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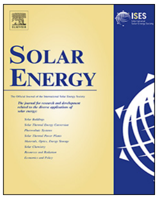

Corrosion resistance of Cr/Ni alloy to a molten carbonate salt at various temperatures for the next generation high-temperature CSP plants

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ABSTRACT

The corrosion behaviour of a commercial HR3C steel in a molten eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 mixture was studied by isothermal immersion tests at 700 °C and 800 °C for 2000 h. It was found that in both cases the corrosion products were arranged in a multilayer structure, with $LiFeO_2$, $LiCrO_2$, NiO and $FeCr_2O_4$ as the main compounds. Similar results to those obtained at 700 °C were reached in the tests performed at 800 °C but 1000 h earlier, which seems to indicate that the process was accelerated at higher temperature. Furthermore, regarding the superficial crystalline phase formed and according to the XRD and SEM examinations, it was found that on increasing the test temperature, a continuous transformation occurred from the rhombohedral to the cubic phase of the $LiFeO_2$ oxide layer. This transformation took place at both temperatures when the tests proceed and it was also accelerated by increasing the temperature from 700 to 800 °C. Thus, the process seems to be slower at 700 °C, which complicates the use of HR3C at 800 °C in the molten eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 salt mixture. These results suggest that the use of protective coatings should be assessed and that this material should be tested at 700 °C under more aggressive conditions, such as flowing salt, in future studies.

1. Introduction

In recent years there has been a substantial change in interest in renewable energy, which has increased greatly, particularly in the field of concentrated solar power (CSP) (Dorcheh et al., 2016; Liu et al., 2016; Lei et al., 2010). CSP plants often use molten salt mixtures as a heat transfer fluid (HTF) and/or as a thermal energy storage (TES) medium (Dunn et al., 2012). Molten nitrate salts are currently considered ideal candidates for heat transfer applications because of their properties. The best industrial compound is considered to be an alkali-nitrate mixture composed of 60 wt% $NaNO_3$/40 wt% KNO_3 (Solar Salt®) (Dorcheh et al., 2016; Zhao and Wu, 2011). However, the development of new molten salt mixtures has been studied by many authors in the last few years (Serrano-López et al., 2013; Fernández et al., 2014; Peng et al., 2010). These studies are searching for new salts with lower melting points and/or higher thermal stabilities, without a considerable increase in cost, viscosity, density, and/or corrosive behaviour. Ren et al. and Olivares et al. recently proposed the replacement of molten nitrate salts by molten carbonate salts, making possible an increase in the operational temperature to between 700 °C and 850 °C (Ren et al., 2011; Olivares et al., 2012).

In this field, corrosion of materials in contact with the molten salt is a very important issue for CSP plants (Fernández et al., 2015). Thus, many authors have studied the corrosion behaviour of numerous steels and other alloys immersed in molten salts (Hofmeister et al., 2015; Trinstancho-Reyes et al., 2011; Shankar et al., 2013; Vignarooban et al., 2014; Goods and Bradshaw, 2004). Due to the strength and oxidation resistance requirements, austenitic steels and Ni-based alloys could be of great interest in these environments. Within the Ni-based alloys, Inconel 617 or 625 and Haynes 230 has been widely studied under molten salt environments and attract a great interest (Turchi et al., 2018; McConothy and Kruizenga, 2014). At this respect, it is supposed that the higher the nickel content, the higher the corrosion resistance and the lower the corrosion rate. However, Gomez- Vidal et al. (Gomez-Vidal et al., 2016) found that IN625 has a higher corrosion compared to iron-based alloys in spite of its higher amount of nickel (> 58 wt%). This fact, together with the higher price of the Ni-based alloys compared to austenitic steels (Dorcheh et al., 2016), leads to consider the latter as good candidates for use at high temperatures under molten carbonate environments. Within them, HR3C is a low-cost alternative (Viswanathan and Bakker, 2001) that appears to be very resistant to high-temperature corrosion and steam oxidation due to its high Cr content (Wen et al., 2017), and also has high creep strength. The presence of chromium in this alloy allows the formation of a protective oxide layer while the presence of nickel improves the stability of the oxide formed (Boulesteix and Pedraza, 2018). HR3C is widely used in

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superheaters and reheaters, where it must resist the extreme conditions in USC boilers (Cao et al., 2011). Fu et al. have just tested this material under applied stress in molten salts (Fu et al., 2015), but to the best of our knowledge HR3C has yet not been widely studied in molten salt environments. Furthermore, corrosion behaviour of HR3C in carbonate molten salt mixtures has not been reported in the literature, except in our previous work (de Miguel et al., 2016). In this previous work, the behaviour of austenitic steel HR3C in a eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 molten salt was studied at 700 °C for 2000 h. However, the analysis was not focused on the outer Li-containing oxide layers that grows during test, which seems to be of great interest. Thus, this work is aimed at determining and comparing the behaviour of HR3C steel in a molten eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3 mixture at two temperatures, 700 °C and 800 °C for 2000 h. Furthermore, an in-depth study of the corrosion products in terms of thickness and crystalline phase formed is performed.

2. Experimental procedure

2.1. Material

2.1.1. Preparation and characterization of the salt mixture

The saline carbonates used as the corrosive agent in this study were Na_2CO_3, K_2CO_3 and Li_2CO_3 (Panreac®). Table 1 shows some properties of interest and the impurity level of the salts, regarding chlorides and sulphates content (Selvduray and Properties, 1991; Jong-Wan and Hae-Geon, 2001).

With the aim of limiting possible modifications of the composition under solid–liquid phase transition cycling, we selected a eutectic salt mixture (Guillot, 2012). The composition in weight percentage of the mixture (Na_2CO_3/K_2CO_3/Li_2CO_3) was 33/35/32 and it was prepared on the basis of the of the ternary phase diagram (see Fig. 1). The ternary phase diagram (Na_2CO_3, K_2CO_3 and Li_2CO_3) shown in Fig. 1 corresponds to pure salts and was developed by using suitable thermochemical software (FactSage®).

The melting point of the prepared ternary salt was determined by differential scanning calorimetry (DSC) and thermal stability was measured by thermogravimetric analysis (TGA). The DSC measurements were performed using a DSC-Q20 calorimeter and the thermogravimetric analysis using a SDT-Q600 both from TA Instruments. To perform each analysis, two different crucibles were employed. The crucibles used in the DSC Q-20 instrument were made of aluminium and were hermetically sealed, whereas the crucibles used in the TGA instrument were made of platinum and were opened to atmosphere. Both tests were conducted at a heating rate of 10 °C·min^{-1}, and in the case of TGA, a flowing air atmosphere of 100 ml·m^{-1} was used. The typical sample mass used in each test was 10 mg. Prior to the analyses, both instruments were calibrated with indium.

2.1.2. Tested substrates

The corrosion tests were performed on commercial HR3C austenitic steel with its composition in weight percent being 0.06% C, 0.52% Si, 1.02% Mn, 0.015% P, 0.004% S, 25.11% Cr, 20.03% Ni, 0.20% Nb, 0.26% N and the balance Fe. Specimens were manufactured with nominal dimensions of 10 × 10 × 2 mm. After manufacturing, the samples were superficially prepared using a size 47 grinding wheel with an average grain diameter of 370 µm. This step was followed by 5 min of ultrasonic cleaning in alcohol and de-ionised water.

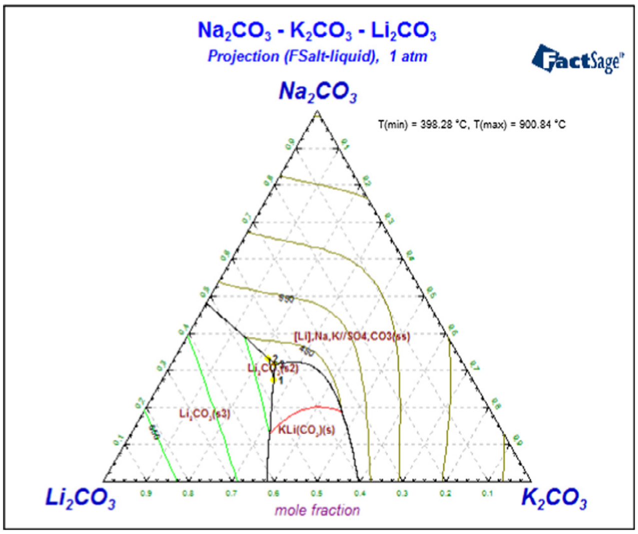

Fig. 1. Na_2CO_3-K_2CO_3-Li_2CO_3 ternary diagram.

Table 1

Relevant parameters of Na_2CO_3, K_2CO_3, Li_2CO_3 (Fu et al., 2015; de Miguel et al., 2016).

Salt	Melting point, °C	Purity, %	Impurity level, ppm	
			Cl^-	SO_4^{2-}
Na_2CO_3	858	98.5	5000	300
K_2CO_3	898	99	100	500
Li_2CO_3	723	98	100	3000

2.2. Corrosion study of the substrates

2.2.1. Corrosion tests

The isothermal corrosion tests were analysed via gravimetric analysis. Previously cleaned specimens were fully immersed in alumina crucibles containing 50 ml of the prepared molten mixtures giving a melt depth of about 3.5 cm. The crucibles together with the solid salt mixture were then set inside a Carbolite® electrical tube furnace with atmospheric air to reach the required temperatures, these being 700 °C and 800 °C. The working temperatures were selected on the basis of the conditions required in the future CSP plants, allowing for a supercritical steam power cycle to improve cycle efficiency (Peterseim and Veeraragavan, 2015; Sakadjian et al., 2015; Osorio et al., 2016).

The isothermal immersion tests were analysed at 24, 72, 168, 250, 500, 1000, 1500 and 2000 h. Thus, three specimens were removed from the ternary mixture for examination and analysis at the selected times. Once the samples were removed from the oven they were cooled slowly in warm distilled water in order to eliminate the salt in which they had been immersed. They were then dried and weighed and an average taken from five values of their weights. Thus, the formula used to calculate the mass gain over time was:

$$\frac{\Delta m}{S_0} = \frac{m_i - m_f}{S_0} \tag{1}$$

where m_i is the initial mass of the specimen, m_f is the mass of the sample at the selected time and S_0 is the initial area of the specimen.

2.2.2. Characterization of the samples

The previously immersed specimens were characterized by Scanning Electron Microscopy – Energy Dispersive X-ray spectroscopy (SEM-EDX) and X-Ray diffraction (XRD) after 1000 h and 2000 h of testing.

In order to study the morphology and chemical composition of the surface and cross-section of the corroded samples, SEM was carried out using a JEOL® JSM-820 scanning electron microscope. For cross-sectional SEM analysis, the cross-section of the corroded samples was mounted in a phenolic resin (Buehler®), then ground using 240, 320, 400, 600, 1000 and 2400-grit silicon carbide papers. Distilled water was sprayed on the papers during the grinding process.

XRD was carried out for the phase analysis of the corrosion products