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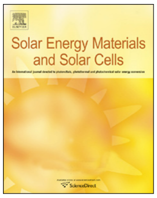

Electrochemical study on the corrosion behaviors of 316 SS in HITEC molten salt at different temperatures

Ming Zhu*, Song Zeng, Huihui Zhang, Junyi Li, Boyuan Cao

College of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, PR China

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ABSTRACT

Corrosion of 316 SS in HITEC molten salt was investigated at 450 °C, 600 °C, and 680 °C by electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. Corrosion products were investigated by XRD and SEM equipped with EDS. Corrosion of 316 SS in HITEC molten salt exhibited active corrosion characteristics at these temperatures. 316 SS exhibited resistance to corrosion in HITEC molten salt at 450 °C, suffered severe corrosion at 680 °C, and demonstrated discontinuously increasing corrosion rate from 600 °C to 680 °C. A thin layer of Cr_2O_3 and Fe-based oxides formed at 450 °C. At 600 °C and 680 °C three distinct oxide layers could be distinguished with a loose outer Fe-based oxide layer. After corrosion at 600 °C and 680 °C for 200 h, Na_2O and K_2O were detected in the HITEC molten salts, which caused the decomposition of the protective Cr_2O_3 layer and enhanced corrosion of 316 SS. EIS results show that the corrosion processes of 316 SS in molten salt at 450 °C and 600 °C are controlled by outward diffusion of metal ions and oxygen vacancies, while corrosion mechanism at 680 °C change to was inward diffusion of oxygen ions. The change in corrosion mechanism became more prominent when corrosion time was prolonged to 197 h.

1. Introduction

Molten salts are widely used as heat transfer media in Concentrating Solar Power (CSP) plants [1–3]. The heat transfer medium used in solar plants is an important component of a thermal energy storage system. Presently molten salts for heat transfer and energy storage are nitrates, chlorides, fluorides, and carbonates [2,4]. Thermal properties of these molten salts including their melt point, working temperature, heat captivity, and corrosiveness have been investigated. Based on cost and corrosiveness considerations, the nitrates and nitrites are the most suitable salts as heat transfer and thermal storage material in solar thermal power plants. HITEC mixture, which is composed of 40 wt% $NaNO_2$–7 wt% $NaNO_3$–53 wt% KNO_3, was first proposed for use as a storage medium in a THEMIS experimental solar plant in France in the 1980s [5].

Although nitrate and nitrate molten salts are less corrosive than chlorides, carbonates, and fluorides corrosion in solar thermal plant industry is the main problem limiting wide application of these salts as a heat transfer fluid [1,6–12]. Effects of alloying elements on resistance of several alloys such as stainless steel [7,11], carbon steel, low Cr or Cr-Mo alloy steel [1,12], and Ni based alloys [6,11] to corrosion in nitrite and nitrate mixture molten salts have been investigated. The results indicate that high Ni or Cr content results in better corrosion resistance in nitrite and nitrate mixture molten salts due to formation of stable NiO or Cr_2O_3 protective oxide scale on the surface of the alloy during corrosion.

Nitrate and nitrite molten salt corrosion test experiments are usually conducted at 400–600 °C temperature range, E.g. 390 °C for parabolic trough and 550 °C for central tower technologies [13]. Higher operation temperatures can increase the cycle efficiencies of the CSP. However, lower operating temperatures of HITEC salts limit the CSP cycle efficiencies. It is reported that the operating temperature of HITEC salt is at least 610 °C in inert atmosphere and may be as high as 650–700 °C in oxidizing atmosphere [14]. Therefore, HITEC salts have the potential to be utilized at temperatures up to about 700 °C if the operating atmosphere is controlled. Few corrosion tests in nitrate or nitrite molten salts above 600 °C have been reported. McConohy and Kruizenga reported a significant increase in corrosion rate of Ni based alloy in solar salt (60% $NaNO_3$ + 40% KNO_3, molar ratio) when the corrosion temperature increased from 600 °C to 680 °C [6]. The increase in corrosion rate was attributed to the decrease of melting point and heat of fusion of the solar salt.

Corrosion tests in nitrate or nitrite molten salts are usually carried out by immersion method. Electrochemical method is widely used for understanding the corrosion mechanism of metal alloys in molten salts [15–20]. Corrosion behavior of 316 SS in HITEC molten salt at 450 °C,

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* Correspondence to: College of Materials Science and Engineering, Xi'an University of Science and Technology, 58 Yanta Road, Xi'an 710054, PR China.
E-mail address: mingzhu@xust.edu.cn (M. Zhu).

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Table 1
Chemical composition of 316 SS (wt%).

C	Si	Mn	P	S	Ni	Cr	Mo
≦0.03	≦1.0	≦2.0	≦0.045	≦0.03	10–14	16–18	2.0–3.0

600 °C, and 680 °C was investigated by electrochemical method to elucidate high temperature corrosion mechanisms in nitrate molten salt, especially at 680 °C.

2. Experimental procedures

Commercially available 316 SS with chemical composition shown in Table 1 was cut into 30 mm × 5 mm × 5 mm samples by an electric spark cutting machine. The specimens were ground with 200, 600 and 1000 grit SiC sand papers, polished by 0.3 µm alumina paste, rinsed with distilled water, ultrasonically degreased with acetone, and dried in a warm air stream. A stainless steel wire was spot welded to one end of the specimen for electrical connection. The specimen was then sealed in an alumina tube with high temperature cement leaving only 20 mm exposed. The cement was dried at room temperature for 24 h and then further cured at 150 °C for 12 h. The exposed surfaces of the specimen were polished again with 1000 grit SiC, rinsed, and dried prior to test as working electrodes.

A ternary nitrate mixture of 53% KNO_3–40% $NaNO_2$–7% $NaNO_3$ (weight percentages, HITECH salt) was used for the study. Each nitrate salt in the mixture was dried prior to being weighed and was added to other salts in an alumina crucible. The mixture was further dried at 200 °C in a reaction chamber first under vacuum, and then in an Ar atmosphere for 20 h prior to placement in the furnace to be heated to experimental temperatures.

The electrochemical tests were conducted in a stainless steel chamber in high purity Ar. Environment. Fig. 1 shows the schematic diagram and object picture of the experimental setup for molten salt corrosion. Electrochemical techniques employed here included potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) measurements. The potentiodynamic polarization tests were conducted using a conventional three-electrode system. Preparation procedure fort he working electrode was described above; the reference electrode was made of a 0.5 mm diameter platinum (Pt) wire inside an alumina tube filled with HITEC salt and sealed with high temperature cement. High purity graphite was used as auxiliary electrode. The electrodes were connected to electrochemical station (AutoLab) when the salt mixture was heated up to the testing temperature, scanning was done at a rate of 20 mV/min. Each sample was tested 3 times.

The EIS measurements were carried out at open circuit potential between 0.01 Hz and 100 kHz using a two electrode system, i.e. two working electrodes. The amplitude of the input sine wave voltage was 10 mV. The impedance spectra were calculated and fitted using Zview software.

Phase composition analysis of the corrosion products and the molten salts after electrochemical tests were determined by x-ray diffraction with Cu Kα. Surface and cross-sections of the samples were studied by a scanning electron microscope equipped with EDS.

3. Results and discussion

3.1. Potentiodynamic polarization results

Potentiodynamic polarization curves are very useful for determining some corrosion mechanisms such as active dissolution, passivation, and pitting potentials. The potentiodynamic polarization curves of 316 SS under Ar atmosphere in molten HITEC salt at 450 °C, 600 °C, and 680 °C when the OCP reached a stable value, are presented in Fig. 2. 316 SS exhibits active corrosion in HITEC molten salt at these three temperatures. The oxidation-reduction reactions at the anode and cathode in molten nitrate salt at high temperature are:

$$M = M^{2+} + 2e^{-} \text{(Anode oxidation reaction, M is metal)} \qquad (1)$$

$$1/2O_2 + 2e^{-} = O^{2-} \text{(Cathode reduction reaction)} \qquad (2)$$

During the course of reaction metal ions, electrons, and oxygen vacancies diffuse outward while oxygen ions diffuse inward, leading to thickening of the corrosion layer.

The anodic and the cathodic Tafel slops of the polarization curves may be determined by Tafel extrapolation technique to obtain corrosion density (I_{corr}) and corrosion potential (E_{corr}). The fitting results are listed in Table 2. The corrosion density increases from 2.02 mA/cm^2 at 450 °C to 8.09 mA/cm^2 at 600 °C and to 34.4 mA/cm^2 at 680 °C. These correspond to an increase by factor of 4 from 450 °C to 600 °C and an increase by a factor of 17 from 450 °C to 680 °C. The results indicate that there is a change in corrosion mechanism of 316 SS in HITEC molten salts from 450 °C to 680 °C, which is in accordance with McConohy and Kruizenga's findings [6].

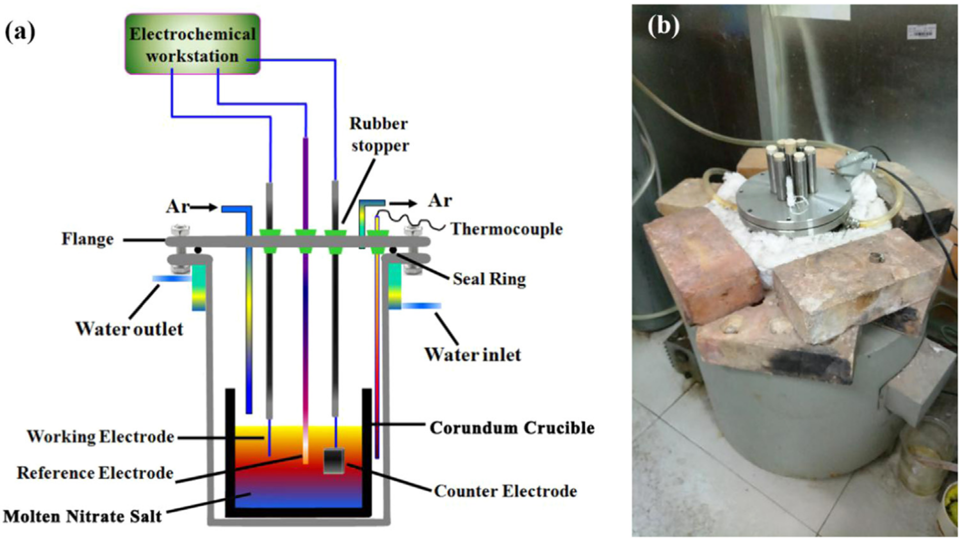

Fig. 1. A schematic diagram(a) and object picture(b) of experimental setup for molten salt corrosion.