

Thermal Energy Storage using Solar Salt at 620 °C: How a reactive gas atmosphere mitigates corrosion of structural materials

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1. Introduction

Molten nitrate salts play a crucial role as storage and heat transfer media in Thermal Energy Storage (TES) systems. In Concentrating Solar Power (CSP) plants molten salt storage allows for generation of dispatchable electricity and in the future, may assist in decarbonizing and prolonging the life-time of coal-fired power plants. The operating temperature range of commonly used Solar Salt, a binary mixture of sodium- and potassium nitrate, is set by the freezing temperature (plus a safety margin) on the lower-, as well as the decomposition temperature on the higher end, which is typically agreed upon as 290-565 °C. At DLR facilities research has been aiming at pushing the high temperature limit of Solar Salt up to, and even above, bulk temperatures of 600 °C. [1, 2] Stabilization of Solar Salt at 650 °C, in terms of a nitrate-nitrite equilibrium has been demonstrated on last year's SolarPaces conference. We demonstrated that the decomposition of Solar Salt depends on the partial pressure of oxygen and/or nitrous gases in the gas phase above the melt, at a certain temperature. In the last months, we have performed long-term exposure experiments to assess the corrosion performance of structural materials in Solar Salt at elevated temperatures. In an attempt to assess the impact of gas phase and temperature, three sets of experiments were performed: 1: Under state-of-the-art conditions of 570 °C in air, 2: At elevated temperatures of 620 °C in air, resembling a case where the salt is not stabilized, and 3: at 620 °C under a purge gas flow of 80 % O₂ and 400 ppm NO (rest N₂), resembling a case where the salt is chemically stabilized (as described in Sötz' work [2, 3]). The metal specimens were analyzed in terms of corrosion rate by descaling and cross-section analysis to evaluate the long-term corrosion performance. Our work constitutes a major contribution to the implementation of Solar Salt storage at higher operating temperatures and supports material and system engineering in the field of TES.

2. Experimental

Solar Salt was produced by mixing and subsequent melting of 60 wt% NaNO₃ (>99 %, Merck, Germany) and 40 wt% KNO₃ (>99 %, Merck, Germany). Metal samples of different alloys (e.g. 316L, 316LN, 310, 347H, A800, In825, In625) were produced from bulk plates with a geometry of 20x10x3 mm, grinded with P600 SiC paper, washed and rinsed with isopropyl alcohol. All samples were placed in alumina sample holders which allow for full isolation of samples and prevent galvanic corrosion, and placed in a furnace-setup described elsewhere.[4] Molten salt samples were extracted at the beginning and at the end of the experiment if not stated otherwise, and were analyzed in terms of the anions: nitrate, nitrite, oxide and chromate, as well as cation composition (Na⁺ and K⁺). Two sets of metal specimens were used for each experimental condition. One set was used to analyze the corrosion rate by descaling following the DIN EN ISO 8047-2014, while another set was used to analyze the cross-sections of the exposed specimens.

3. Results & Discussions

The stability of molten nitrate salts is mainly determined by the level of decomposition products formed at a specific temperature and gas phase compositions, mainly the concentrations of nitrite- and corrosive oxide-ions. In general, the lower the concentration of nitrites and oxides, the higher the stability and the lower the corrosivity of the nitrate salt (e.g. Solar Salt). With increasing temperature, it is not sufficient to operate nitrate salts under air, because the oxygen partial pressure is too low, to allow for reasonably low nitrite and oxide ions levels. A nitrate salt can therefore only be "stabilized", if it is purged under gas flow enriched with oxygen and/or nitrous gases, especially at temperatures exceeding 600 °C.

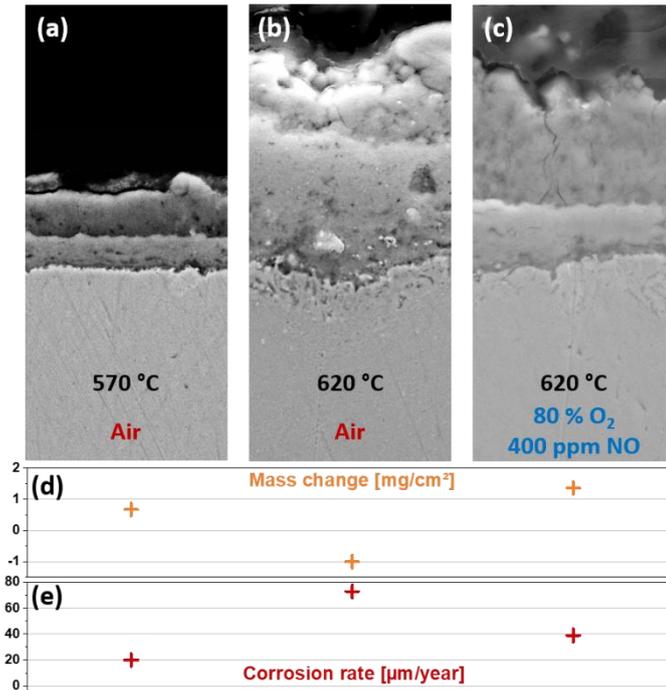


Figure 1 Cross-sections of SS 316LN (1.4910) after corrosion in Solar Salt for 1000 h at (a) 570 °C in a purge gas of air, (b) 620 °C under air and (c) 620 °C under a purge gas containing 80%O₂ and 400ppm NO (rest N₂). (d) shows the mass change (after washing and drying), as well as (e) the corrosion rate after descaling.

The effect of temperature and gas phase on corrosion of the alloys is best described looking at the cross-sections of SS 316LN, a boron stabilized 316L-type, shown in Figure 1. The corrosion rate under state-of-the-art conditions (570 °C, air) is in the range of 20 µm/year and the corrosion layer consists of inner iron-chromium oxide and outer hematite or sodium-iron oxide phases. At 620 °C under air flow, the salt decomposes excessively (salt data not presented here), leading to aggravated corrosion and also partial spalling of oxide scales as resembled by mass loss of the samples (Fig. 1(d)) and enhanced corrosion rates (Fig. 1 (e)). When applying a salt-stabilizing gas atmosphere with higher O₂ and NO partial pressures, the corrosion rate decreases significantly while and the corrosion scales are strongly adherent and more protective, as displayed by a decreasing corrosion rate and homogeneous oxide layers from cross-section analysis. The stabilizing character of the gas phase is outlined by salt analysis, which reveal unusually low nitrite- and oxide ion concentrations, resembling the salts' low corrosivity. At this years' SolarPaces conference we will present a coherent set of corrosion data on stainless steels (e.g. 316-types, 321, 310, 347) and Ni-based alloys (In825, In625) in Solar Salt at 620 °C, with a particular investigation of the link between molten salt chemistry and corrosion mechanisms, underlying the importance of gas phase control in TES systems. It will be highlighted, that the smart control of the gas phase allows for efficient corrosion mitigation and the use of economic stainless steels even at elevated hot tank temperatures of 620 °C.

Acknowledgements

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4. References

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