

Corrosion Characteristics of Iron-Nickel-Chromium Alloys in Molten Nitrate Salts under Isothermal and Thermal Cycling Conditions

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ABSTRACT

The corrosion degradation of metallic components in Concentrated Solar Power Plants (CSP) with molten salt poses significant threat to the continuous safe operation at high temperature. Updated understanding of the corrosion behavior, mechanisms and the properties of corrosion products formed are needed to explain and optimize the corrosion performance of metals. In this study, the corrosion behavior of 321 SS, 347 SS, Alloy 625 and Alloy 825, are investigated in nitrate salt for 7, 14 and 28 days under isothermal; at 565°C, and thermal cycling conditions (between 565 and 290°C) in air. Several corrosion and advance surface evaluation techniques were implemented to characterize the corrosion process. The results show that the corrosion rate after thermal cycles is lower than in isothermal condition. This was due to increased spallation of corrosion products under isothermal test condition than during thermal cycling tests; particularly in stainless steel samples after 28 days. Multilayer corrosion products were observed on the surface of stainless steels and Ni-based alloys from both isothermal and thermal cycling tests. For stainless steels, an outer layer of sodium iron oxide, intermediate iron oxide and an inner layer of iron chromium spinel were found. NiO and Cr-rich oxides that were detected on the surface of Ni-based alloy, serve as protective layers against further corrosion processes.

Key words: Thermal cycling; Corrosion evaluation; Multi-layer; Spallation

INTRODUCTION

The drive towards renewable energy, requirement for reduction in fossil fuel consumption and emission of carbon dioxide has received substantial attention from governments and researchers worldwide during the last few decades [1]. The exploration of renewable sources of energy has been grouped into wind, geothermal, tidal and solar energy. Solar energy has shown great promise due to the abundant amount of energy reaching the Earth [2, 3]. Electricity generation from solar irradiation can be achieved by photovoltaic (PV) and photothermal conversion [4]. Concentrated solar power plant (CSP) has played a significant role in large-scale solar thermal electricity generation from photothermal conversion [5], due to high potential efficiency, low operation cost and low environmental impact. In current CSP systems, molten salts (especially mixture of NaNO_3 and KNO_3) are widely used as heat transfer fluids (HTF) and sensible heat storage materials to collect, transfer and store energy in heat collectors, heat transfer pipes and hot storage tanks, respectively. The high operating temperature of next generation CSPs (typically ranging from 550-850°C) with molten salt inevitably poses a significant corrosion threat to all exposed metallic components [6]. Most candidate materials are more vulnerable to high temperature oxidation [7] and intergranular corrosion (IGC) at the metal-salt interface [7].

Due to the potential for corrosion degradation of candidate materials to occur, it is important to deploy materials with a resilient molten salt – metal interface for mitigating the risk of catastrophic failure of metal components used in CSP plants. Stainless steels and Ni-based alloys are widely used in CSP plants due to their good mechanical properties, high corrosion resistance and oxidation resistance [3]. Significant research has been carried out to investigate the corrosion performance of low-alloy steels, stainless steels, and Ni-based alloys with molten salt. Many of these studies have been focused on the effect of temperature and molten salt chemistry on the corrosion rate of the selected alloys [8] [9]. But the effect of thermal cycling on the corrosion behavior of alloys with molten salt has not received sufficient research attention to date; particularly in the presence of excess amount of oxygen (air). This is critical because oxygen is often considered an impurity in molten salt systems because it increases the risk of corrosion [6]. Bradshaw [10] first performed thermal cycling tests in air with a 7.5-hour hot salt and 0.5-hour cold salt cycle, and found that thermal cycling moderately increased the corrosion rate of three stainless steels compared with isothermal condition. However, this methodology did not consider and accurately simulate the real condition for CSPs in operation, which includes day-time heating and night-time cooling.

Studies on corrosion behavior of alloys and the evolution of the corrosion products in molten salt under thermal cycling conditions are limited. This study aims to investigate and understand the corrosion behavior of two stainless steels and two Ni-based alloys under isothermal and thermal cycling conditions in a molten nitrate salt under air atmosphere. The test protocols were developed to closely simulate the real condition during 12-hour day-time heating and 12-hour night-time cooling in the heat transfer pipes and heat storage tanks. The results from this study could provide an empirical basis and guide for appropriate materials selection for molten salt based CSP applications.

EXPERIMENTAL PROCEDURE

The materials tested in this study are 321 SS (UNS S32100) and 347 SS (UNS S34700) austenitic stainless steels, Ni-based alloy 625 (UNS N06625). and alloy 825 (UNS N08825). The as-received samples were supplied by Zhejiang JIULI Hi-tech Metals Co., Ltd China, with dimension 10mm x 10mm and 3mm thick. The chemical compositions of these alloys is listed in Table 1. The samples were first wet-ground using silicon carbide (SiC) paper up to 2000 grit and followed by polishing with diamond suspension. Polished samples were then degreased with acetone, ethanol, and deionized (DI) water in the sequence, followed by hot-air drying. The prepared samples were kept in a desiccator and weighed (m_0) on an analytical balance (0.01mg, Ohaus Analytical Plus balance, New Jersey, United States) prior to being tested. The samples for cross-section analysis were embedded in epoxy resin before being abraded and polished. Prior to cross-section analysis, the prepared samples were sputtered with Ir to enhance the conductivity of the specimens.

Four samples of each alloy were placed horizontally in each Al₂O₃ crucible in order to ensure the same contact surfaces between the samples and the molten salt. Solar salt (60 wt.% NaNO₃ and 40 wt.% KNO₃) were selected for this study and were purchased from Alfa Aesar with analytical reagent purity. The salts were weighed to achieve the required ratio, mixed to achieve homogeneity and dried at 120°C for 24 h in a furnace before the experiments. The homogeneous salts were poured into each sample-containing crucible before being transferred into the furnace to dry for 12 hours at 180°C. The furnace was gradually heated up to test temperature before the start of the tests.

The isothermal corrosion tests were performed at a constant temperature of 565°C. Under thermal cycling conditions, the temperature was controlled to fluctuate between 290°C and 565°C, representing peak-time heating of molten salt and night-time cooling of molten salt in CSP storage tanks and flow lines. The exposure duration of materials to molten salts in these configurations was designed to replicate, as closely as possible, a real-time CSP cycle between daytime 12-hour heating and night-time 12-hour cooling. The temperature range to be explored was chosen based on the melting point at 220°C and stability limit at 565°C for the molten salt (solar salt). The thermal cycling profile is shown in Figure 1. The duration for the tests were 7 days, 14 days and 28 days (cycles). The corrosion products formed on the surfaces of studied alloys were investigated.

After the experiments, the samples were taken out from the salt and were descaled to remove the corrosion products using a standardized procedure of 20-min washing with 10% HNO₃ at 60°C for austenitic stainless steels and 10% H₂SO₄ at 20-25°C for Ni-based alloys, as described in ASTM G1-03 [1] and BS EN ISO 8407:2014 [2]. Mass change before and after immersion test were calculated via Equation 1 and thus corrosion rate was estimated by Equation 2, assuming the uniform corrosion occurred on the interface between salt and metal.

$$\frac{\Delta m}{S} = \frac{m_0 - m_1}{S} \quad \text{Equation 1}$$

$$CR(\mu\text{m/y}) = \frac{87600 \Delta m}{\rho S t} \quad \text{Equation 2}$$

Where m_0 represents the initial mass and m_1 is the mass of specimen after corrosion. S is the specimen surface area, $\Delta m/S$ is descaled mass loss per unit area (mg/cm²), ρ is alloy density in g/cm³, t is the immersion time (h). Three parallel samples were used to determine the mass loss data to ensure accuracy.

RESULT AND DISCUSSION

The comparison of corrosion rate measurements

Figure 2 shows the mass loss and corrosion rate of the studied alloys after isothermal and thermal cycling immersion test in solar salt. Stainless steels always exhibited higher mass loss and corrosion rate than Ni-based alloys under all conditions tested. In general, the corrosion resistance of four alloys are in this order: 625 > 825 > 347 SS > 321 SS. The mass loss and corrosion rate of isothermal samples are higher than thermal cycled samples, indicating more severe corrosion processes occurring in isothermal conditions. Regardless of isothermal or thermal cycling, the mass loss of stainless steels increased steadily with prolonged immersion time while the mass loss of Ni-based alloys increased only slightly, and the corrosion rate decreased with increased immersion time over 28 days. This is consistent with similar corrosion studies in the literature [3]. According to the literature [4], the corrosion process can be divided into two regimes; early impurity driven corrosion could lead to an initially high corrosion rate until the impurities are exhausted and corrosion becomes driven by a different mechanism [4]. It is known that the formation of a corrosion product layer could provide protection against further corrosion because of the low diffusion rate of oxygen and metal ions through the film [5], and hence reduce the kinetics of

corrosion. Under the thermal cycling conditions explored in this study, the results presented in Figure 2 shows a lower corrosion rate under thermal cycling conditions than in isothermal tests over 28 days. This is an indication that the range of temperature used for the cooling phase and the long residence time during this period helps to slow down the kinetics of corrosion and oxide formation, thereby reducing overall material loss rate. This intermittent cooling effect is believed to have also provide a break in the aggressive molten salt - metal interaction typically enhanced by high temperature to improve the adherence of initially formed corrosion oxide layers at 565°C. Also, the metal ion solubility and diffusion of alloy elements can be temperature dependent. This implies that thermal cycling process in this study could also affect the corrosion process by altering element distribution of the bulk material towards the molten salt – material interface.

Identification of corrosion products via XRD and Raman spectra

The XRD patterns confirmed that the oxide layers formed on the surface of 321 SS and 347 SS in solar salt are chromium oxide (Cr_2O_3), iron chromium spinel (FeCr_2O_4), iron oxide (Fe_2O_3), and a less dense, and less protective layer of sodium ferrite (NaFeO_2). Nickel oxides formed on the corrosion surface of 625, while various forms of iron chromium spinel, chromium oxide and iron oxide were observed on the surface of 825 due to its higher iron content and lower nickel content. Evidence of these corrosion products are presented in Figure 3. It is worth noting that the corrosion products formed on isothermal samples after 1-week immersion test, were similar to those formed on the samples from thermal cycling tests.

Raman spectroscopy results, shown in Figure 4, showed that Fe_2O_3 , Cr_2O_3 and FeCr_2O_4 spinel were detected on the surface of stainless steels after isothermal and thermal cycling condition. The corrosion products formed on the surface of 625 were a mixed oxide of Fe and Ni and were identified as NiFe_2O_4 ($\text{NiO-Fe}_2\text{O}_3$). The main corrosion products formed on the 825 surface were identified as Fe_2O_3 , Cr_2O_3 and $\text{NiO-Fe}_2\text{O}_3$, which shows good agreement with XRD results.

SEM surface observation

The oxide layer formed on the surface of the alloys specimens can protect base metal against molten salt infiltration. To better understand the corrosion process and mechanism, the corrosion layer was examined with SEM. The SEM images and corresponding magnified images are shown in Figure 5, as well as EDX data.

For 321 SS, as shown in Figure 5 (a) – (f) the corrosion surface show evidence of coarse morphology with increase immersion time under isothermal and thermal cycling condition. However, the corrosion surfaces from isothermal tests were coarser than that from thermal cycling tests. From the EDX result, the corrosion products are identified as iron oxide, iron chromium spinel and sodium ferrite. It's worth noting that NaFeO_2 was only found on the surface of 2-week isothermal sample. In addition, higher Cr content was observed on the samples after 1-week isothermal and thermal cycling tests, indicating a mild corrosion process under these conditions. Thermal cycling suppresses the kinetics of corrosion process through the formation of corrosion products and its transformation into a porous layer. A similar trend was observed on the surfaces of 347 SS samples.

With increase of isothermal immersion time, the corrosion surfaces became coarser, with evidence of increase coverage by crystalline corrosion oxide layer identified as Fe_2O_3 and NaFeO_2 . For the samples of thermal cycling, the content of Fe, Cr and Ni decrease from 1-week to 4-week thermal cycling, while the O content continued increasing from 7.7wt % after 1-week to 33.1 wt.% after 4-week thermal cycling tests. Na was also observed after 4-weeks of thermal cycling tests, indicating the formation of NaFeO_2 . This shows the dynamic growth and evolution of the corrosion products on the surface of samples under thermal cycling conditions. The spallation behavior of corrosion products on stainless steel surface has been reported by several researchers [6-8], which is attributed to the stress due to the mismatch of

thermal expansion and Young's modules between bulk steel and corrosion scales. In this study, no spallation of oxide layer was observed on all surfaces of stainless steels, indicating that the corrosion layer was dense and protective compared to that in literature.

The corrosion surface of 625 after 4-week isothermal and thermal cycling immersion tests are shown in Figure 5 (m) – (r). No obvious corrosion products or corrosion layer was found on the smooth surface. Referring to XRD results, the NiO was the primary oxide layer on the surface of isothermal samples, where the polishing marks are apparent on the surface as shown in Figure 5 (m)-(o). In Figure 5 (p)-(r), the corrosion surface of sample from thermal cycling test is covered by randomly scattered crystals, which were a mixture of Ni and Fe oxides. According to mass loss and XRD results, the corrosion rate and formation of oxide layer are minor, and the surface observation confirmed this conclusion. For 825, polishing marks were apparent on the surfaces after 1-week isothermal and thermal cycling immersion tests. With increasing test duration, more crystalline products formed on the samples, which are identified as NiO, Fe₂O₃ and FeCr₂O₄ via XRD patterns and Raman spectra.

Cross-sectional observation

Figure 6 shows the cross-section images of studied alloys after 4-week corrosion immersion tests in molten salt under isothermal and thermal cycling conditions. A thin layer (~ 3µm) was found on the 321 SS surface, which was identified as Fe₂O₃ via EDX line scan in Figure 6 (a) and (b). The corrosion product was scattered on the surface without forming a continuous layer. The corrosion reaction is not considerably more severe under this temperature. A continuous oxide layer (~3µm) was found on the surface of 347 SS after 4-week isothermal immersion, mainly Fe₂O₃. As a comparison, Fe₂O₃ crystal was scattered on the surface of 347 SS sample from thermal-cycling test as shown in Figure 6 (d). It can be inferred that the thermal cycling suppresses the kinetics of corrosion and oxide layer formation due to the intermittent cooling effect, providing a means limiting the progressive increase in the corrosiveness of molten salt linked to the thermal stability of molten salt at high temperature. Non-obvious oxide layers were found on the surface of 625 after isothermal or thermal cycling test as shown in Figure 6 (e) and (f). 625 exhibited highest corrosion resistance against molten salt both in isothermal and thermal cycling. As a comparison, mixed oxides of Fe, Ni and Cr formed on the surface of 825 after 4-week immersion test in molten salt, shown in Figure 6 (g) and (h).

Discussion

Referring to the 20-40 µm/yr of corrosion rate to provide a 30-year lifetime service for CSP plants [9], the corrosion performance of stainless steels and Ni-based alloys are acceptable at 565°C under isothermal and thermal cycling conditions in a long-run operation for CSP plants. Considering the cost of these alloys, it's wise to choose relatively cheaper stainless steels rather than Ni-based alloys as the main alternative material for CSP plants.

As noted previously, the higher corrosion rate recorded for isothermal tests than from thermal cycling test is mainly linked to the lower time (12 hours per 24 hours experiment time) at maximum temperature of 565 °C under thermal cycling condition. Also the cooling effect during thermal cycling, and by extension the lower residence time at peak temperature helps to reduce the kinetics of outward diffusion of key metallic elements within the bulk material; Fe and Cr for oxide formation at the corrosion interface. This is likely to reduce metal loss rate and hence lower corrosion rate than isothermal conditions. Similarly, the intermittent cooling process also helps to prevent the rapid breakdown and spallation of initially formed oxide layers. This occurs by the tempering effect of extended cooling on the continuous thermal stress build up in isothermal conditions. This helps in maintaining the protective properties of the oxide layers. The intermittent cooling effect also reduces the rate of progressive increase in corrosiveness of molten salts as result of decomposition of molten nitrate salts to form nitrites and oxide ions [4]. These three pathways are directly linked to effect of intermittent cooling during thermal cycling experiments.