



Corrosion of stainless steel 316 in eutectic molten salts for thermal energy storage

Madjid Sarvghad*, Theodore A. Steinberg, Geoffrey Will

Science and Engineering Faculty, Queensland University of Technology (QUT), Queensland 4001, Australia

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ABSTRACT

Stainless steel 316 was examined for compatibility with the eutectic mixtures of NaCl + Na₂CO₃ and NaCl + Na₂SO₄ at 700 °C and Li₂CO₃ + K₂CO₃ + Na₂CO₃ at 450 °C in air for thermal energy storage. Electrochemical measurements combined with advanced microscopy and microanalysis techniques were employed. NaCl + Na₂CO₃ was found as the most aggressive salt at 700 °C. The attack morphology on the surface was uniform corrosion with no localized degradation at 450 °C. Microscopy observations showed grain boundary oxidative attack as the primary corrosion mechanism at 700 °C with depletion of alloying elements from grain boundaries.

1. Introduction

Thermal Energy Storage (TES) is a critical component in Concentrated Solar thermal Power (CSP) plants through providing dispatchability and increasing the capacity factor of the plant (Liu et al., 2016, 2012; Gomez-Vidal et al., 2016; Gomez-Vidal and Morton, 2016). To fulfil the recent interests in raising the working temperature of these plants, considerable improvement in material compatibility between the containment material (tank) and storage medium is a prerequisite (Kuravi et al., 2013; Cabeza et al., 2015; Kenisarin, 2010; Sarvghad et al., 2018b). Some TES systems employ eutectic mixtures of molten salts with high thermal capacity as Phase Change Materials (PCM) to store the thermal energy (Gomez, 2011; Bauer et al., 2013; Sarvghad et al., 2017a).

Steel alloys, as economic candidates for containment materials, are subject to hot corrosion and oxidation from the molten media in TES systems (Gomez-Vidal et al., 2016; Gomez-Vidal and Morton, 2016; Kuravi et al., 2013; Cabeza et al., 2015; Kenisarin, 2010; Gomez, 2011; Bauer et al., 2013; Sarvghad et al., 2017a; Guo et al., 2015; Lovegrove and Csiro, 2012; Lovegrove and Pye, 2012; Federsel et al., 2015; Mehrabadi et al., 2016; Sridharan and Allen, 2013; Olson, 2009; Olson et al., 2009; Rebak, 2011, 2008; Ruiz-Cabañas et al., 2016). Molten eutectic mixtures of carbonate, chloride-carbonate, and chloride-sulfate salts are also considered as PCM candidates that provide high heat capacity and energy density (Gomez-Vidal et al., 2016; Molten Salt Corrosion, 2007). The solubility of corrosion products and oxidation potential of the alloy are key factors that affect compatibility between the containment material and molten medium (Sohal et al., 2010). In

steel alloys, the development of protective oxides on the material surface promotes resistance against corrosion where the material chemistry, temperature and atmosphere determine the scaling rate (Young, 2008a; Khanna, 2002). However, in molten salts, protective layers consisting of components like chromium oxide are often dissolved into the salt mixture by fluxing. Once the oxide film is removed, the least noble constituent of the exposed metal will be attacked (Sohal et al., 2010; Lantelme and Groult, 2013; Sarvghad et al., 2017b). For example, the corrosion of Fe-based alloys at 450 °C in ZnCl₂-KCl was shown to be due to the separation and spallation of the oxide films (Li et al., 2003).

Intergranular corrosion of steel alloys in contact with molten chloride and chloride-carbonate salts has been reported previously (Sarvghad et al., 2017b; Groll et al., 1990). Other studies confirm that intergranular attack in Fe-Ni-Cr alloys is more severe than metal loss in molten chlorides (Molten Salt Corrosion, 2007). Depletion of Cr from grain boundaries in molten salts has been commonly identified as a key corrosion mechanism in various molten salts for high Cr alloys (Sarvghad et al., 2017a,b; Gomez-Vidal and Tirawat, 2016; Sarvghad et al., 2017c). However, recent research showed acceptable resistance of stainless steel 310 to molten carbonate salts at 750 °C (Gomez-Vidal et al., 2016). Generally, steel alloys with around 20 wt% Cr and/or high nickel content show a greater resistance to high-temperature corrosion (Young, 2008a; Schütz et al., 2015).

This study will examine the compatibility of stainless steel 316, as TES vessel, with some eutectic mixtures of molten salts, as PCM, for the purpose of developing economic and functionally efficient CSP systems.

* Corresponding author.

E-mail address: madjid.sarvghadmoghaddam@hdr.qut.edu.au (M. Sarvghad).

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Table 1
Chemical composition, melting point and test temperature of the salt mixtures.

Eutectic salt mixture	Composition (wt%)	Melting point (°C) <i>Collection of Phase Diagrams, 2016; Sarvghad et al., 2017d</i>	Test temperature (°C)
Chloride sulfate	26.5 NaCl + 73.5 Na ₂ SO ₄	626	700
Chloride carbonate	40 NaCl + 60 Na ₂ CO ₃	632	700
Ternary carbonate	33.4 Na ₂ CO ₃ + 32.1 Li ₂ CO ₃ + 34.5 K ₂ CO ₃	397	450

2. Experimental procedure

Austenitic stainless steel 316 (SS316), supplied by M D Lewis & Company Pty. Ltd, with the nominal chemical composition of (in wt%) 67.45% Fe, 12% Ni, 17.5% Cr, 3% Mo and 0.05% C was examined for compatibility in three eutectic mixtures of molten salts.

Powders of sodium chloride (CAS No.7647-14-5), sodium sulfate (CAS No. 7757-82-6), sodium carbonate (CAS No.497-19-8), potassium carbonate (CAS No.584-08-7) and lithium carbonate (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 1. The eutectic mixtures melting points and test temperatures have been also provided in the table. Test temperature for each salt was selected close to its melting point assuming the salt will be used as a PCM.

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 × 5 × 1 mm) as pseudo reference and counter electrodes (Bhatt and Snook, 2013; Inzelt, 2013; Chen et al., 2000; Nohira et al., 2003). 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 of -400 to +500 mV with respect to the open circuit potential. Tafel fit tool of EC-Lab software was used to fit PDP curves and calculate Tafel slopes, corrosion current density and corrosion potential.

2.2. Static corrosion

Fresh metal coupons were cut to around 25 × 7 × 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. Cylindrical alumina crucibles were used as salt vessels and the furnace temperature was set to 700 ± 10 °C for chloride carbonate and chloride sulfate salts and 450 ± 10 °C for the 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 and then removed after 120 h of exposure. All coupons were then mounted exposing the right (or left) side 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. It is worthy to note that although 120 h does not seem long enough to study the corrosion rate and related

phenomena, the aggressive nature of molten salts makes studying short-term impacts like attack morphology and corrosion mechanisms possible.

2.3. Microstructural investigations

Optic microscope model Leica DMi8A (magnification 1.25 × - 50 ×) equipped with Leica Application Suite software was used to take macro and micro-images for microstructural and corrosion observations.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were also employed for further microstructural investigations using a field emission SEM; model: JEOL 7001F, with automated feature detection equipped with secondary electron and EDS analysis system.

3. Results and discussion

3.1. Electrochemistry

OCP graphs of the alloy specimens in the studied molten salts are represented in Fig. 1a. In chloride sulfate, SS316 shows an initial rapid drop followed by more noble OCP values after 1000 s and ending to stable values over the 1 h of exposure. In chloride carbonate at 700 °C and ternary carbonate at 450 °C it shows more noble potential values over time. This could be attributed to the gradual development of films on the surface.

E_{corr} values in PDP plots in Fig. 1b reflect OCP values in Fig. 1a. Data extracted from PDP curves are summarized in Table 2 depicting the corrosion current density values in Fig. 2b.

SS316 represents the least I_{corr} value in ternary carbonate at 450 °C. Between the two high temperature salt mixtures at 700 °C, chloride carbonate seems the most aggressive one with a corrosion current density value of around 3.3 times higher than that of chloride sulfate. This could be attributed to the high solubility of Cr and other alloying elements in chloride carbonate and the subsequent dissolution of oxide films into the molten salt as reported previously (Sarvghad et al., 2017d). The significant changes in I_{corr} and E_{corr} values could also indicate changes in mechanism between the molten salts because of dissimilar compositions and test temperatures.

The corrosion mechanisms of steel alloys in the studied molten salts have been previously discussed in detail (Sarvghad et al., 2017b, 2018a). It has been shown that the corrosion mechanism in molten carbonate salts varies widely with temperature and the salt composition while the salt becomes less corrosive at lower temperatures (Molten Salt Corrosion, 2007). Because of their ionic nature, molten salts interact electrochemically with metals leading to Redox reactions (Carter et al., 1989; Young, 2008b; Liu et al., 2014; Nishikata et al., 1991) with corrosion highly dependent on the solubility of metal oxides in the liquid salt (Tzvetkoff et al., 1995). Solubility of oxygen and the subsequent oxidation of metals (and alloying elements) has been previously shown in molten carbonates (Sarvghad et al., 2017b,c,d; Azzi and Rameau, 1984). Formation of a variety of iron oxides, such as FeO, Fe₂O₃ and Fe₃O₄, is a consequence of the interaction between molten carbonates and steel alloys (Tzvetkoff et al., 1995; Azzi and Rameau, 1984). However, molten chlorides have been reported to destabilize the oxide film due to the formation of HCl and Cl₂ gas that penetrate the

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