Corrosion of steel alloys in eutectic NaCl + Na$_2$CO$_3$ at 700 °C and Li$_2$CO$_3$ + K$_2$CO$_3$ + Na$_2$CO$_3$ at 450 °C for thermal energy storage

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ABSTRACT

Stainless steel 316, duplex steel 2205 and carbon steel 1008 were examined for compatibility with the eutectic mixtures of NaCl + Na$_2$CO$_3$ at 700 °C and Li$_2$CO$_3$ + K$_2$CO$_3$ + Na$_2$CO$_3$ at 450 °C in air for thermal energy storage. Electrochemical measurements combined with advanced microscopy and microanalysis techniques were employed. Oxidation was found as the primary attack in both molten salt environments. However, the availability of O$_2$ controlled the degree of oxidation. Alloy 316 showed the lowest corrosion current densities in each molten salt owing to the formation of films on the surface. The attack morphology on the surface of all materials was uniform corrosion with no localized degradation at 450 °C. Microscopy observations showed grain boundary oxidative attack as the primary corrosion mechanism for all studied alloys at 700 °C with depletion of alloying elements from grain boundaries in alloys 316 and 2205. The protective nature of austenite phase reduced selective oxidation of the underlying ferrite layers of alloy 2205 in chloride carbonate at 700 °C.

1. Introduction

Recent interest in increasing plant efficiency requires improved compatibility between structural alloys and molten salts for Thermal Energy Storage (TES) used in Concentrated Solar Thermal (CST) power plants [1–3]. Hot corrosion and oxidation from retained storage media (molten salts) as Phase Change Materials (PCM) causes significant deterioration to containment materials used in TES systems [1–14]. Whilst steel alloys are considered as economic candidates for containment materials in TES systems, eutectic compositions of molten chlorides, nitrates, carbonates and fluorides are favorite candidates as storage medium [15–20]. Oxyanions like carbonates have recently attracted more attention not only owing to their great heat capacity, but also for their high energy density and less corrosive behavior compared to traditional chlorides [2,21]. Even the mixture of carbonate and chloride have been reported to be less corrosive than pure chlorides [21].

The compatibility of structural alloys with molten salts depends on the metal's potential for oxidation, passivating nature and the solubility of corrosion products in the salt [22]. In steel alloys, scaling rate depends on three variables: steel chemistry, temperature and atmosphere [23]. Based on the working temperature low-alloyed carbon steels, Cr-Mo steels and Cr-Ni stainless steels might be employed in combination with molten salts [10]. Groll et al. [24] reported intergranular corrosion of steel alloys in contact with molten chloride salts

at temperatures up to 420 °C. Other studies confirm that intergranular attack in Fe-Ni-Cr alloys is more severe than metal loss in molten chlorides [21]. Ferritic steel has shown to oxidize more easily than austenitic steel in hot chloride containing atmospheres [25]. However, recent research on a group of metal alloys also showed acceptable resistance of stainless steel 310 to molten carbonate salts at 750 °C [2]. Steel alloys with around 20 wt% Cr and/or high nickel content show a greater resistance to high-temperature corrosion [23,26].

The stability of oxide layer should also be taken into consideration when using carbon or stainless steels. Most metals oxidize over a wide range of conditions at elevated temperatures. Thus, oxidation rate and morphology are of importance to determine the material lifetime. Corrosion resistance in many high-temperature environments is achieved by the formation of a protective oxide film on the material surface [27]. An early study by Azzi et al. [28] showed that the corrosion rate of iron in molten carbonate is limited by the diffusion of oxidizing species through the corrosion products rather than in the melt; where FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ were determined as the general corrosion products formed on the material surface. Hot corrosion behavior of steel alloys in molten Li$_2$CO$_3$-K$_2$CO$_3$ showed the formation of a porous layer composed of Fe$_2$O$_3$ and LiFe$_5$O$_8$ on the material surface [29]. However, the usually thick Fe$_2$O$_3$ layer has shown not to be protective in molten salt environments [30]. Al and Si also contribute to the development of self-healing protective oxide films on the alloy surface acting as diffusion barriers against further oxida-

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Table 1
Nominal elemental composition and crystal structure of the studied alloys (wt%).

Alloy	Structure	Fe	Ni	Cr	C	Mo	Mn	S	P
SS316	fcc	Bal	12	17.5	0.05	3	...	...	...
DS2205	fcc/bcc	Bal	6.5	23	0.03	3.5	...	...	...
CS1008	bcc	Bal	...	...	0.14	...	0.5	0.04	0.04

tion [15]. Cr and Al oxides have also proved to be more stable than those of iron and thus Cr_2O_3 and Al_2O_3 are thermodynamically favored [31].

The compatibility of containment material with molten salt and its stability is a concerning issue in TES systems [8]. The selection of appropriate and optimum structural materials as Thermal Energy Storage vessel, subject to corrosive molten salts as PCM and high temperature atmospheres, is essential in developing economic and functionally efficient systems. This study will examine the corrosion behavior of three commercial steel alloys in two eutectic mixtures of molten salts for the next generation of TES applications.

2. Experimental procedure

Austenitic stainless steel 316 (SS316), ferritic carbon steel 1008 (CS1008) and ferritic/austenitic duplex steel 2205 (DS2205) were examined in two eutectic mixtures of molten salts. Table 1 summarizes the structures and nominal compositions of the alloys used in the current study.

Sodium carbonate anhydrous LR (CAS No. 497-19-8), sodium chloride AR (CAS No. 7647-14-5), potassium carbonate anhydrous LR (CAS No. 584-08-7) and lithium carbonate 99% (CAS No. 554-13-2) were placed for 24 h in a 180 °C furnace to dry and then were measured and mixed according to Table 2. The eutectic mixtures melting points and test temperatures are also provided in the table. Test temperature for each salt was selected close to its melting point based on the assumption that the salt will be used as a PCM in a CST plant.

2.1. Electrochemical corrosion investigation

Electrochemical experiments were conducted using a three-electrode cell containing the molten salts in alumina crucibles open to air at 700 °C and 450 °C in a preheated cylindrical furnace. Test coupons of 25 mm long, 5 mm wide and 1.4 mm thick were mechanically wet ground and polished down to 0.04 μm by colloidal silica, washed with ethanol and dried in air. Measurements were implemented by means of a VMP3-based BioLogic instrument controlled by EC-Lab® software. The three-electrode cell was implemented with the polished sample as the working electrode and two same sized platinum sheets ($25 \times 5 \times 1$ mm) as pseudo reference and counter electrodes [33–36]. Samples were subjected to open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements in this order to avoid sample deterioration. Equilibrations of potentials (OCP) were carried out for 1 h immediately after immersion. EIS measurements were then obtained using a frequency range of 100 kHz–100 mHz with the amplitude of ± 10 mV. Finally, PDP was conducted at the potential scan rate of 10 mV/min and potential range

Table 2
Chemical composition, melting point and test temperature of salt mixtures.

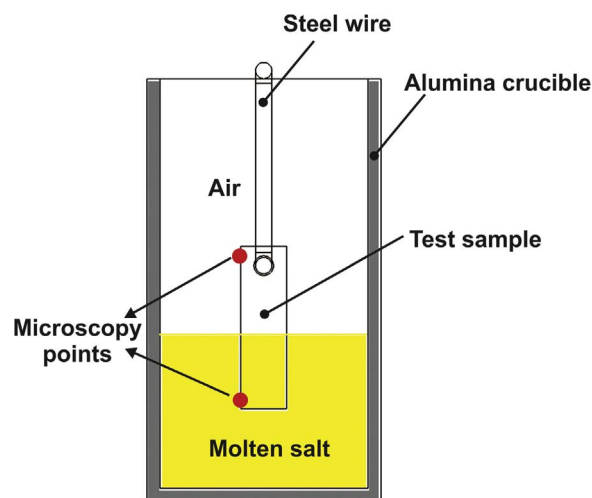| Salt mixture	Composition (wt%)	Melting point (°C) [32]	Test temperature (°C)
Chloride carbonate	40 NaCl + 60 Na_2CO_3	632	700
Ternary carbonate	33.4 Na_2CO_3 + 32.1 Li_2CO_3 + 34.5 K_2CO_3	397	450

Fig. 1. Schematic of the corrosion vessel and a sample inside the furnace.

of -400 to $+500$ mV with respect to the open circuit potential. ZFit analysis of EC-Lab software was used to fit successive impedance cycles.

2.2. Static corrosion

Fresh metal coupons were cut to around $25 \times 7 \times 1.4$ mm for static corrosion tests while the front sides were mechanically wet polished down to 1 μm in colloidal silica using standard grinding and polishing procedures. A schematic representation of the test condition and alignment of samples in the furnace is shown in Fig. 1. Cylindrical alumina crucibles were used as salt vessels and the furnace temperature was set to 700 ± 10 °C for chloride carbonate and 450 ± 10 °C for ternary carbonate.

The salt containing vessels were placed into the furnace at room temperature and then gradually heated up to the test temperature. Once the salt melted and the chamber conditions stabilized, the metal coupons were immersed so that the top half was exposed to the air and bottom half submerged into the molten salt. Such a configuration enabled us to make a comparison not only between the impact of the salt and that of the oxygen from the environment, but also the decomposition gases of the salt which are expected to increase the corrosive impact in this atmosphere. Metal coupons were removed after 120 h of exposure. All coupons were then mounted exposing the side indicated in Fig. 1 into a conductive resin, ground and polished down to 0.04 μm from the side of the sample in colloidal silica using standard procedures, washed with ethanol and finally dried in air. Microscopy points in Fig. 1 provide us with a view of the material close to the polished side. It is worthy to note that although 120 h does not seem long enough to study corrosion rate and related phenomena, aggressive nature of molten salts makes studying short-term impacts like attack morphology and corrosion mechanisms possible.

2.3. Metallography samples

Small coupons of each alloy were selected and mechanically wet ground and polished down to 0.04 μm by colloidal silica, washed with ethanol and finally dried in air. These coupons were used to study the corroded metal morphology and short-term impacts of the molten salts on the microstructure. The coupons were submerged into the molten salts for only 3 min and then were ultrasonically cleaned for 15 min in demineralized water for corrosion product residues to be removed from the surface. The samples were then studied under an optic microscope from the surface.