



# Effects of exposing temperature on corrosion performance of weld joint of a Ni–Mo–Cr alloy



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## ABSTRACT

Corrosion tests of weld joint of a Ni–Mo–Cr alloy were performed in a eutectic LiF–NaF–KF molten salt for 400 h at different temperatures (550 °C, 700 °C, 850 °C). Results indicate that the joints exhibit Cr depletion and Fe enrichment in corrosion layer at 700 °C and 850 °C, that the structural differentiation caused by welding has little impact on the diffusion of the elements in the alloy. The thickness of the Cr depleted layer induced by the corrosion in the molten salt increases with the temperature. The grains of the alloy sample become coarser due to the annealing at higher temperature, which may also enhance the corrosion of the alloy in the salt.

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## 1. Introduction

Molten Salt Reactor (MSR), one of the Generation IV Initiative nuclear reactors, offers a potentially safer, more efficient and sustainable form of nuclear power [1,2]. In a MSR, molten fluoride salts have been proposed for use as primary reactor coolants [1,2]. Eutectic salt, such as LiF–KF–NaF (46.5–11.5–42 mol.-%, common referred to as FLiNaK), is a candidate for the coolants of MSRs, because FLiNaK exhibits a high thermal conductivity, a high specific heat, a low viscosity, and a high boiling point [3,4]. However, most of the molten fluoride salts are highly corrosive, and the corrosion behavior of the material in the molten FLiNaK salt has hence been recognized as a severe issue of the material in a MSR. The structural material, Hastelloy N alloy which possess exceptionally outstanding corrosion resistance to the molten salts and good oxidation resistance, for example, is required for a MSR [5,6].

Corrosion behaviors of materials in molten salt environments have been extensively investigated. The active alloying elements are selectively attacked by dissolution, which results in the surface pitting of the alloy samples. In the study of Hastelloy-N and Incoloy-800H exposed to FLiNaK, some of the Cr in these alloys was

selectively attacked and the weight loss is correlated directly to the initial Cr contents of the alloys [4,7,8]. It's widely accepted that the corrosion of the alloys containing Cr in molten fluorides is controlled by the Cr dealloying of the alloys. Corrosion rate is, thus, much dependent on the diffusion rate of Cr in the alloys. Based on the Arrhenius law, the temperature-dependent diffusion coefficient  $D$  is expressed as  $D = D_0 \exp(-Q/RT)$ . Where  $D_0$  is a pre-exponential factor depending on ingredient [9–11];  $Q$  is the apparent activation energy which is proportional to the melting temperature of the material [12];  $R$  is the universal gas constant. According to the diffusion equation, key factors that influence  $D$  will affect the diffusion controlled corrosion. The directly influencing factors of diffusion coefficient  $D$  are the material composition, structure and environmental temperature. For a specific material, temperature plays an important role on corrosion. In a MSR, temperature gradients exist across the whole components parts, which affects the diffusion of elements in the components. Moreover, the temperature influences the solubility of Cr in molten salts. The Cr equilibrium solubility in FLiNaK increases from  $1.1 \times 10^{-3}$  mol/L at 600 °C to  $2.7 \times 10^{-3}$  mol/L at 800 °C [1,13]. Thus, it's significant to investigate the corrosion behaviors of the MSR materials in molten fluorides under different temperatures.

Nickel-base alloys have been utilized extensively as structural materials and fabricated into pressure vessels, heat exchangers, tanks, and other reactor components to handle the various corrosive liquids [5]. Several literatures have showed that

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Hastelloy-N alloy was used as the promising candidate material for MSR metallic structures due to its excellent corrosion resistance [2,13]. Other similar Ni-based alloys had been developed as well, such as Chinese GH3535 alloy. The GH3535 alloy possesses similar [14] composition, and comparable performance with those of Hastelloy-N alloy [15].

Welding technique has been applied in nuclear reactors to connect and fix up tubings and plates [14]. Plant experiences and laboratory experiments have shown, in water reactors, that the weld joints of Ni-based alloys and stainless steels are more susceptible to corrosion failure. Local changes in composition and structure of the weld joint due to fusion welding affect corrosion process [16,17]. For the materials in molten fluorides, the corrosion of the materials is affected by the composition gradient through diffusion. Thus, composition changes caused by welding will result in effects on corrosion performance. Few reports, however, were available in literature for the study on the weld joint corrosion in molten fluorides [18].

In this work, a detailed study was undertaken to investigate the corrosion behavior under different temperatures of the weld joint of a Ni–Mo–Cr alloy in FLiNaK melt. The microstructure of the weld joint was analyzed by a scanning electron microscope (SEM), an electron-backscatter-diffractometer (EBSD) and a transmission electron microscope (TEM). The metallographic properties were also investigated.

## 2. Results and discussion

The metallurgical microstructure of the alloy joint was observed using an optical microscope, as shown in Fig. 1. The base zone exhibits an equal axis structure with an average grain size of about 60  $\mu\text{m}$  (Fig. 1(a)), while a typical dendritic structure is formed in the fusion zone (Fig. 1(c)). The large dendritic grains are approximately perpendicular to the fusion boundary. The heat-affected zone (HAZ) presents both equal axis grains with smaller average size, relative to the base zone, and dendritic grains (Fig. 1(b)). Some very small precipitations are also found at the grain boundary in both fusion zone and base zone. Compared Fig. 1(a) and 1(c), the fusion zone presents more intergranular precipitations than the base zone.

The composition and structure of the intergranular precipitates were examined using a TEM. In Fig. 2(a), the TEM bright-field image shows that the intergranular precipitates are elongated. The EDS spectrum of a particular precipitate (Fig. 2(b)) indicates that C and Mo are enriched in this intergranular precipitate. The selected area electron diffraction (SAD) pattern (Fig. 2(b)) shows the structure of this intergranular precipitate is in a fcc structure. Based on these results and the previous study [19], we suggest that the intergranular precipitates are  $\text{M}_6\text{C}$  carbides.

The surface of corroded weld joint was observed using a SEM. The fusion zone and base zone exhibit a similar smooth surface after corrosion. As shown in Fig. 3, the surface is much smoother after exposed to FLiNaK at 550  $^{\circ}\text{C}$ , while becomes rougher at higher exposure temperature of 700  $^{\circ}\text{C}$  and 850  $^{\circ}\text{C}$ . The rough surface is mainly caused by grain spalling due to corrosion dissolution. Diffusion rate increases rapidly with increasing temperature. Higher temperature enhances the Cr diffusion in the body of the alloy and therefore, the corrosion attack becomes heavier at higher temperature.

The cross sections of the corroded specimen were observed using a SEM. The base zone and fusion zone were both examined for each exposing temperature, as shown in Fig. 4. The corrosion attack is much slighter after exposure at 550  $^{\circ}\text{C}$  (Fig. 4(a)). More pitting are observed at 700  $^{\circ}\text{C}$  (Fig. 4(b)), compared to the corroded sample at 550  $^{\circ}\text{C}$ . Whereas, corrosion attack is not getting heavier as expected at 850  $^{\circ}\text{C}$  (Fig. 4(c)), with respect to the corroded

sample at 700  $^{\circ}\text{C}$ . It is assumed that the corrosion involves a reaction as follows [20]:



Considering the Cr and Fe concentration of the salts before and after the corrosion tests (Table 1), the result reveals the Cr dissolution from the alloy and the Fe deposition from the salt onto the surface of the alloy samples during the corrosion process. The Cr concentration increases with the temperature. The Fe concentration in the salt changes little during the corrosion process at

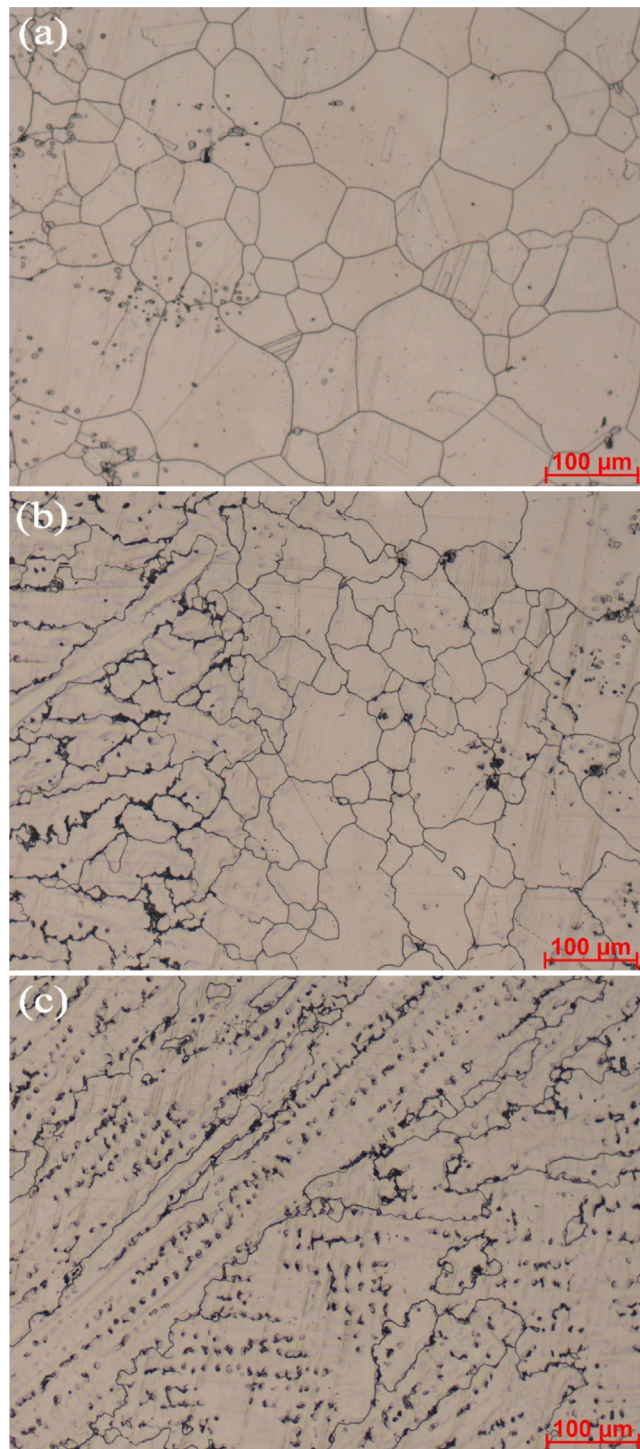


Fig. 1. Metallographic observation of the different parts of the alloy weld joint: (a) base zone, (b) HAZ and (c) fusion zone.

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