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Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Slurry aluminizing: A solution for molten nitrate salt corrosion in concentrated solar power plants



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ARTICLE INFO

Article history:

Received 13 August 2015

Received in revised form

6 October 2015

Accepted 13 November 2015

Available online 27 November 2015

Keywords:

Nitrate salt

Concentrated solar power

P91

Aluminizing

Slurry

Solar salt

ABSTRACT

Molten nitrate salts ($\text{KNO}_3\text{--NaNO}_3$) are used extensively as heat transfer fluids in concentrated solar power (CSP) applications. The oxidative character of nitrate salts at high temperature conditions leads to challenges in the corrosion protection of CSP installations in contact with molten salts. This work reports efforts to protect low-cost ferritic–martensitic P91 (Cr9–Mo1) and austenitic stainless steel 304SS materials against molten salt corrosion using slurry aluminizing. The gravimetric results show a significant improvement for aluminized alloys up to 1700 h immersion in molten nitrate salt at 600 °C. The extent of protection in P91 becomes comparable with the most competitive resistant materials e.g. Inconel 625. Metallographic investigations and scanning electron micrographs reveal no sign of corrosion in the substrates beneath the aluminide coatings during the immersion test. Electron probe micro-analysis results reveal Na(Fe,Al)O_2 as the protective corrosion product forming on the surface of both aluminized steels.

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1. Introduction

Concentrated solar power (CSP) has recently gained increased interest as a major renewable energy technology. It provides not only clean electricity, but can also provide continuous, reliable and flexible power systems using an unlimited source of energy i.e. Sun. The most common CSP technologies are parabolic dishes, power towers, parabolic troughs, and linear Fresnel reflectors which are based on point focus and line focus concentration of solar radiation. To date, more than 95% of the CSP systems are based on parabolic trough collectors [1,2]. However, recent trends show that the solar power tower system is the preferred CSP system for the future due to its capability to achieve higher temperatures [2]. Fig. 1 demonstrates the schematic cycle for a solar power tower system. The principle of this technology is based on the concentration of solar radiation using mirrors focused on the receiver tank. Inside the receiver the heat transfer fluid (HTF) absorbs the heat and transfers it to a storage tank (hot tank). This stage is followed by a heat exchange process which finally ends with a conventional steam power generating process. The cold fluid is transferred to the cold tank and is again pumped to the receiver tank [3]. Based on basic thermodynamic principles, the amount of heat produced in a central receiver CSP can be

calculated as:

$$Q = mC_p(T_H - T_C)$$

where Q is the heat energy, m is the mass, C_p is the specific heat of the storage medium i.e. HTF (which is assumed to be independent on temperature), T_H is the temperature in the hot storage, and T_C is the temperature in the cold storage.

Thus, higher energies can be stored by a) high density storage media, b) HTFs with higher specific heat, and c) higher temperatures in the hot storage tank. All of these parameters are related to the characteristics of heat transfer fluids. To date, molten nitrate salts (so called solar salt) based on alkali nitrates with a composition of 40 wt% $\text{KNO}_3\text{--}60$ wt% NaNO_3 are the main HTFs used for CPS applications. They offer a combination of high density, high specific heat (C_p), low melting point, high thermal stability, and low vapor pressures. The physical properties of the solar salt are listed in Table 1.

Currently, the thermal efficiency of the power tower CSP plants is between 30% and 40% [1]. Increasing thermal efficiency requires lower salt melting points and elevated hot storage temperatures. Efforts to develop novel salt mixtures with lower melting points and higher heat capacities are increasing [2,7,8]. However, degradation of nitrate salts which starts above 600 °C does not allow an increase in the hot storage temperature beyond the stability of such molten salts [2].

The circulation of salt in the power cycle relies on the molten state of the nitrate salts and this can only be granted by keeping the temperature in all transport and storage parts above the

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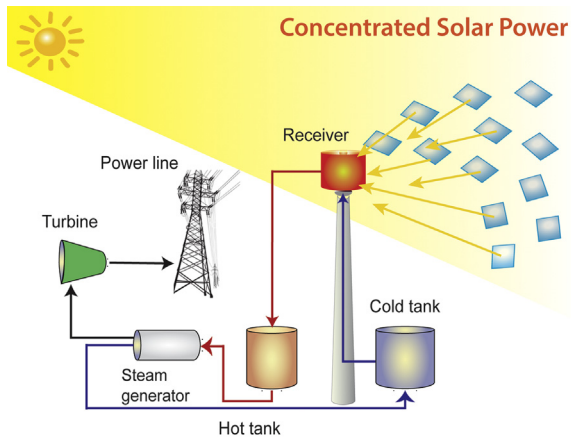
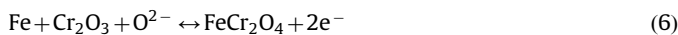
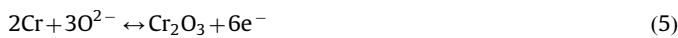
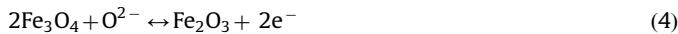


Fig. 1. Schematic of the energy conversion cycle in a concentrated solar power plant.

Table 1
Physical properties of the solar salt (60 wt% NaNO₃–40 wt% KNO₃).

Property	Melting point (°C)	ΔH_{fusion} (J/g)	Thermal stability (in air, °C)	Viscosity (at 300 °C, cP)	Heat Capacity (at 300 °C, J/kg K)
Value	221	123.9	650–700	3.26	1495
Reference	[4]	[4]	[5]	[6]	[6]

freezing point of the salt (~ 225 °C). In this condition, the corrosion resistance of the storage tanks and piping in CSP installations is one of the most challenging engineering issues in CSP plants [4,9–13]. Molten nitrate salts contain oxidizing agents such as NO₂⁻ and NO₃⁻ oxide species, and O₂ (from air). Corrosion of steel parts in contact to molten nitrate salts at high temperatures can occur via the following reactions:



Moreover, commercial salts contain levels of impurities which can accelerate the rate of corrosion. Thus, the mechanism of corrosion has to be investigated and the life time of these materials has to be correctly estimated.

The performance of different materials in molten salt corrosion at different temperature ranges has been studied [12,14]. It has been found that high chromium Ni-base alloys (e.g. IN625) and high chromium austenitic steels (e.g. 304 and 316) have lower corrosion rates in molten salt compared to the low chromium steels [11–13,15–17]. The influence of chromium on molten salt oxidation behavior is controversial. It is known that high chromium alloyed steels show higher corrosion protection via formation of a slow growing continuous chromium oxide or chromate spinel layer [4,12]. On the other hand, depletion of chromium in the substrates and Cr-dissolution in molten salt (however slow) has been evident [13]. In addition, alloys with high chromium contents are usually more expensive than the low-chromium

steels (e.g. P91 or X20CrMo-V11-1) which significantly affect the price of the output electricity [1].

More than 75 years ago iron-aluminides emerged as resistant materials for highly oxidative environments [18–28]. The high Al concentration of these alloys induces the formation of a protective aluminum oxide scale which guarantees their high resistance to oxidation [22], sulfidation [23,29] at high temperatures and hot corrosion in molten salts [27,30,31]. Tortorelli et al. showed that iron aluminides show significant resistance to molten nitrate salt corrosion [13,31]. They reported that aluminides with more than 30 at% Al show superior oxidation resistance in KNO₃–NaNO₃–Na₂O₂ molten salt at temperatures lower than 600 °C.

In iron-based alloys, aluminizing can significantly increase corrosion resistance by promoting alumina scale formation in oxidizing atmospheres [18,19,21,23,26,28,32–35]. Pack cementation (chemical vapor deposition) and slurry process are the major aluminizing techniques. Recently, interest in slurry aluminizing processes has increased due to its simplicity, economic efficiency, environmentally friendly process, and higher flexibility compared to a pack cementation method [36]. The process starts with spraying or painting of a suspension of Al particles on the substrate surface followed by a heat treatment process which forms an aluminide diffusion layer on the substrate surface. The classical heat treatment is performed under an inert atmosphere at moderate temperatures. Recent technical advances, however, increased the process flexibility including on-site treatment (e.g. post welding treatment) by utilizing local induction, hot blanket, and flame treatment under atmospheric conditions [37].

Experimental results on the effect of aluminizing on molten salt corrosion resistance of ferritic and austenitic steels are very limited. Carling et al. studied the molten salt corrosion behavior of pack cemented aluminized steels [38].

In this work, slurry aluminizing is used to enhance the molten salt corrosion of ferritic–martensitic steel P91 and austenitic stainless steel 304 materials in NaNO₃–KNO₃ molten salt mixtures. The focus is primarily on the comparative corrosion performance of uncoated and aluminized steel substrates. Furthermore, the evolution of coating microstructure and corrosion products during the corrosion test is evaluated.

2. Experimental

2.1. Substrate materials

Rectangular coupons of ferritic–martensitic steel P91 and stainless steel 304 with $25 \times 10 \times 4$ mm³ dimensions were cut by an electric discharge machine. Coupons were ground to 320 grit SiC paper, sand blasted, degreased with acetone in an ultrasonic bath, and finally dried in air. The compositions of the studied alloys were obtained using optical emission spectroscopy (OES) (see Table 2).

2.2. Slurry aluminizing procedure

Two groups of specimens from both steels were used for the slurry coating process. To prepare the coating slurry, aluminum powder was mixed with polyvinyl alcohol and distilled water. The slurry was air brushed onto the specimen's surface. Dried samples were heat treated at 300 °C for 4 h (to cure the binder) and then heat treated at 700 °C for 10 h under an Ar atmosphere. After heat treatment samples were washed and weighed before being used in the corrosion test.

Two different salt mixtures composed of NaNO₃ (60 wt%) and KNO₃ (40 wt%) were used for the corrosion test. The salt mixtures were different in the level of impurities, primarily the chloride

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