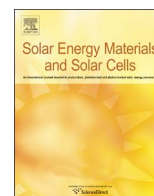




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Corrosion of alloys in a chloride molten salt (NaCl–LiCl) for solar thermal technologies



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ABSTRACT

Next-generation solar power conversion systems in concentrating solar power (CSP) applications require high-temperature advanced fluids in the range of 600–800 °C. Current commercial CSP plants use molten nitrate salt mixtures as the heat transfer fluid and the thermal energy storage (TES) media while operating with multiple hours of energy capacity and at temperatures lower than 565 °C. At higher temperatures, the nitrates cannot be used because they decompose. Molten chloride salts are candidates for CSP applications because of their high decomposition temperatures and good thermal properties; but they can be corrosive to common alloys used in vessels, heat exchangers, and piping at these elevated temperatures. In this article, we present the results of the corrosion evaluations of several alloys in eutectic 34.42 wt% NaCl – 65.58 wt% LiCl at 650–700 °C in nitrogen atmosphere. Electrochemical evaluations were performed using open-circuit potential followed by a potentiodynamic polarization sweep. Corrosion rates were determined using Tafel slopes and Faraday's law. A temperature increase of as little as 50 °C more than doubled the corrosion rate of AISI stainless steel 310 and Incoloy 800H compared to the initial 650 °C test. These alloys exhibited localized corrosion. Inconel 625 was the most corrosion-resistant alloy with a corrosion rate of 2.80 ± 0.38 mm/year. For TES applications, corrosion rates with magnitudes of a few millimeters per year are not acceptable because of economic considerations. Additionally, localized corrosion (intergranular or pitting) can be catastrophic. Thus, corrosion-mitigation approaches are required for advanced CSP plants to be commercially viable.

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1. Introduction

Thermal energy storage (TES) is a key component of concentrating solar power (CSP) plants and grid integration of renewable energies as a whole. Although energy may be stored by several different methods such as pumped hydro, batteries, or supercapacitors, TES has the advantages of lower capital costs and high operating efficiencies [1]. The most obvious benefit of TES is that it allows for power generation not only during peak solar irradiance, but also, during peak demand that occurs later in the day. TES also stabilizes energy generation from fluctuations such as cloud cover. This makes concentrating solar power with thermal energy storage (CSP/TES) a dispatchable resource. In addition, the nature of the CSP/TES power plant allows for fast ramp rates. The flexibility inherent to solar fields with TES allows greater penetration of other non-dispatchable renewable resources such as solar photovoltaics (PV) [2]. As PV penetration increases, increased strain is placed on conventional systems to rapidly ramp power

generation to compensate for the reduced solar output at the end of the day. In addition to the problem of the ramp rate, conventional systems are limited in the overall ramp range. The dispatchable power provided by CSP/TES fields can accommodate these demands, thus allowing for greater PV use in addition to the benefits of the CSP plants themselves.

Molten-salt TES may be used in several configurations in a CSP field. In active storage systems, the storage media is actively circulated for heating; in passive storage systems, the heat transfer fluid (HTF) flows through the storage for charging and discharging [3]. Active systems are further classified into direct and indirect systems. In direct active systems, the HTF is also the storage media and is heated directly from the source. For indirect active systems, the HTF is heated in the field, and thermal energy is transferred to the storage media through a heat exchanger. Active systems will either employ a two-tank system, where the hot and cold storage media are separated, or a single-tank system, where the hot and cold fluids are stored together. The hot and cold fluids remain separated by buoyancy effects, with a thermocline region established between the fluids at different temperatures [1]. Thermocline systems typically require a filler material to help maintain the temperature gradient. Generally, the two-tank system is more

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widely implemented, but advances by Sandia National Laboratories are promising for single-tank systems. Currently, seven parabolic trough systems use a two-tank indirect configuration, one trough system uses a two-tank direct system, and a central receiver with a two-tank direct configuration is operating that implements a TES application with molten salts [1]. The nominal maximum operating temperatures for those plants are 386°, 550°, and 565 °C, respectively.

Molten salts can be used as HTF and TES as sensible or latent-heat media. Current CSP plants use nitrate molten salts and can operate with multiple hours of energy storage capacity. Next-generation solar power conversion systems in CSP applications are targeting high-temperature, advanced fluids to operate in the range of 600–800 °C, which are temperatures that exceed the range of nitrate stability. Chloride molten salts are promising candidates, but are corrosive to common alloys used in vessels, heat exchangers, and piping at these elevated temperatures [4]. Containment material degradation is a major concern to meet commercial viability of next generation CSP plants [5]. The chemical interactions between these fluids and the metallic containments must be evaluated and understood to determine the degradation and lifetime of the containment material. Therefore, we must establish corrosion performance limits under various conditions and material systems to select the most cost-effective materials for these plants. The chemical (or electrochemical) reactions and transport modes are complex for molten salt corrosion in systems involving multi-component alloys and salts; but some insight can be gained through thermochemical models to identify major reactions [6]. Electrochemical techniques for molten salt corrosion can be used to rapidly identify the best-performing alloys. Recently, these techniques have been used for a better understanding of the fundamentals behind the molten salt corrosion mechanisms for thin-film molten salts in gas-turbine engines and electric power generation [7–10]. Molten-salt corrosion of Inconel 625 (IN625) in salts containing sulfates, oxides, and chlorides at 600°, 700°, and 800 °C reported corrosion rates of 1.80 ± 0.33 , 14.25 ± 2.01 , and 26.54 ± 1.69 mm/year, respectively. IN625 was not able to passivate under the conditions tested; specifically, the oxide scale produced was not protective against the corrosive salt [11].

It has been reported that Cr is not an effective element for improving corrosion resistance of Fe-based and Ni-based alloys. Because Cr_2O_3 has a higher solubility than iron and nickel oxides, it will react more readily with chloride salt [12,13]. This high solubility is reported for KCl-containing molten salts in oxidizing atmospheres, in which soluble K-chromates are formed. The higher the Ni content, the higher the corrosion resistance against molten chlorides [7]. Intergranular corrosion is the major corrosion type found in alloys exposed to molten chlorides in oxidizing atmospheres [6].

Potentiodynamic polarization sweep (PPS) is a powerful electrochemical technique that has been used to measure molten salt corrosion of stainless steels (SS) because it generates data quickly and is sensitive to very low corrosion rates [7]. Before the PPS, the open-circuit potential (OCP) must be established. The OCP is the stable electric potential obtained between the metal surface and the electrolyte (molten salt). To initiate the PPS, the metal/electrolyte system is first cathodically polarized (negative overpotential from the OCP), followed by a sweep in applied potential toward anodic polarization (positive overpotential from OCP). The polarization curves (applied potential vs measured current density) are then used to find the cathodic and anodic Tafel slopes. These slopes are usually found between ± 30 –120 mV relative to the sample-OCP [14]. The intersection of the Tafel slopes provides the corrosion potential (E_{corr}) and corrosion current density (j_{corr}), which is the corrosion current (i_{corr}) divided by the exposed area

(A).

The corrosion rate (CR) in millimeters per year can be calculated using the Stern-Geary equation through Faraday's law [15,16]:

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

where K is a constant equal to 3272 [mm/(A cm year)], EW is the equivalent weight of the alloy [g/mole- e^-], and ρ is the alloy density [g/cm³].

The equivalent weight of the alloy is calculated using its composition and the following equations:

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

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

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.

In addition to identifying corrosion currents and potentials, the polarization curves may also be used to determine the corrosion behavior of the sample. If the current constantly increases with the applied potential, then the sample has active corrosion. If the current decreases to values lower than i_{corr} and remains at that value for a certain potential range, then the sample is showing passivation produced by the formation of protective scales at the surface.

Using these techniques, scientists at the National Renewable Energy Laboratory (NREL) evaluated several alloys in eutectic 34.42 wt% NaCl – 65.58 wt% LiCl at 650° and 700 °C in a nitrogen atmosphere.

2. Experiment

2.1. Preparation of salt mixture

The eutectic 34.42 wt% NaCl – 65.58 wt% LiCl with a melting point of 554 °C was selected because it has a high heat capacity of 1.44 J/g. K. The eutectic salt mixture was prepared using ACS grade anhydrous NaCl and LiCl, each with a purity greater than 99 wt%, as received from Alfa Aesar. The unmixed salts were placed in a drying oven (DK-42, American Scientific Products) at 120 °C in air for at least 24 h to ensure low moisture content. The salts were weighed and mixed to the proper ratio in 125-g batches. The salts were then placed in an alumina crucible because this material has been shown to be stable in chloride molten-salt systems. The crucible containing the salt mixture was kept in a vacuum furnace at 120 °C for 24 h and then transferred to a muffle furnace (Vulcan 3-1750), heated and held at 300 °C for three hours. The temperature was then raised to 850 °C, where it was maintained for 30 min to completely melt the components. To avoid moisture absorption after cooling, the pre-melted and solidified salt mixture was stored at 120 °C in the vacuum furnace until needed for testing. Since the CSP plants cannot pursue very complicated and expensive mixing and melting procedures of the salts, the salt preparation followed here did not consider any further purification of the mixture.

2.2. Preparation of alloys

The alloys tested were SS347, SS310, Incoloy (In) 800H, and Inconel (IN) 625. The nominal composition of the alloys is shown in Table 1. Cylinders of 8-mm diameter and 12-mm height were

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