



Corrosion performance of Ni-16%wt.Mo-X%wt.SiC alloys in FLiNaK molten salt

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ABSTRACT

The corrosion performance of Ni-16%wt.Mo-X%wt.SiC (X = 0.5, 1.5, 2.0, 2.5 and 3.0) alloys prepared via mechanical alloying followed by consolidation using spark plasma sintering (SPS) from pure Ni, Mo and SiC powders is investigated. Corrosion testing at 650 °C/200 h in FLiNaK molten salt showed that increasing the volume fraction of SiC in the initial Ni-Mo-SiC powder mixture leads to formation of large amount of Mo₂C precipitates, which readily dissolve into FLiNaK molten salt. Hence, only the corrosion resistance of NiMo-SiC alloys with a low SiC content (< 2 wt.%) is comparable to that of Hastelloy-N[®] alloy.

1. Introduction

Molten Salt Reactor (MSR) is one of the next generation (Generation IV) of nuclear reactors selected by the Generation IV International Forum (GIF) [1,2]. MSR employs a circulating liquid molten salt (FLiBe, FLiNaK) containing fission material (fuel) as the fuel and coolant at the same time. The fuel is dissolved in the carrier molten salts, so it can be easily transported by pumps via pipes between a reactor core and a heat exchanger [1,2]. However, the molten salt is highly corrosive to the structural materials, especially at high temperatures [3,4]. Unlike the protective function of oxide products, which are formed on the surface of alloys in oxygen-containing environment, the corrosion products (e.g. metallic fluorides) forming in molten-salt environment are unstable and easily dissolvable in molten salt [5]. According to Gibbs free energies of common alloying elements present in most of structural materials, the tendency of formation of metallic fluorides increases in the following order: W, Mo, Ni, Fe, Cr, Al [6]. In addition, to highly corrosive environment of molten salt and high temperature, the neutron irradiation is also a problem for the structural materials in MSR systems. It has been shown the radiation damage of reactor materials may further promote molten salt corrosion [5,7]. Hence, successful structural materials employed in MSRs are expected to withstand a combination of challenging operation conditions of high temperature, neutron irradiation and molten salt corrosion [8,9].

Nickel-based alloys possess by far the best corrosion resistance in fluoride molten salts (FLiBe, FLiNaK) comparing to any other readily available structural materials, and are thus considered as candidate structural materials for MSR systems. Hastelloy-N[®] (UNS N10003), a Ni-based alloy with low Cr content and no Al, has been developed by Oak Ridge National Laboratory (ORNL, USA), and it has been used as the main structural material for 5 years in the experimental MSR at ORNL [10]. However, it has been found during the operation of this experimental MRS that the Te-induced intergranular cracking significantly deteriorates its mechanical properties [11]. Cheng et al. [12] showed that Te, which is a fission product, reacts with Cr in the alloy forming a cubic CrTe at grain boundaries, which then leads to the Te-induced intergranular cracking. In addition, the face-centered cubic (fcc) structure of the Ni matrix is vulnerable to He embrittlement, which is caused by the accumulation and coalesce of He bubbles formed as a result of neutron irradiation [13]. Last but not least, the low thermal stability of mechanical properties limits the application of Hastelloy-N[®] to temperatures below 700 °C [14].

In order to address some of the shortcomings of the currently available alloys for MSR applications, a new type of NiMo-SiC alloys has been developed by Shanghai Institute of Applied Physics (SIAP). These novel NiMo-SiC alloys are prepared using mechanical alloying (MA) of pure Ni, Mo and SiC powders followed by consolidation via spark plasma sintering (SPS) [15,16]. They do not contain Cr in order to

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avoid Te-induced intergranular cracking as well as commonly observed Cr depletion during the exposure to fluoride molten salts. The effects of SiC content on microstructure and mechanical properties have been investigated in Refs [15,17]. – these results showed an excellent strength and thermal stability of SiC nano-particles in the NiMo matrix at temperatures up to 850 °C [18]. Hence, SiC particles not only strengthen the alloy matrix but also act as He trapping sites and thus effectively inhibit the growth of He bubbles greatly reducing the He embrittlement [19,20]. However, the molten salt corrosion of these new NiMo-SiC alloys has not been investigated.

In the present study, the corrosion behaviour of Ni-16 wt.%Mo-Xwt.% SiC (X = 0.5, 1.5, 2.0, 2.5 and 3.0) alloys is investigated. The molten corrosion performance of prepared alloys was tested in a eutectic mixture of LiF–NaF–KF (FLiNaK) at 650 °C for 200 h under Ar atmosphere. The extent of corrosion was examined from a direct weight loss measurement, and by studying the effect of molten salt on the microstructure. The corrosion performance of prepared Ni-16wt.%Mo-Xwt.% SiC alloys is then compared with that of Hastelloy-N[®] alloy, and the corrosion mechanisms in fluoride molten salt are discussed.

2. Experimental

2.1. Material

High purity Ni, Mo and SiC powders were mixed and mechanically alloyed in a high-energy ball mill before being consolidated using the spark plasma sintering (SPS). The ratio of powders in the initial powder mixture varied as follows – the amount of Mo was always constant at 16 wt.%, while we were varying the amount of SiC between 0.5–3.0 wt.% (0.5, 1.5, 2.0, 2.5, 3.0 wt.%), and thus also the balance amount of Ni. After consolidation using SPS specimens were annealed at 1100 °C for 15 min and water quenched. The detail procedures and parameters for fabricating of these NiMo-Si alloys are described in details in Ref. [15,17]. High-resolution neutron diffraction (HRND) measurement a range of microscopy techniques was used to identify the constituent phases present in prepared alloys [15,17].

2.2. Molten salt corrosion testing

The corrosion testing was conducted at Australian Nuclear Science and Technology Organisation (ANSTO), Sydney, Australia. The specimens with dimensions of 10 × 5 × 1 mm were wire cut from prepared Ni-16wt.%Mo-X wt.%Si and Hastelloy-N[®] alloys. The specimens were then polished to a 50nm-Al₂O₃ finish before being exposed to FLiNaK molten salt. 200 g of the FLiNaK molten salt was prepared in a glow box under a N atmosphere from commercially available LiF (62497), NaF (201154) and KF (60239) salts supplied by Sigma-Aldrich (≥ 99.0% pure). The maximum amounts of impurities in the prepared 200 g of FLiNaK salt were calculated based on the supplier datasheets and are shown in Table 1. No additional purification of the salt was applied in order to test the samples in the molten salt containing commonly present impurities. A vitreous (glassy) carbon crucible (7 mm in diameter, 7 mm in height and with the volume capacity of 250 ml) was filled with the prepared FLiNaK molten salt mixture in the glove box under a N atmosphere before being transferred to pre-heated furnace (150 °C). Then a bake-out sequence of FLiNaK salt was carried out to minimize the water content in the salt prior to the actual corrosion experiment. The salt was heated at a rate of 3 °C/min up to 100, 200, and 300 °C with a holding time of 2 h at each temperature under vacuum. In the final bake-out stage, the salt was heated up to 400 °C for 16 h followed by slow heating to 650 °C, while maintaining vacuum. Once the vacuum of 0.5–0.6 mbars was achieved at the 650 °C, the furnace was purged with Ar gas (99.997%) at a pressure of 34 kPa – this overpressure of Ar was maintain during the entire experiment to prevent oxygen entering into the furnace. The Ni-16wt.%Mo-X wt.%Si specimens were introduced into the molten salt only after the bake-out procedure was

Table 1

Impurity details of used LiF–NaF–KF (FLiNaK) molten salt, which was prepared in-house from the raw chemical constituents (LiF (62497), NaF (201154) and KF (60239)) supplied by Sigma-Aldrich (≥ 99.0% pure).

	NaF (ppm)	LiF (ppm)	KF (ppm)	FLiNaK (ppm)
Cl	50	100	50	65
S	300	500	100	240
Fe	30	50	5	21
Ag	–	–	5	3
Al	–	200	5	61
As	–	5	–	1
Ba	–	50	5	18
Bi	–	20	5	9
Ca	–	500	10	152
Cd	–	5	5	4
Co	–	5	5	4
Cr	–	10	5	6
Cu	–	50	5	18
Fe	30	50	5	21
Mg	–	100	5	32
Mn	–	5	5	4
Mo	–	5	5	4
Ni	–	100	5	32
Pb	30	10	5	9
Sr	–	100	5	32
Zn	–	10	5	6
Li	–	–	5	3
Ti	–	–	5	3

completed. The specimens were fully submerged in FLiNaK, whilst not being in direct contact with any side of the crucible. Note that the corrosion testing of the Hastelloy-N[®] alloy sample was carried out separately but in the same experimental set-up so that the direct comparison can be made. In order to minimize experimental errors during corrosion testing, three specimens of each alloy were simultaneously tested in the FLiNaK molten salt at 650 °C for 200 h under Ar atmosphere.

After the corrosion experiment, the samples were soaked for 24 h in Al(NO₃)₃ aqueous solution (20 wt.%) to remove the residual FLiNaK salt from the sample surface. All specimens were weighted before and after the corrosion test (after cleaning) so the overall weight loss could be recorded. The elemental analysis of the salt after the testing was conducted using an Analytic Jena (formerly Varian) 820-MS Inductivity Coupled Plasma - Mass Spectrometry (ICP-MS) instrument, fitted with a Micromist[®] concentric glass nebulizer and Peltier cooled glass spray chamber. The SEM/EDS (Zeiss Auriga 60, 20KV), EPMA (Shimadzu EPMA-1720, 15KV) and TEM (JEM-2200FS at ANSTO and Tecnai G²F20 at SINAP, 200 kV) were employed to examine the impact of molten salt corrosion on the microstructure of tested alloys.

3. Results

3.1. Microstructure

The MA followed by SPS consolidation process of Ni-16wt.%Mo-X wt.%Si powder mixtures resulted in a NiMo matrix containing unreacted SiC nano-particles and Mo₂C, Ni₃Si precipitates, which were formed by reaction between Mo and SiC powders during MA and SPS processes [15,17]. Fig. 1 presents high-resolution neutron diffraction (HRND) patterns of prepared alloys. The main diffraction peaks in collected HRND patterns are those corresponding to the fcc NiMo matrix (black) and hcp Mo₂C (red) precipitates. Note that due to a small volume fraction of both Ni₃Si nano-precipitates and unreacted SiC nano-particles in the microstructure of prepared alloys [15,17] their presence cannot be evaluated from HRND patterns.

Analysis (Rietveld refinement) of HRND patterns has been conducted using the GSAS software package [21–23]. The results of GSAS

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