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Galvanic corrosion of pure metals in molten fluorides

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ABSTRACT

The corrosion of structural materials is a great challenge for the development of a molten salt reactor using molten fluorides as fuel or coolant. The corrosion of materials in molten fluorides occurs mainly through the dissolution of alloying elements into the melt. In the present investigation, the galvanic corrosion behavior of pure Ni, Fe, and Cr as the common alloying constituents in an eutectic LiF–NaF–KF melt at 700 °C has been investigated. The experimental results indicate that the corrosion potential of the three metals decreases significantly by the order of Ni, Fe and Cr, with the largest potential difference observed between Ni and Cr. Their great potential differences lead to the occurrence of significant galvanic corrosion. The galvanic corrosion effects of the couples Ni/Cr, Ni/Fe and Fe/Cr are significantly larger than 1, with the most remarkable effectiveness obtained for the couple Ni/Cr, then Fe/Cr and Ni/Fe.

1. Introduction

Molten fluoride salts appear to be excellent candidates as primary reactor coolant, liquid fuel, and solvent for the reprocessing of spent fuel in many nuclear reactors, such as Molten Salt Reactor (MSR) and Advanced High-Temperature Reactor (AHTR), with the advantages of good thermal conductivity, large specific heat, low viscosity, low vapor pressure at operating temperatures, low melting point, high boiling point, relatively good chemical inertness, etc. [1]. However, an immediate challenge for using molten fluoride salts in these nuclear reactors is the corrosion of structural materials at the desired operating temperatures between 650 and 850 °C. In most conventional high temperature processes, materials derive their corrosion resistance through the formation of a dense protective oxide film such as Cr_2O_3, Al_2O_3 or SiO_2 on the surface. In molten fluorides, however, these oxides are thermodynamically unstable, and generally converted to the corresponding fluorides. The corrosion in molten fluorides mainly occurs through the dissolution of alloying elements into the melts. Due to the fact that the free energy of salt constituents such as LiF, NaF, KF, etc., is more negative than that of the fluorides for the constituents of alloys, the driving forces for the corrosion in molten fluorides are generally involved with the impurities in fluorides, temperature gradients and activity gradients. As the main oxidizing impurity, H_2O is among the most deleterious contaminants in fluorides, and is hard to be removed completely. H_2O can react with the fluoride ions to generate HF that then attacks metals to form metal fluorides.

Large amounts of investigations on the material compatibility with various molten salts have been conducted in ORNL (Oak Ridge National Laboratory-USA), the University of Wisconsin, and National Institute for Fusion Science (NIFS), etc. [1–3]. The weight loss of Ni-based alloys due to corrosion has been shown to increase with the increase in the Cr content. Therefore, some Ni-based alloys with a low Cr content have been considered as the most suitable structure materials for MSR, among which Hastelloy-N (Ni–17%Mo–7%Cr–5%Fe, mass percent) developed by ORNL exhibits a great potential for long-term application [1,4].

The design consideration for a MSR system may involve the use of various materials which may exhibit different potentials, and thus be susceptible to galvanic corrosion. As an important corrosion topic, galvanic corrosion has received wide attention. It usually happens as a macroscopic process when two metals or alloys with different electromotive potentials are in electrical contact in molten salts. It can also occur as a microscopic process, such as between the alloy matrix and the precipitates [1,5]. Galvanic corrosion can be influenced by many factors, such as temperature, the anode–cathode area ratio and spacing. The driving force for galvanic corrosion is the potential difference between metals or alloys in molten fluoride salts. Electromotive potential rankings have been developed for common metals in aqueous solutions [6,7], while similar rankings have not been developed for metals in molten salts. Up to now, there are very limited reports on the galvanic corrosion of metals or alloys in molten salts, mainly involving the evaluation of the corrosion behavior of metals or alloys by measuring the galvanic current of

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coupled metal-platinum in molten salts [8–10]. Salih et al. [8] studied the corrosion behavior of some stainless steels in molten alkali carbonates by measuring the galvanic current between the working electrode and a Pt electrode. In a study of the galvanic corrosion behavior of the coupled nickel-platinum in molten Na_2CO_3 under O_2 and Ar, respectively [9], Hara et al. observed that the galvanic current passed from platinum to nickel under both atmospheres. Nickel and platinum became the anode and cathode, respectively, and the galvanic current under O_2 was larger than that under Ar, suggesting O_2 was dissolved in the melt and hastened the galvanic corrosion. Mo et al. [11] also measured the galvanic current density between a Ni sample and a Ni–Cr sample in molten Na_2SO_4 at 900 °C.

In a study of the corrosion mechanism of two-phase Ni–20Cr–20Cu and Ni–20Cr–30Cu (mass percent) alloys in a eutectic $(Li,K)_2CO_3$ melt at 650 °C, Zeng et al. suggested that the significantly faster corrosion rates of the two-phase alloys with respect to the single-phase Ni–20Cr and Ni–20Cr–10Cu alloys were attributed to the electrochemical galvanic corrosion mechanism [12].

Galvanic corrosion is an important corrosion mechanism and also a great challenge in molten fluorides of MSR where any protective scales cannot be expected to form on the alloy surface. In a study of the corrosion performances of reduced activation ferritic steel, JLF-1 (8.92Cr–2W) in LiF–BeF_2 and (Li,Na,K)F salts, Kondo et al. observed that the corrosion rate of the steel in nickel crucible is three times larger than that in JLF-1 crucible [13]. Olson et al. also found that the corrosion rate in molten fluorides for Incoloy 800H was greater by 20 times in a graphite crucible compared to an Incoloy 800H crucible [1]. Some investigations have indicated that the galvanic corrosion rate might be one or two orders of magnitude higher than the intrinsic corrosion rate, and is comparable to the temperature/concentration gradient induced corrosion rate [1,2,13].

In the present study, the galvanic corrosion behavior of pure metals Ni, Fe and Cr in molten fluorides was investigated in an attempt to understand the corrosion mechanism of metallic materials in molten fluorides.

2. Experimental procedures

The materials used in the present investigation are industrially pure Ni (with a purity of 99.96 wt%), Fe (99.87 wt%), and Cr (99.19 wt%). The bulk metals were cut into specimens with a size of 5 mm × 30 mm × 2 mm by an electric spark cutting machine, followed by grinding down to 1000 grit SiC paper, cleaning with distilled water and then drying. A Fe–Cr wire was spot welded to one end of the specimens for electrical connection. The sample was sealed in an alumina tube with high-temperature cement, with a length of 15 mm exposed. The cement was dried at room temperature for 24 h and then further solidified at 300 °C for 2 h. The exposed surfaces of samples were polished again with 1000 grit SiC paper, rinsed, and dried before tests.

All experiments were conducted in a closed stainless steel chamber under the protection of a circulating high-purity argon, as shown in Fig. 1. All electrochemical measurements were undertook at 700 °C in an eutectic 46.5%LiF–11.5%NaF–42%KF (mol%) melt with the CS310 electrochemical workstation. Electrochemical experiments include free corrosion potential (E_{corr}) and galvanic corrosion measurements, with a Pt electrode as the reference electrode. In the galvanic corrosion experiments, three galvanic couples, i.e. Ni/Fe, Fe/Cr and Ni–Cr were selected. The galvanic potential (E_g) and current (I_g) of the couples were simultaneously recorded.

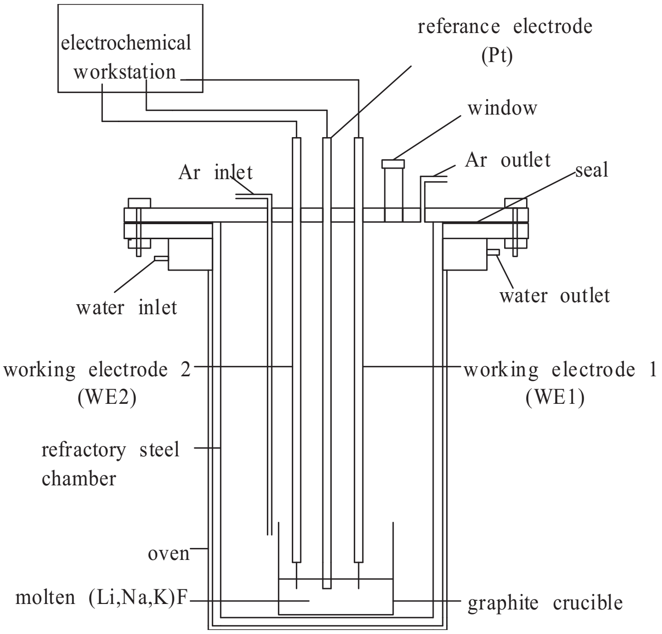

Fig. 1. A schematic diagram of experimental setup.

After drying LiF, NaF and KF, respectively, at 200 °C in vacuum, a mixture of (Li,Na,K)F of 178 g was prepared and then put into a graphite crucible. After drying the mixed salts again at 200 °C in vacuum for 2 h, the furnace was then heated to the experimental temperature under the protection of Ar, and then the electrodes were dipped into the melt to begin the experiments.

After galvanic corrosion, the corroded samples covered with the remaining salts were mounted in epoxy resin and then their metallurgical sections were prepared using kerosene as coolant for grinding and polishing, with an attempt to examine the corroded metal/salt interface. Additionally, some of the corroded specimens were also cleaned with deionized water to remove the remaining salts. X-ray diffraction (XRD) and scanning electron microscope (SEM) coupled with an energy dispersive X-ray microanalysis (EDX) were used to characterize the corroded metals.

3. Results and discussion

3.1. Free corrosion potential measurements

Fig. 2 shows the change of free corrosion potential with exposure time for pure metals Ni, Fe and Cr in molten (Li,Na,K)F at 700 °C. E_{corr} for pure Ni decreases slightly to around −105 mV vs. Pt

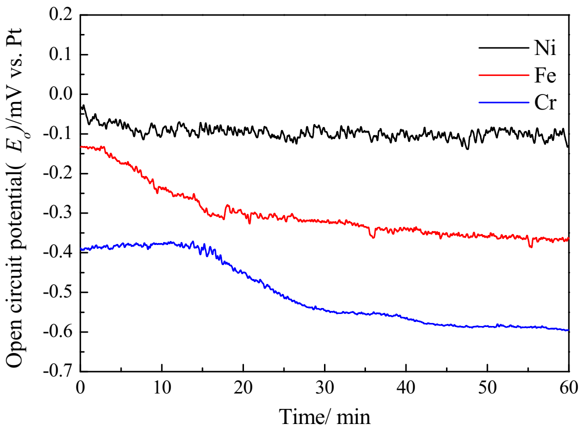

Fig. 2. Free corrosion potential of pure Ni, Fe and Cr in molten (Li,Na,K)F at 700 °C.