



Unexpected effect of nanoparticles doping on the corrosivity of molten nitrate salt for thermal energy storage

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ARTICLE INFO

Keywords:

Corrosion
Thermal energy storage
Concentrated solar power
Molten salt

ABSTRACT

Molten nitrate salts are currently the most common mature solution for thermal energy storage at the concentrated solar power (CSP) plants. Enhancing heat capacity and thermal conductivity of molten salts via doping by inorganic nanoparticles has attracted an explosively increasing interest due to the possibility of a considerable decrease of the investment costs for CSP technology. However, to the best of our knowledge there is almost no information on the effect of such doping on the corrosivity of the molten salts. In this work we demonstrate that adding small amounts of nanoparticles into the molten nitrate HitecXL salt considerably increases its corrosivity and modifies the corrosion mechanisms. A set of advanced techniques such as SEM-EDX, XPS and XRD are applied to get insights into the effect of inorganic nano-additives on the corrosion phenomenon.

1. Introduction

Thermal energy storage (TES) represents an important route for increasing the dispatchability of the concentrated solar power (CSP) technology [1–4]. Currently, molten salts (nitrate salts in particular) are frequently used as storage media as well as heat transfer fluids. Corrosive degradation of the construction materials due to the contact with molten salts can lead to a power plant failure and negative environmental impact. Understanding the corrosion mechanism as well as effect of different factors on the corrosion rates allows to improve the safety, while decreasing the investment costs.

With these regards, compatibility of different molten salts with potential construction and storage [7] materials is often addressed in scientific literature. In particular, Fernández et al. [5] performed a corrosion study between the HitecXL salt and several stainless and carbon steels. They have shown acceptable compatibility and corrosion rate dependence on the steel composition. Moreover, they have found out that the HitecXL salt is less corrosive compared to the commonly used solar salt [5]. Additionally, they detected the incorporation of the magnesium atoms (impurity in the salt) into the carbon steel corrosion layer. In [6], the authors presented a corrosion testing device and used it for solar salt with carbon steel A516Gr70 system. They demonstrated that the corrosion rates are acceptable for practical use and they also confirmed the incorporation of magnesium into the corrosion layer. In [8] the corrosion resistance of the Hastelloys in molten metal-chloride

heat-transfer fluids was studied showing dependence of the corrosion rates on steel composition. Federsel et al. [17] conducted a compatibility study between the Hitec salt and several types of steel revealing a negative effect of chlorides on the corrosion behaviour. Cheng et al. [25] performed a corrosion study between molten $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$ salt and several steels. The corrosion resistivity was found to be proportional to the Cr concentration in the steel and that the main mechanisms of corrosion are oxidation and lithiumization. Miguel et al. [26] investigated the compatibility between HR3C steel and $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ carbonate salt demonstrating multi-layer formation of different oxides as corrosion products. García-Martín et al. [9] presented a device for dynamic corrosion studies demonstrating that the dynamic conditions increase the corrosion rates compared to static ones. The stability and corrosion aspects of molten salts doped with carbon based nanomaterials were addressed in [27,28]. For the recent review on the corrosion of some PCM materials the interested reader can refer elsewhere [29].

On the other hand, there is a growing interest in molten salt based nanofluids development, due to their enhanced thermophysical properties (thermal conductivity and heat capacity) [30–33]. However, there are almost no studies demonstrating how such doping with nanoparticles affects the corrosion behaviour of molten salts. Some information can be found in [13,24]. In these studies, adding 1%wt of silica nanoparticles into 42.7% $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic salt at 520 °C was claimed to considerably reduce the corrosion rates compared to that of

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the pure salt. Formation of a protective layer of silica nanoparticles during the immersion corrosion tests was put forward in [13,24] as an explanation of the improvement mentioned above. However, the authors arrived to this conclusion solely based on mass variation of the samples of SS304 in the corrosion tests, while referring to the work of Suegama et al. [23], where bis-[trimethoxysilylpropyl]amine anti-corrosion coating filled with silica nanoparticles was developed. Further investigations are needed to support this explanation.

The effect of nanoparticles on the corrosion and erosion in water and in ethylene glycol based nanofluids was studied in more details in [18–22]. Particularly, Celata et al. studied erosion and corrosion of the metal surfaces by water based nanofluids containing TiO₂, Al₂O₃, SiC, ZrO₂ nanoparticles under dynamic conditions [18]. They have concluded that these nanofluids had no effect on the erosion of the stainless steel pipe, while the aluminium pipe had demonstrated increased erosion [18]. Rashmi et al. studied water and ethylene glycol based nanofluids containing carbon nanotubes [19] and they have found that, regardless of the fluid used, the corrosion rate of the tested materials increases in the order: aluminium, stainless steel, copper. The corrosion rate was increasing with temperature (27–90 °C) for all the materials [19]. In another work of the same authors, an increase of erosion and corrosion for nanofluid formed by alumina nanoparticles and sea water was demonstrated [20]. Bubbico et al. [22] investigated the corrosion and erosion of stainless steel 316, copper and aluminium by nanofluids based on different aqueous solutions and have found that the pH played an important role in the corrosion process. Among the investigated construction materials, only the aluminium was affected. Recently, Fotowat et al. [21] have studied the impact of pH on the corrosivity of water + Al₂O₃ nanofluid with the same materials (aluminium, copper and stainless steel). Among the three investigated construction materials, copper was found to be the most corroded one while the stainless steel 316 was the most corrosion resistant [21]. However, to the best of our knowledge there are no studies focused on the effect of nanoparticles on the corrosion behaviour of molten inorganic salts.

In this work, we studied the effect of adding the inorganic nanoparticles on the corrosivity of the molten salts. In particular, the corrosion tests were carried out for nanofluids based on the commercial HitecXL salt in direct contact with carbon steel. It was demonstrated that the presence of nanoparticles in this nitrate salt affects the corrosion rate noticeably. This finding can have far reaching implications for the practical use of nanodoped molten salts.

2. Materials and techniques

2.1. Materials and preparation

In this work, carbon steel A516. Gr70 with the following chemical composition was used: 98.68% Fe, 0.97% Mn, 0.31% C and 0.04% P (weight concentrations). Small pieces of the material were successively washed in acetone, ethanol and water in ultrasonic bath prior to the corrosion tests. As was demonstrated in our previous work [11], the initial state of the material has strong effect on the corrosion behaviour. For that reason, the samples were not polished before the corrosion tests as such treatment activates the surface, removing the oxide and carbon-rich layers, providing the initial state of the material far from the one corresponding to the application.

The above indicated material was tested with HitecXL salt consisted of 15% of NaNO₃, 43% of KNO₃ and 42% of Ca(NO₃)₂ (weight concentrations), which was prepared using commercial compounds (NitCal from YARA [14], KNO₃ and NaNO₃ from SQM) with the chemical composition presented in Table 1S. All the components were completely dried at 200 °C over 24 h prior to weighing under controlled conditions inside the glove box.

Two types of commercial nanoparticles were used to prepare the nanofluids. The Al₂O₃ nanoparticles produced by Aerioxide® with particle size of 13 nm and the SiO₂ nanoparticles delivered by Sigma-

aldrich with particle size of 12 nm.

To prepare the nanofluids a dry method was used. A quantity of 2 g of the mixture of HitecXL salt (99%wt) and the nanoparticles (1%wt) were introduced into a 50 ml aluminium bottle and subjected to dynamic shaking by means of ball milling machine during 15 min. The proper distribution of the nanoparticles was verified by different techniques and is a topic of a separate paper.

2.2. Corrosion tests protocol

For the corrosion experiments, around 6 g of salt were placed inside an alumina crucible and then a piece of 3 mm x 10 mm x 20 mm of carbon steel was immersed completely into the salt. Then, the alumina crucible was placed inside the furnace and kept at a constant temperature of 310 °C under air atmosphere for exposure times of 500, 1000 and 1500 h. The test temperature was selected in view of the operation conditions of the pilot CSP plant developed within ORC-Plus project [10], where the HitecXL salt is considered as one of storage material candidates to be used in the thermocline storage system, where, no controlled atmosphere on the top of TES tank is envisaged.

After the corrosion tests, the carbon steel samples were removed from the salt and carefully washed with hot water in order to remove the salt residues stuck at the surface.

2.3. Characterization techniques

2.3.1. Scanning Electron Microscopy - SEM

The surface and a cross section of the samples were imaged by means of a scanning electron microscope Quanta 200 FEG operated in high vacuum mode at 30 kV featured with a back scattered electron detector (BSED). In addition, energy-dispersive X-ray spectroscopy (EDX) analyses were carried out for elemental mapping. The images of the oxidation/corrosion layers were recorded along the whole perimeter of the samples' cross sections and average values are presented.

The cross sections of the samples were obtained following the simplified scheme shown in Fig. 1S. The carbon steel piece was immersed in rubber prepared by mixing KEM 90 Harz resin and KEM 90 Harter catalyst in 2:1 proportion, which upon solidification creates a proper holder for SEM imaging and helps to avoid possible removal of the corrosion and/or oxidation layers during the cutting and polishing of the cross section of the sample. A comparison of the SEM results of samples with and without the resin holder confirms that such holder does not bring any detrimental information, but helps to keep the separated corrosion/oxidation layer close to the surface of the material.

2.3.2. Fourier Transform Infrared spectroscopy – FTIR

The FTIR was used to identify any degradation or contamination of the salt upon testing with the carbon steel. The FTIR measurements were performed with a Bruker Vertex 70 spectrometer equipped with diamond ATR and DLaTGS detector. The FTIR spectra of the salts before and after the corrosion tests were recorded at room temperature in the range of 4000 – 450 cm⁻¹ in transmission mode.

2.3.3. X-ray photoelectron spectroscopy characterization – XPS

XPS characterization was performed in an ultra high vacuum system described elsewhere [15] to follow composition changes in the surface layer of carbon steel. The XPS spectra were acquired by means of a hemispherical electron energy analyzer PHOIBOS 150 (SPECS). A twin Al/Mg anode X-ray source XR50 (SPECS) operated at 12 keV and 100W power was used to excite the photoelectron spectra. The XPS spectra were acquired in the fixed analyzer transmission mode with pass energies of 20 eV and 100 eV for detecting elemental spectral lines with high resolution and survey spectra, respectively. The XPS spectra were peak-fitted using CasaXPS data processing software. The quantification has been done using sensitivity factors provided by the elemental library of the CasaXPS software [16].

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