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Effect of grain refinement on the corrosion of Ni-Cr alloys in molten (Li,Na,K)F

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ABSTRACT

The corrosion of cast coarse grain and laser-remelting fine grain Ni-Cr alloys in molten (Li,Na,K)F at 700 °C under Ar has been investigated by electrochemical and thermogravimetric methods with an attempt to understand the effect of grain refinement on the corrosion of the alloys. The results indicate that grain refinement remarkably accelerates the dissolution of Cr, leading to the formation of a wider Cr-depleted zone. The enhanced corrosion of fine grain Ni-Cr alloys could be ascribed to the laser remelting treatment decreasing greatly the grain size of the alloys, and thus significantly increasing the overall effective diffusion coefficient of Cr.

1. Introduction

Molten fluoride salts have been chosen as the fuel and coolant in high temperature molten salt reactors (MSR) due to their desirable thermophysical and thermochemical properties. Of fluoride salts, LiF-BeF_2 is often used in the experimental molten salt reactors [1]. However, beryllium is extremely toxic and environmentally harmful. Fortunately, a eutectic 46.5%LiF-11.5%NaF-42%KF (mole percent) melt, showing similar characteristics with LiF-BeF_2, is often used as simulator fluid and experimental salts [2–5]. So far the corrosion of structural materials in molten fluoride salts at high temperatures is considered to be an immediate challenge for the development of MSR [6]. Over the past 60 years, the corrosion behavior of structural materials in molten fluorides has been investigated by many research institutions, such as ORNL, NASA, the University of Wisconsin, and National Institute for Fusion Science (NIFS) [1,7,8]. Their results show that the major materials problem of MSR is the preferential dissolution of chromium in molten fluoride salts due to its higher chemical activity than other composition metals of the alloys.

Thermogravimetric is one of the most common experimental methods to investigate the effect of Cr on the corrosion behavior of the materials used in MSR [9–11]. An investigation by Olson indicates that the weight loss of Ni-based alloys increases with the increasing of the initial Cr content, and the weight-loss of the alloys is affected by their carbon content due to the connectivity of Cr carbides at grain boundaries that are attacked directly by the (Li,Na,K)F [3]. Fabre et al. calculated the theoretical oxidation potential for the selective dissolution of Cr from the binary Ni-Cr alloys and pointed out that a critical Cr activity should exist to make the alloy stable in molten LiF-NaF and other melt [12]. Furthermore, a minimum Cr content is also needed for the oxidation resistance of the outside of air exposed piping.

The dissolution of Cr in molten fluorides is intrinsically an electrochemical process. Therefore, the corrosion of material in molten fluorides can also be investigated by some electrochemical techniques, such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) by which more information can be obtained to understand the reaction mechanism and kinetics. Fabre et al. have successfully obtained the oxidation potentials for concurrent dissolution of Cr and Ni from the $Ni_{1-x}Cr_x$ electrodes in LiF-NaF at 1173 K [12].

Usually, lattice diffusion will tend to predominate at high temperatures. However, solid state diffusional transport also occurs along grain boundaries and dislocations (easy diffusion paths) [13–15]. Olson [3] suggests that the corrosion rate of alloys in molten (Li,Na,K)F can be accelerated at grain boundaries where the distance for the penetration of (Li,Na,K)F into the alloys can be shorten. Therefore, the contribution of grain boundary diffusion to the corrosion of materials in molten fluorides may be related to the

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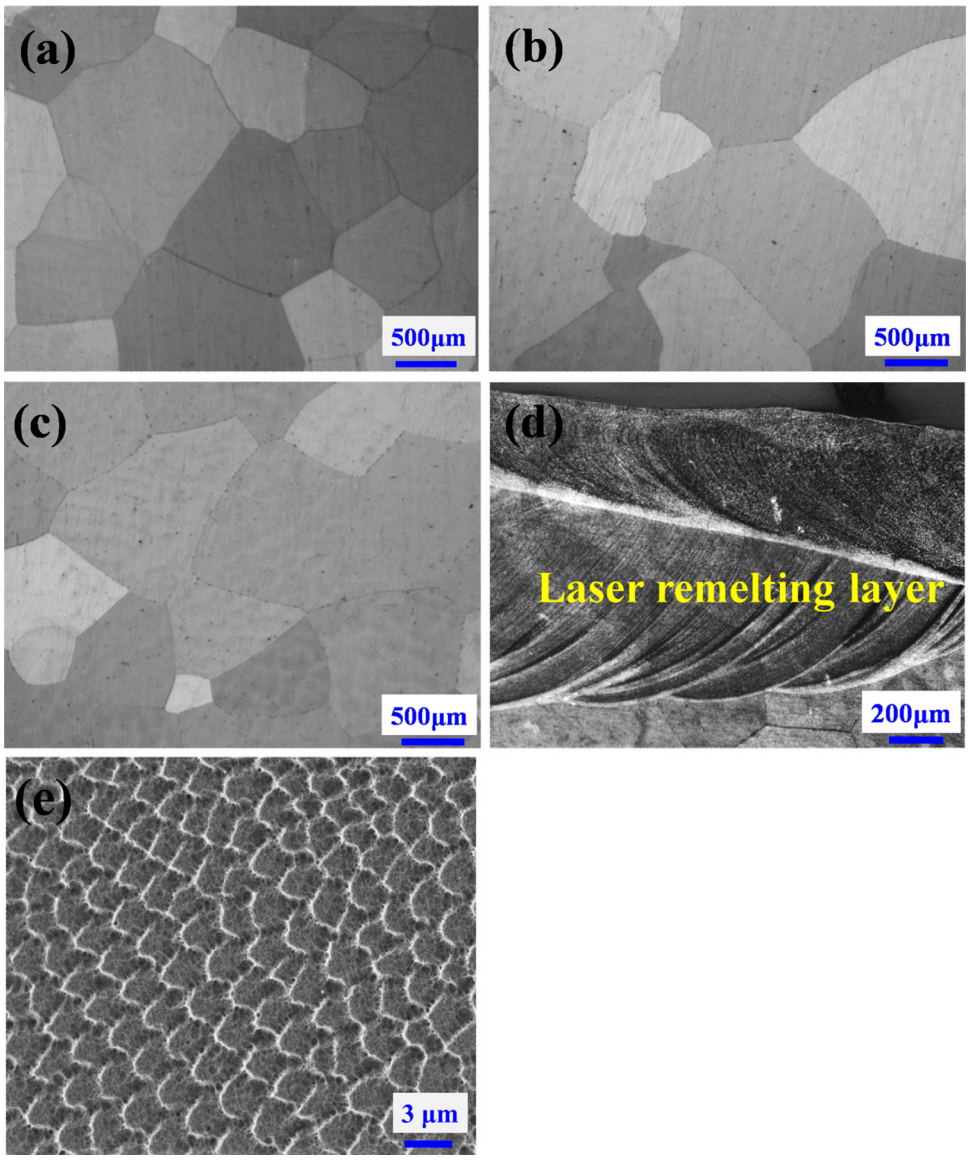

Fig 1. Microstructures of coarse-grain Ni-5Cr (a), Ni-10Cr (b) and Ni-15Cr (c) and fine-grain (d, e) alloy. (d): cross-sectional image of the laser remelting Ni-5Cr; (e): amplified image for the laser remelting layer in (d).

grain size. However, there are limited reports on the effectiveness of grain size in recent years [3,10]. In the present study, the corrosion behavior of coarse-grain and fine-grain Ni-Cr alloys are comparatively investigated in molten (Li,Na,K)F at 700 °C in an attempt to understand the effect of grain size on the corrosion behavior of Ni-Cr alloys.

2. Experimental procedures

Ni-Cr alloys containing 5, 10, and 15 at.% Cr, respectively, were used in the present study. The alloys were prepared by repeatedly arc-melting mixtures of Ni and Cr under argon. The alloy ingots were heat treated at 950 °C in vacuum for 30 h, followed by cooling with furnace. In accord with the phase diagram [16], the alloys exhibit a single-phase microstructure, with a coarse grain (denoted as CG) size ranging from 800 to 1500 μm, as shown in Fig. 1a–c. The alloy ingots 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, rinsing with distilled water and then drying. Meanwhile, fine grain (denoted as FG) Ni-Cr alloys were prepared by laser-remelting the above CG Ni-Cr alloys, with around 1 mm thick laser-remelted layer. Fig. 1d and e shows the cross-sectional morphology of the laser-remelted Fe-5Cr and microstructure of the remelted zone, respectively. The average grain size of the FG Fe-5Cr is about 3 μm, which is significantly lower than that of the CG Fe-5Cr. The laser remelting layer of the alloys was cut into specimens with a dimension of 4 mm × 30 mm × 0.4 mm. For electrochemical measurements, a Fe-Cr wire was spotwelded to one end of the specimens for electrical connection. The sample was then sealed in an alumina tube with high-temperature cement, with a length of 15 mm exposed. The cement was kept at room temperature for 24 h and then solidified at 200 °C for 12 h. The exposed surfaces of the specimen were ground again with 1000 grit SiC paper, rinsed with distilled water and dried prior to electrochemical tests.

A ternary eutectic 46.5LiF-11.5NaF-42KF (mole percent) mixture was used for the corrosion study. After drying LiF, NaF and KF, respectively, the mixture of (Li,Na,K)F of 178.6 g was prepared and then placed in a graphite crucible. The mixed fluorides were further dried at 200 °C in the reaction chamber under vacuum for 48 h, and