanding the fundamentals of corrosion mechanisms in molten salts is imperative for finding ways to protect materials from the attack of these fluids at high temperatures.

Fig. 4. Corrosion rates of bare and coated alloys in $\text{Na}_2\text{CO}_3 - 34.55 \text{ wt}\% \text{K}_2\text{CO}_3 - 32.14 \text{ wt}\% \text{Li}_2\text{CO}_3$ in bone-dry CO_2 and N_2 atmospheres. Data from Table 4.

Two coatings after pre-oxidation treatment had very low corrosion rates. Coating Diamalloy 4700 (wt. %: 38.5Co-32Ni-21Cr-8Al-0.5Y) deposited using HVOF and pre-oxidized (air, 800°C, 24 h, 0.5°C/min) corroded at 46 $\mu\text{m}/\text{year}$. Coating SPM4-2667 (wt. %: 47.6Ni-22Co-17Cr-12Al-0.5Hf-0.4Si-0.5Y) deposited using APS and pre-oxidized (air, 900°C, 24 h, 0.5°C/min) had the lowest corrosion rate of 34 $\mu\text{m}/\text{year}$. This decrease in the corrosion rate is likely associated to the formation of protective oxide scales that act as barriers, separating the metal substrate from the corrosive environment. These results are very promising and show that the degradation of alloys in a molten carbonate HTF can be controlled by depositing coatings that form protective oxides that passivate the coating's surface.

It seems that Hf and Si (in SPM4-2667) have a better corrosion resistance against molten carbonates than Ta, which is present in the A9 coating. Both coatings have similar composition except for containing Ta, Hf, and Si. Based on vendor's recommendation, SPM4-2667 was deposited using APS in which usually higher deposition temperatures are obtained. Further evaluation should be performed to determine the best deposition parameter to increase the corrosion resistance of the two best down-selected coatings.

The best-performing coating, pre-oxidized SPM4-2667 (NiCoCrAlHfSiY), was cross-sectioned and prepared for metallographic characterization. Results of light microscopy (LM) characterization are shown in Fig. 5. The coating NiCoCrAlHfSiY deposited on In800H with a thickness of 700–800 μm appeared well adhered and essentially free of fissures or cracks (see Fig. 5a). The coating was characterized by a relatively low

density of equiaxed pores. These pores are not connected, so they are not expected to cause a problem during exposure to the molten carbonate. The coating is characterized by dark wavy or swirly oxide scales associated with sprayed particles (see Fig. 5b). Close scrutiny of the light-contrasted constituent of the coating indicates a multi-phase microstructure. In addition, there appears to be a layer (35 μm) of internal precipitation in the substrate beneath the coating, in the coating/substrate interface (see Fig. 5c).

Fig. 5. Light-microscopy (LM) images of unetched NiCoCrAlHfSiY coating on In800H substrate exposed to molten carbonates: (a) low magnification showing carbonate solidified scale; (b) higher LM magnification showing both coating/solidified-scale and coating/substrate interfaces and some non-connected porosity; and (c) detail for higher magnification of (b) at the coating/substrate interface.

Electron microscopy using ESEM coupled with EDS for elemental analysis was also performed to characterize the sample at much higher resolution. EDS analyses are summarized in a table in Fig. 6c and the locations of analyses are indicated on the images. The chemical composition of NiCoCrAlHfSiY was confirmed via EDS. The presence of spheroidal porosity (not connected) in the coating was confirmed via ESEM. The carbonate scale/coating interface is extremely flat, with no indication of relatively coarse pitting or corrosion attack. The metallographic characterization showed that the sample was stable against corrosion in molten Na,K,Li- CO_3 at 700°C and the pores did not allow the penetration/permeation of the molten salt (Figs. 6a and 6b). The particle oxide scales were again confirmed as aluminum oxide via EDS. An $\sim 3\text{-}\mu\text{m}$ -thick aluminum oxide layer exists on the flat outer surface of the coating (2cEDS in Fig. 6b).

The presence of a layer of fine precipitates at the coating/substrate interface is confirmed via SEM (see Fig. 7). The precipitates (Pptn zone in Fig. 7a) are rod- or needle-like and polyhedral in morphology. EDS analyses (6a- and 6b-EDS in Fig. 7d) indicate that they could be AlN. The source of N is unknown, but it seems likely that it could be from the substrate. Analysis of the coating region (6c-EDS) is consistent with the coating's chemical composition. Also, the analysis of the substrate was consistent with the elemental analysis reported in 6d-, 6-e, and 6f-EDS. Comparing these analyses among different phases, it appears that the region in the vicinity of the interface is consistent with interdiffusion of Al, Fe, and Co from the substrate and the coating (Fig.

7b). Coarse alumina particles are also present in the interface. The coating/substrate interface appears intact all along its length.

Fig. 6. Coating NiCoCrAlHfSiY near interface with carbonate scale. (a) SE-SEM, (b) BSE-SEM, (c) EDS.

Fig. 7. Coating NiCoCrAlHfSiY near interface with substrate. (a) BSE-SEM, (b) detail of (a)Pptn area, (c) BSE-SEM of multi-phase microstructure of SPM4-2667 coating, and (d) EDS elemental analysis.

The multi-phase microstructure (7aEDS) within the light constituent (7bEDS) of the coating particles is characterized by coarse light and dark BSE phases (Figs. 7c and 67d). The dark phase (7aEDS) is Al- and Ni-rich and Cr- and Co-poor and vice versa for the light phase (7bEDS). The dark phase could be an unreacted β -phase and the light-phase γ solid solution.

Oxalic acid electroetching revealed the microstructure of SS310 and In800H substrate (Figs. 8 and 9, respectively). Heavy and continuous etching or "ditching" of the grains and twin boundaries and deformation bands was revealed. Boundary ditching generally occurs because the microstructure has been sensitized by precipitation of Cr-rich carbides at the boundary. Sensitization occurs because this precipitation leaves the steel matrix locally depleted in Cr in areas near the grain boundaries. This sensitized condition has been reported to likely produce intergranular corrosion in aqueous acid solutions [30,31]. Sensitization is likely with relatively high C levels in the steel and a sufficiently long time in the temperature range of 700°C to 900°C. A long time can also be associated with slow cooling in the same temperature range. 310SS has a relatively high maximum carbon content of 0.25 wt%, compared to other 300-series stainless steels. It is also possible that sensitization occurred during coating deposition or pre-treatment.

Fig. 8. LM image of SS310 microstructure near coating/substrate interface showing sensitized structures with precipitation at deformation bands, 10% oxalic acid electroetching. (a) Lower magnification, and (b) higher magnification showing recrystallization and grain growth.

Even though In800H has a much lower C concentration, this alloy also showed a sensitized matrix (Fig. 9). The grain boundaries of an equiaxed grain structure, as well as an intragranular deformation structure of slip lines and deformation bands, has been subjected to heavy precipitation of Cr carbides. In addition, a relatively precipitate-free zone (PFZ) (125 μm) exists at the interface with the coating. The PFZ could be due to diffusional depletion of Cr in this region. A thin layer of fine recrystallized grains (35 μm)

exists at the coating interface. It is likely that a deformed substrate surface prior to coating was recrystallized during coating.

Fine-scale microstructural features have been produced in the immediate vicinity of the coating/steel interface (Figs. 8b and 9b). Fine-scale microstructure at the interface is associated with a layer of localized deformation that has apparently undergone recrystallization to produce a layer of very fine grains and some grain growth immediately at the interface. The deformation in the vicinity of the interface was produced by sand-blasting pre-treatment of 310SS required to facilitate coating adhesion. The fine recrystallized grain structure at the interface appears to have been facilitated by precipitate pinning of grain boundaries.

Fig. 9. LM image of In800H substrate near coating/substrate interface, 10% oxalic acid electroetching. (a) lower magnification, (b) higher magnification of (a).

The pre-oxidation processing has left the stainless-steel substrates in a condition that, if exposed to aqueous acid solutions, will likely produce intergranular corrosion. This type of localized corrosion of sensitized alloys in molten salts has not been reported. Because of this lack of information, more evaluations will be required if these alloys are employed in high-temperature molten salt CSP applications in the temperature range of 700°C to 900°C.

4. Conclusions

Alloys SS310 and In800H were selected as the substrates to be coated with Ni-based coatings. Their corrosion rates in molten carbonates, the high mechanical resistance, and low cost were considered in down-selecting them as the alloys of special interest for CSP applications. The corrosion rates obtained in bare alloys show that understanding the fundamentals of corrosion mechanisms in molten salts is imperative for finding ways to protect materials from the attack of these fluids at high temperatures.

Ni-based MCrAlX coatings are able to protect common alloys (SS310 and In800H) from the attack of molten carbonates ($\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--Li}_2\text{CO}_3$) in bone-dry CO_2 atmosphere at 700°C . Two pre-oxidized coatings reduced the corrosion rates in two orders of magnitude from $\sim 2,500\text{ }\mu\text{m/year}$ to only a few tens of micrometers per year. The best-performing coating was SPM4-2667 (wt. %: 47.6Ni-22Co-17Cr-12Al-0.5Hf-0.4Si-0.5Y) deposited using APS and pre-oxidized (air, 900°C , 24 h, 0.5°C/min) with a corrosion rate of $34\text{ }\mu\text{m/year}$. The second-best coating was Diamalloy 4700 (wt. %: 38.5Co-32Ni-21Cr-8Al-0.5Y) deposited using HVOF and pre-oxidized (air, 800°C , 24 h, 0.5°C/min) with a corrosion rate of $46\text{ }\mu\text{m/year}$.

From metallographic characterization, we concluded that this decrease in the corrosion rate is likely associated with the formation of protective oxide scales that act as barriers, separating the metal substrate from the corrosive environment. These results are very promising and show that the degradation of alloys in a molten carbonate HTF or TES fluid can be controlled by depositing coatings that can form protective oxides that passivate the coating's surface.

Thermal sprayed coatings presented some internal porosity due to the nature of powder thermal spray processes. The porosity was not open or interconnected, which means that it did not participate in the permeation of molten salts through the metallic substrate once the pores are exposed to the fluid.

Because of the sensitization of the substrates SS310 and In800H, further studies should be carried on these alloys if their use is considered for high-temperature application in the range of 700°C to 900°C .

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Tables' captions

Table 1. Nominal composition of tested bare alloys.

Table 2. Nominal composition of commercially available gas atomized raw powders for MCrAlX coatings. Deposition technique (DT): high-velocity oxyfuel (HVOF) and atmospheric thermal plasma spray (APS). Substrates are SS310 and In800H.

Table 3. Corrosion rates (CR) of tested alloys in molten $K_2CO_3 - 53.82 \text{ wt\% } Na_2CO_3$ at 750°C in N_2 atmosphere vs. pseudo-PtRE. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}).

Table 4. Corrosion rates (CR) of substrate alloys and coatings (in as-deposited and pre-oxidized conditions) in eutectic $Na_2CO_3 - 34.55 \text{ wt\% } K_2CO_3 - 32.14 \text{ wt\% } Li_2CO_3$ ($T_e = 398^\circ\text{C}$) at different temperatures and carrier gases. HVOF: high-velocity oxyfuel; APS: atmospheric thermal plasma spray.

Table 1.

Alloy	Composition [wt.%]							other
	Fe	Ni	Cr	C	Mn	Si	Al	
SS310	~51	20.5	25	0.25	2	1.5		
SS321	~49.8	10.5	18	<0.08	<2	<1		
SS347	~68.5	9.6	17.7	0.05	1.66	0.77		Cu:0.4; Mo:0.4; Co:0.2; Ta:0.021; Nb:0.72
In800H	~46.2	33.2	19.6	0.06	0.8	0.3	0.5	Cu:0.2; Ti: 0.3-0.7
AFA-OC6	~51.9	25	13.8	0.11	1.99	0.13	3.56	Cu:0.5; Mo:0.2; Ti:0.53; W:0.2; Ti:0.05; Nb: 2.5
IN625	5	58	21.5					Mo: 9; Ta: 3.55

AFA-OC6 was provided by Oak Ridge National Laboratory. A commercial version of it may be available from Carpenter Technology Corporation.

Table 2.

Coating	DT	T _{smax} [°C]	Composition [wt.%]					
			Ni	Co	Cr	Al	Y	Other
Amdry 510 (A5)	HVOF	980	66		22	10		2 max.
Amdry 997 (A9)		1050	44.4	22	20.5	8.5	0.6	Ta: 4
Diamalloy 4700 (D4)		850	32	38	21	7.5	0.5	1 max.
Diamalloy 4008NS (D4NS)		800	95			5		
SPM4-2667 (SPM4)	APS	1050	47.6	22	17	12	0.5	Hf: 0.5; Si: 0.4

T_{smax}: maximum service temperature

Table 3.

Alloy	E_{corr} , mV	I_{corr} , $\mu\text{A}/\text{cm}^2$	CR_{Alloy} , $\mu\text{m}/\text{year}$
SS310	-334 ± 91	149 ± 7	$1,530 \pm 80$
SS321	-129 ± 30	440 ± 36	$4,640 \pm 380$
SS347	-451 ± 98	224 ± 37	$2,360 \pm 390$
In800H	-449 ± 70	105 ± 3	$1,080 \pm 40$
AFA-OC6	-656 ± 196	173 ± 49	$1,750 \pm 490$
IN625	-330 ± 80	272 ± 62	$2,600 \pm 590$

Table 4.

Substrate/ Deposition/Coating	Condition	CR _{alloy} , μm/year
In800H	N ₂ (g), 600°C	451 ± 156
	bone dry-CO ₂ (g), 650°C	990 ± 82
	bone dry-CO ₂ (g), 700°C	2,577 ± 273
SS310	N ₂ (g), 600°C	632 ± 20
	bone dry-CO ₂ (g), 650°C	589 ± 29
	bone dry-CO ₂ (g), 700°C	2,456
SS310 / HVOF / A9: NiCoCrAlTaY	bone dry-CO ₂ (g), 700°C	687 ± 152
	bone dry-CO ₂ (g), 700°C, Ox: air, 800°C, 24 h, 0.5°C/min	512
	bone dry-CO ₂ (g), 700°C	344 ± 124
SS310 / HVOF / D4: CoNiCrAlY	bone dry-CO ₂ (g), 700°C	228 ± 9
	bone dry-CO ₂ (g), 700°C, Ox: air, 800°C, 24 h, 0.5°C/min	46
	bone dry-CO ₂ (g), 700°C	1,150 ± 42
In800H / APS / SPM4: NiCoCrAlHfSiY	bone dry-CO ₂ (g), 700°C	1,150 ± 42
	bone dry-CO ₂ (g), 700°C, Ox: air, 900°C, 24 h, 0.5°C/min	34
	bone dry-CO ₂ (g), 700°C	34

Figures' captions

- Fig. 1. Potentiodynamic polarization sweep plot used to calculate the corrosion current density (i_{corr}) using the intersection of Tafel slopes [26].
- Fig. 2. Three-electrode arrangement (PtCE, pseudo-PtRE, and WE/sample) showing a coated sample.
- Fig. 3. Electrochemical PPS curves for: (a) tested alloys in molten K_2CO_3 – 53.82 wt% Na_2CO_3 at 750°C in N_2 atmosphere vs. pseudo-PtRE, and (b) AFA-OC6 polarized at higher anodic overpotentials.
- Fig. 4. Corrosion rates of bare and coated alloys in Na_2CO_3 – 34.55 wt% K_2CO_3 – 32.14 wt% Li_2CO_3 in bone-dry CO_2 and N_2 atmospheres. Data from Table 4.
- Fig. 5. Light-microscopy (LM) images of unetched NiCoCrAlHfSiY coating on In800H substrate exposed to molten carbonates: (a) low magnification showing carbonate solidified scale; (b) higher LM magnification showing both coating/solidified-scale and coating/substrate interfaces and some non-connected porosity; and (c) detail for higher magnification of (b) at the coating/substrate interface.
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