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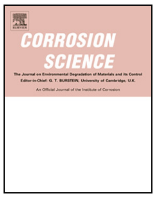

The high-temperature corrosion of Hastelloy N alloy (UNS N10003) in molten fluoride salts analysed by STXM, XAS, XRD, SEM, EPMA, TEM/EDS

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ABSTRACT

The effect of Fe ion impurity on the corrosion behavior of Hastelloy N (UNS N10003) alloy in molten FLiNaK salts at 850 °C has been investigated by combined synchrotron radiation and other characterization techniques. Results showed that Mo and Cr were depleted from the alloy surface, where Fe-rich layer formed. The corrosion process was mainly controlled by the redox reaction between Fe ion and Cr, and no new compound with high valence state formed in the alloy surface. The loss of Mo and Cr in $M_{12}C$ carbide occurred due to the presence of a concentration-gradient between $M_{12}C$ carbide and matrix.

1. Introduction

Interests in use of molten fluoride salts are increasing for various applications such as thermal storage, electrolyte, coolant or fuel in a molten salt reactor (MSR) [1–3], but corrosion of structural materials in molten fluorides still poses a radical challenge for the application of molten fluorides [4–6]. Unlike high temperature applications of alloys in oxygen-containing environments, in which the formation of self-healing protective surface oxide films such as Cr_2O_3 and Al_2O_3 can reduce the rate of further oxidation, in fluoride salts systems, the products of corrosion, metallic fluorides, are unstable in the salt. Accordingly, passivation is precluded and corrosion depends directly on the thermodynamically driven dissolution of alloy elements whose free Gibbs energies of fluoride formation are more negative [5,7]. The tendency for common alloying elements to form fluorides increases in the following order: W, Mo, Ni, Fe, Cr, Al, Na [7]. Therefore, nickel-base alloys with low Cr and no Al are considered as structural materials for molten salt systems, among which Hastelloy N (UNS N10003) alloy, originally designed for only successfully operated experimental molten salt reactor (MSRE) by ONRL, is well proven to be promising candidate for long-term applications [5,8]. In fact, from the thermodynamic opinion, any corrosion of elements in Hastelloy N alloy could be minimal in pure molten fluoride salts because the main components of the salt (LiF, BeF_2, NaF, KF) are more stable than any potential corrosion product. Nevertheless, the general corrosion of Hastelloy N alloy was still estimated to be with a global metal loss about 5 μm per year in MSRE [9]. Several studies have demonstrated that the corrosion behavior of the alloys is significantly affected by the presence of oxidizing impurities such as H_2O, HF, and polyvalent metallic ions (Ni^{2+}, Fe^{2+}) in molten fluoride salts [9–12]. Moreover, oxidizing impurities can also aggravate other corrosion processes such as mass transfer driven by thermal gradient [13,14] and galvanic corrosion caused by materials with differing electromotive potentials [7,15]. Ouyang et al. [10] demonstrated that FLiNaK salts with higher H_2O content would increase intergranular corrosion and pitting of Hastelloy N alloy at 600 °C and 700 °C in molten FLiNaK salts. The good explanation for this is that H_2O can react with the fluoride ions to generate HF that

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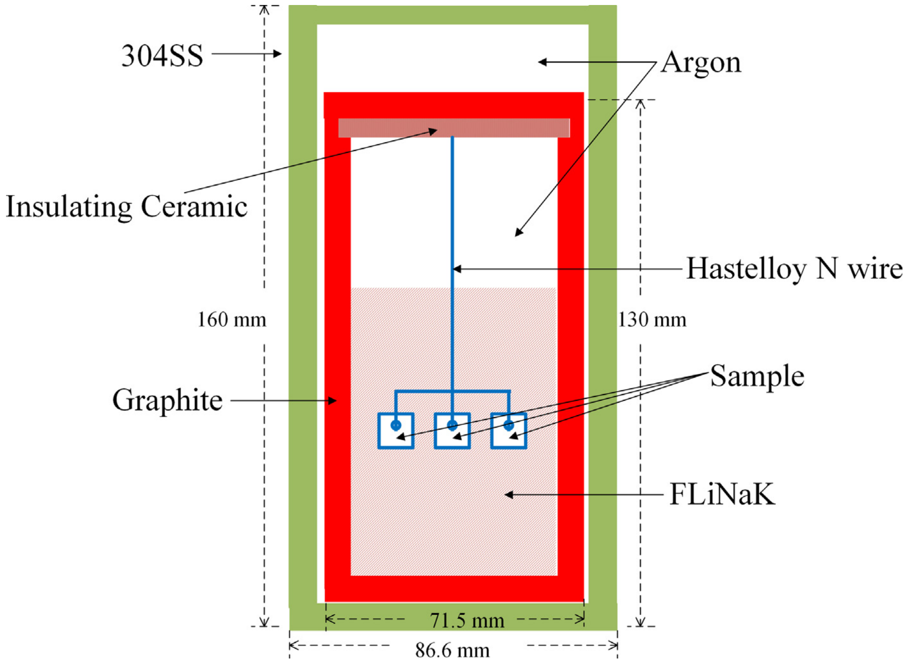

Fig. 1. Schematic diagram of experimental setup.

Table 1
Compositions of Hastelloy N alloy (wt.%), examined by inductively coupled plasma atomic emission spectrometry.

	Ni	Cr	Mo	Fe	Mn	Al	W	Si	C
Hastelloy N	Bal.	7.01	16.80	4.16	0.52	0.28	0.20	0.36	0.06

Table 2
Compositions of FLiNaK salt before and after corrosion (unit: ppm by weight, mg/kg). Each composition value is averaged over six data, expressed in terms of a mean and standard deviation.

Molten salts	Fe	Ni	Cr	Mn	Mo
FLiNaK (46.5LiF-11.5NaF-42KF mol.%, H2-HF purified)	149.5 ± 7.5	60.8 ± 10.4	26.3 ± 0.6	12.9 ± 0.4	21.4 ± 3.0
FLiNaK after corrosion	29.7 ± 7.5	91.5 ± 11.6	37.5 ± 1.3	6.4 ± 0.1	32.5 ± 4.6

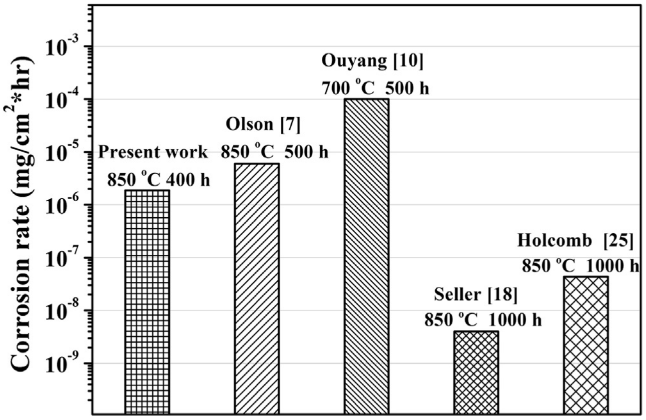

Fig. 2. Average corrosion rates of Hastelloy N alloys in FLiNaK salts at different condition [7,10,18,25]. They are calculated according to net weight loss divided by the immersion time.

will attack most elements of the alloys to form metal fluorides. Kondo et al. investigated the corrosion characteristics of some Ni-based alloys [11] and JLF-1 ferritic steel [12] under molten FLiBe salts and pointed out that HF can accelerate the corrosion rate of alloys, leading to changes in corrosion mechanism. Since H_2O and HF are among the most deleterious contaminants in fluorides, several physical and chemical methods have been applied to purify the fluoride salts and the H_2O content could be reduced to less than 10 ppm [2,16,17]. However, in contrast with the breadth of studies about the effect of H_2O in fluoride salts on alloys, our knowledge about the corrosion effect of metallic ion impurity is still limited. Since metallic ions will also become the main source for the corrosion when the content of H_2O is controlled, understanding how metallic ions affect the corrosion in the molten fluoride salts for Ni-based alloys is crucial.

In addition, for applications like a reactor-to-hydrogen-production-plant heat transfer system, the temperature of the hot side is expected to 850 °C [2]. The performance of Hastelloy N alloy in fluoride salts at such high temperature gained increasing attentions, requiring more characteristics. Olson et al. [7] investigated the corrosion characteristics on several Ni-base alloys including Hastelloy N alloy at 850 °C in FLiNaK salts and pointed out impurities can dramatically influence corrosion. Sellers et al. [18] compared the performance of Hastelloy N alloy and 316L stainless steels in the similar condition, although the emphasis was put on the galvanic corrosion caused by interaction with graphite.

With above ideas in mind, in the present work, corrosion tests of Hastelloy N (UNS N10003) alloys, were performed in molten fluoride salts at 850 °C. FLiNaK salts (LiF–NaF–KF: 46.5–11.5–42 mol.%) with relatively high content of Fe impurities were selected for this study to investigate the effect of the metallic ion impurity on the corrosion behavior. Additionally, FLiNaK salts has also been con-

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