



Effect of moisture on corrosion of Ni-based alloys in molten alkali fluoride FLiNaK salt environments

Fan-Yi Ouyang*, Chi-Hung Chang, Bo-Chien You, Tsung-Kuang Yeh, Ji-Jung Kai

Department of Engineering and System Science, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

HIGHLIGHTS

- High-temperature corrosion behaviors of Ni-based alloys in molten FLiNaK salts.
- Effect of different residual moistures of FLiNaK salts on corrosion behaviors.
- Mass loss of tested alloys is primarily determined by the purity of FLiNaK salts.
- Original Mo content of alloys affects mass losses in moisture-containing salts.
- Higher moisture content in salts aggravates intergranular corrosion and pitting.

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ABSTRACT

We investigated the corrosion characteristics on several selected alloys at 600 and 700 °C in FLiNaK molten salts with different moisture contents. Hastelloys-N and Hastelloys-B3 exhibited better corrosion resistances, while Haynes 263 showed the poorest corrosion resistance. The mass loss of the tested alloys is primarily determined by the purity of FLiNaK salts; however, the effect of temperature becomes more important on the mass loss of the tested alloys in the non-purified FLiNaK salts. When the residual moisture is present in the FLiNaK salts, the mass losses of the tested alloys varied linearly with original Cr content plus one-third of Mo content. The results of structural characterization revealed that the tested alloys in the FLiNaK salts with higher moisture content would aggravate intergranular corrosion and pitting.

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1. Introduction

The molten salt reactor (MSR) has been selected as one of the Gen-IV (Generation Four Initiative) nuclear reactors, due to its desirable properties of online refueling and burning of minor actinides in spent fuels, along with the capability with hydrogen production [1]. A MSR can operate at near atmospheric pressures to reduce mechanical stresses experienced by the structural components, thereby simplifying the reactor design and improving the operation safety. However, MSRs operate at much higher temperatures than water cooled reactors (i.e. boiling water reactors and pressurized water reactors) for a higher thermodynamic efficiency, while staying at a lower vapor pressure. In addition, molten salts can be highly corrosive, especially at high temperatures. Therefore, the structure components in an MSR are expected to face more severe degradation challenges, caused by high operating temperatures and corrosive environments of molten salts [2,3].

A MSR mainly uses molten salt mixtures as a coolant in the primary circuit. General specifications for molten salts used in nuclear applications have been included in Ref. [4]. In comparison with chloride salts, fluoride salts are preferred in MSRs because fluorine does not require an expensive isotope separation process, nor does it easily become radioactive under neutron irradiation. Potential coolants for MSRs are BeF₂-salts (e.g. FLiBe salts), and alkali fluoride salts [5]. However, beryllium is extremely toxic and environmentally harmful. On the other hand, alkali fluoride salts show desirable fluid transport and thermochemical properties, particularly for FLiNaK [6]. Nevertheless, alkali fluoride salts are highly corrosive in nature; in particular, the corrosivity of a molten salt environment will be much greater in the presence of the chemically reactive and radioactive HF gas, produced in the nuclear reactor core through the combination of hydrogen ions (from impurity water) with fluoride ions.

Corrosion behaviors of materials in molten alkali fluoride salt environments have been extensively investigated [7–9]. Several literatures [7,8] have showed that Hastelloy-N and similar Ni-based alloys were resistant to corrosion at temperatures up to about 700 °C. Olson et al. found that corrosion mainly occurred

* Corresponding author. Tel.: +886 3 5715131x34321; fax: +886 3 5720724.

E-mail address: fyoyang@ess.nthu.edu.tw (F.-Y. Ouyang).

Table 1
The compositions of each alloy used in this study.

Alloy/wt.%	Ni	Cr	Mo	Fe	W	Co	Mn	Al	Ti	Si	C	Others
Hastelloy-N	71	7	16	3	0.5	0.2	0.8			1	0.08	Al + Ti:0.35 Cu:0.35
Hastelloy-B3	65	1.5	28.5	1.5	3	3	3	0.5	0.2	0.1	0.01	
Haynes-242	65	8	25	2		2.5	0.8	0.5			0.03	Cu:0.5
Haynes-263	52	20	6	0.7		20	0.6	0.6	2.4	0.4	0.06	Cu:0.2
TZM	0.005		99.4	0.01					0.4	0.005	0.04	

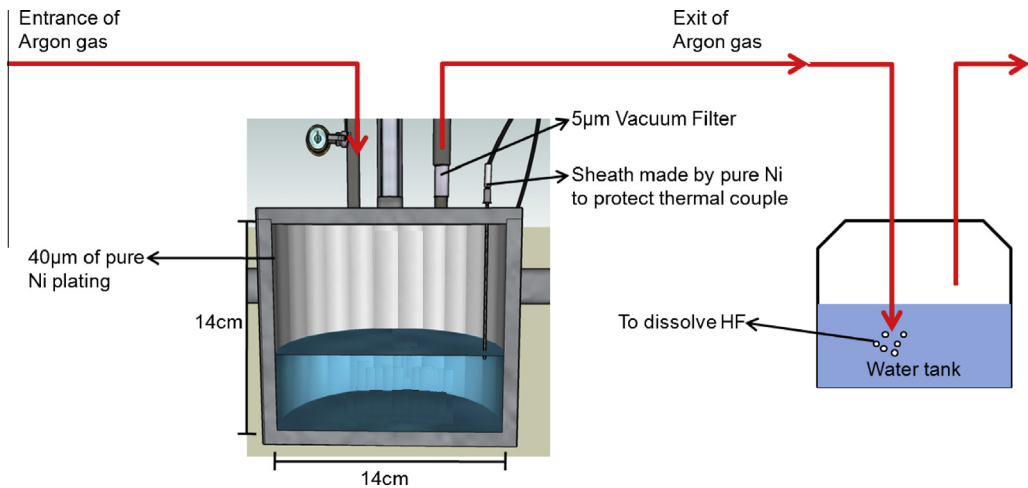


Fig. 1. The schematic of experimental set up.

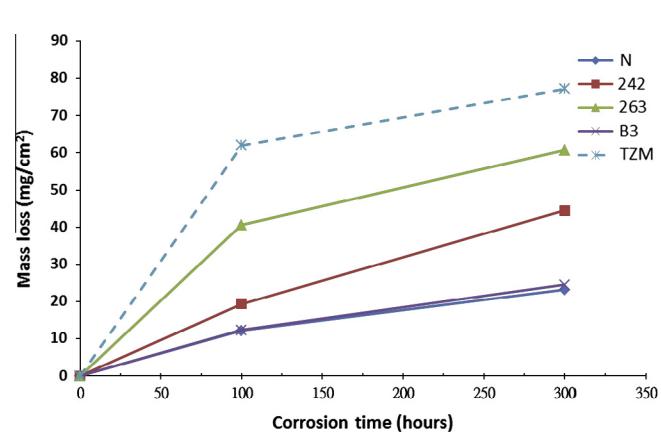


Fig. 2. The results of mass loss of tested alloys after different periods of corrosion tests at 600 °C with moisture content of 3.19 wt.%

Table 2
The experimental conditions for corrosion tests in this study.

Test conditions	Temperature (°C)	Residual moisture content in FLiNaK salts (wt.%)	Tested alloys	Tested duration (h)
A	600	3.19	Hastelloys-N, Hastelloys-B3, Haynes 263, Haynes-242, TZM	100, 300
B	700	3.19	Hastelloys-N, Hastelloys-B3	100, 200
C	700	1.91	Hastelloys-N, Hastelloys-B3	100, 200

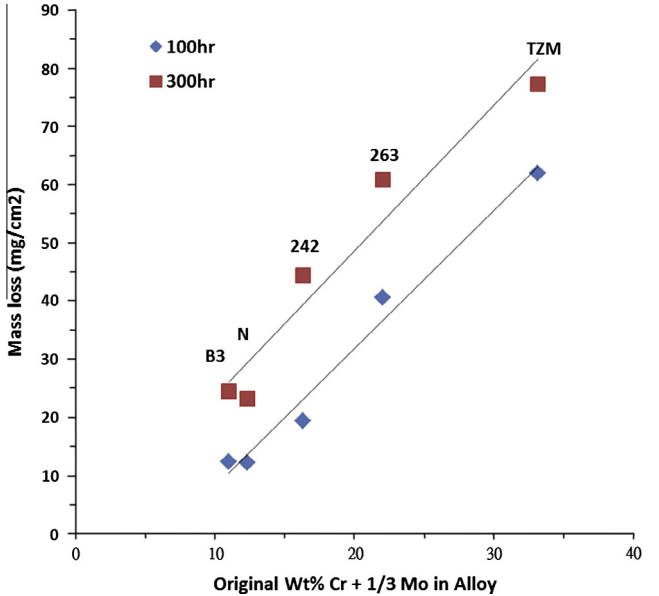


Fig. 3. The relationship between the mass losses and original contents of Cr content and Mo, showing mass losses of the tested alloys varied linearly with Cr content plus one-third of Mo content (Cr wt.% + 1/3 Mo wt.%).

at the grain boundaries of these alloys and the corrosion rates were dependent on the initial Cr-content of these alloys [7]. Additionally, several researches have also demonstrated that the corrosion behaviors are highly affected by the presence of impurity in the molten salts [10–14]. Kondo et al. [11] pointed out that non-purified molten salt may accelerate the corrosion rate of ferritic martensitic steel JLF-1 alloys and accordingly lead to changes in corrosion mechanism. Thus, understanding how moisture and/or

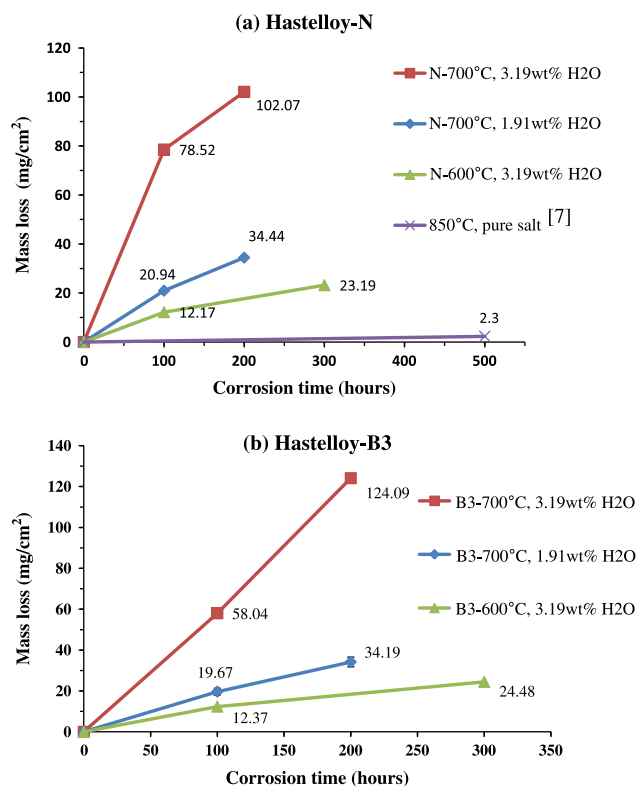


Fig. 4. The comparison of mass loss of (a) Hastelloys-N and (b) Hastelloys-B3 after different periods of corrosion tests for different moisture contents and temperatures.

impurities affect the corrosion in molten FLiNaK salts for Ni-based alloys is crucial. This study investigated the corrosion characteristics of several Ni-based alloys in high-temperature molten alkali fluoride salt (LiF–NaF–KF) environments in terms of different moisture contents. The corrosion behaviors in non-purified and purified molten alkali fluoride salts are discussed and compared. The resulting microstructures of the scale are also characterized.

2. Experimental

Four Ni-based alloys were selected as the target materials for corrosion tests. Table 1 lists the composition of each alloy. Prior to corrosion tests, the samples were ground with SiC papers down to 2500 grit (0.5 mm) and polished progressively with 0.5 mm diamond pastes and 0.01 Al₂O₃ powders. The samples were then ultrasonically cleaned in deionized water and acetone, respectively.

The FLiNaK salt used in this study was composed of LiF, NaF, and KF at ratios of 46.5%, 11.5%, and 42%, respectively, to maintain a lowest melting temperature of 454 °C. To investigate the effect of moisture on the corrosion behavior of the tested alloys, the FLiNaK salt was pre-heated in a furnace at 150 °C for 3 h and at 300 °C for 12 h, respectively, and then promptly poured into a pre-heated autoclave at 100 °C for subsequent corrosion tests. Their corresponding moisture content in the FLiNaK salts in our test system was recorded as high as 3.19 wt.% and 1.91 wt.%.

The schematic of the experimental setup is shown in Fig. 1. Since nickel has been shown to exhibit excellent corrosion resistance in the molten FLiNaK salts [8], the autoclave was made of alloy 625 with a pure nickel liner of 30 mm in thickness to prevent the autoclave from being corroded in the molten FLiNaK salts during the corrosion tests. A thermal couple, protected by a pure Ni sheath inside the autoclave, was used to measure the salt temper-

ature. A dry Ar gas stream was injected into the autoclave to maintain an inert surface environment for the molten salt and to carry possible gaseous HF away from the autoclave.

Corrosion tests were performed by immersing the samples into the FLiNaK salt at an ambient temperature of 600 °C and 700 °C for different periods of time, respectively. Test durations included 100 h, and 200 h, to 300 h. Table 2 summarizes the experimental condition for corrosion tests. After the corrosion tests, the retrieved samples were cleansed in a boiling 1 M Al(NO₃)₃ solution to remove residual FLiNaK salts [15] and then ultrasonically cleansed in deionized water and acetone for 5 min, respectively. Mass changes of the samples were measured using a high precision balance. Microstructural evolution and elemental composition of the samples were examined using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

3. Results and discussion

3.1. Mass changes

The results of mass change in the samples after different periods of corrosion tests at an ambient temperature of 600 °C with moisture content of 3.19 wt.% in FLiNaK molten salts are presented in Fig. 2, showing that the mass loss of the samples increased with increasing corrosion time. Among the tested alloys, Hastelloys-N and Hastelloys-B3 exhibited relatively better corrosion resistances for tested durations of 100–300 h, while Haynes 263 showed the poorest corrosion resistance. The mass loss of Haynes-263 was more than 2 times of those of Hastelloys-N and Hastelloys-B3 alloys after 300-h corrosion test. Since Cr is the major constituent in these Ni-based alloys and possesses lower Gibbs free energy to form Cr fluorides [16], the original contents of Cr in the Ni-based alloys play a dominant role in the corrosion resistance. Literature data also suggested that the Ni-based alloys containing lower Cr contents would have improved corrosion resistances in fluoride salt environments [17]. In the study by Olsen et al. [7], they conducted corrosion tests at 850 °C for 500 h in the purified molten FLiNaK salts and found that the mass losses in alloys resulting from corrosion increased with increasing Cr contents.

However, the effect of the original Cr content alone in these tested alloys fails to explain the discrepancy of mass change between four Ni-based alloys in our study. This proposition can be supported by that the Hastelloy-B3 has similar mass losses as Hastelloy-N at different corrosion durations although the Cr contents of Hastelloy-B3 was lower than that of Hastelloy-N by 5.5 wt.%. In principle, a lower Cr content in an alloy would enhance the corrosion resistance of this alloy in molten salts. Additionally, the Cr contents in Haynes-242 and Hastelloy-N were close to each other, however, Haynes-242 showed a comparatively greater mass loss than Hastelloys N. We found that, as shown in Table 1, Hastelloy-B3 had a relatively high Mo content of 12.5 wt.% as compared to Hastelloy-N. Meanwhile, the Mo content of Haynes-242 was actually 9 wt.% higher than that of Hastelloy-N. It is noted that the residual moisture content of molten salts in this study is 3.19 wt.%, which is much higher than that in the study by Olsen et al. [7]. Thus we speculate that the large deviation of mass loss in corrosion tests was possibly because Mo is easy to corrode in moisture-containing molten salts. Fig. 3 shows an empirical relationship between mass loss and original Cr and Mo contents in the alloys based on the current results. We find that the mass losses of the tested alloys varied linearly with original Cr content plus one-third of Mo content ($\text{Cr wt.\%} + 1/3 \text{ Mo wt.\%}$) under the non-purified molten salt environments.

To further verify the effect of moisture on the mass loss of Mo, the TZM alloys (with 99.4% of Mo) were subject to corrosion test at

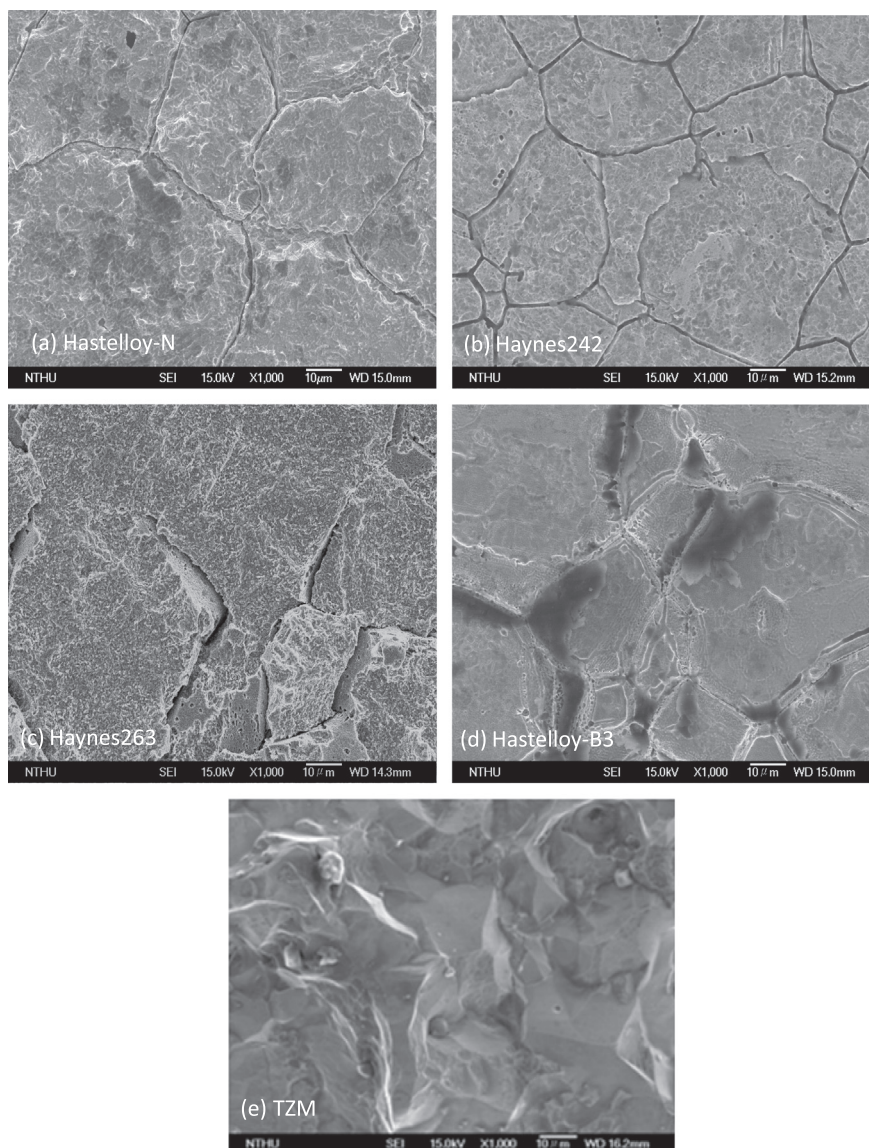


Fig. 5. The morphological SEM images of (a) Hastelloy-N, (b) Haynes-242, (c) Haynes-263, (d) Hastelloy-B3 and (e) TZM after 300 h of corrosion tests in FLiNaK salts with moisture content of 3.19% at 600 °C.

an ambient temperature of 600 °C with moisture content of 3.19 wt.% in FLiNaK molten salts for 100 h and 300 h, respectively. They experienced a mass loss of 61.99 mg/cm² after a 100-h test, which exhibited the highest mass loss in comparison with other four Ni-based alloys (Fig. 2). These results suggest that the presence of residual moisture was likely to preferentially enhance the oxidation of Mo in the FLiNaK salts. Tyreman et al. [18] have conducted a corrosion test for several pure metals in a pure HF gas environment at 850 °C for 10 h and found that Mo was most corrosion resistant material among all tested metals. Conversely, when they repeated the corrosion test in a diluted 50% HF solution, the corrosion rates of all materials decreased except for Mo. In fact, the corrosion rate of Mo increased by a factor of four. Thus, these data further support why Mo is involved in the corrosion under the non-purified molten salt environments.

In addition to moisture induced tendency change of corroded constituents, another interesting finding is that the mass-losses of our samples in the non-purified molten salts are remarkably larger than what have been observed in the literatures with purified FLiNaK [7]. To provide a better view of the effect of moisture on corrosion behavior of Ni-based alloys, Hastelloys-N and Hastel-

loys-B3 were selected for the corrosion tests at 700 °C with moisture content of 3.19 wt.% and 1.91 wt.% in FLiNaK molten salts, respectively. Fig. 4a presents the results of mass change of Hastelloy-N after different periods of corrosion tests for different moisture contents in the molten salts. As compared with samples in the non-purified molten salts at lower ambient temperatures (600 °C and 700 °C), the mass loss of the samples in the purified FLiNaK salts were significantly lowered by at least 25 times, even though the corrosion tests in the purified salts were run at higher temperature (850 °C) for longer exposure time (500 h). These results can infer that the introduction of moisture in the FLiNaK salt would significantly increase the oxidizing power of the salt and accordingly lead to increased corrosion rates of the alloys that are exposed to it. Additionally, these results suggest that the purity of salts plays the dominant role on the mass loss of the samples; the influence of temperature seems not so significant when comparing the mass loss of the samples in terms of purified and non-purified molten salts. When samples were subject to non-purified molten salts at 700 °C, the corrosion tests performed with moisture content of 3.19% exhibited approximately 3 times larger mass loss of samples than that with moisture content of 1.91%, which further

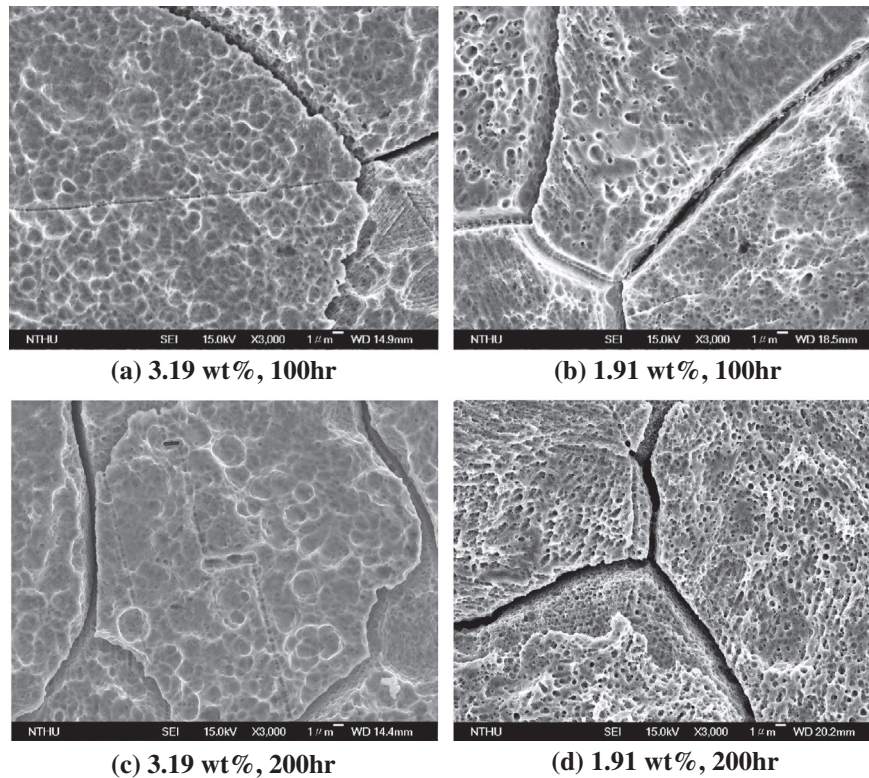
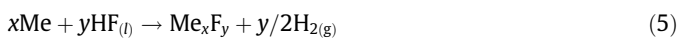
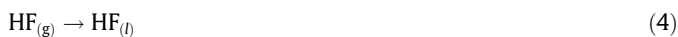
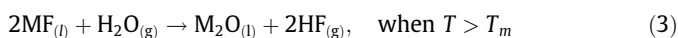
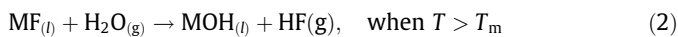


Fig. 6. The morphological SEM images of Hastelloy-N after (a) 100 h with moisture content of 3.19 wt.%, (b) 100 h with moisture content of 1.91 wt.%, (c) 200 h with moisture content of 3.19 wt.% and (d) 200 h with moisture content of 1.91 wt.%, of corrosion tests at 700 °C.

supports that higher moisture in the FLiNaK salt would accelerate the corrosion rates. However, the effect of temperature seems to become more important in the cases of non-purified molten salts. The proposition can be evidenced by that the larger mass loss of samples at 700 °C with 1.91% moisture content of molten salts was observed as compared to that at 600 °C with 3.19% residual moisture of FLiNaK salts. Similar trends were also observed for Hastelloys-B3 (Fig. 4b), showing that the weight loss of samples performed at 700 °C is larger than that at 600 °C. It is also evident that increasing the residual moisture of molten salts results in an enhancement of mass loss of Hastelloys-B3 samples.

When moisture or air impurities are present in the molten salts (non-purified), water in the alkali fluoride salts (represented as MF) will react with fluoride ion and lead to the generation of an HF gas. A portion of the HF gas will be dissolved into the molten salt and transformed into a liquid state, which tends to more easily accelerate the corrosion rates of metals (represented as Me). Possible reactions involved in the foregoing phenomenon are suggested as follows [6]:



where M represents as K, Li and Na; and Me represents as Ni, Mo, Fe, Cr, Ti etc. The water content in the fluoride salts we used in this study was recorded as high as 3.19 wt.% and 1.91 wt.%, respectively. The content of HF generating via Eqs. (1)–(4) was thus sufficient in

quantity to induce significant corrosion in all alloying elements. Accordingly, the enhanced oxidizing power of the salts results in remarkably increases in mass losses of the tested samples.

3.2. Microstructural morphology

Fig. 5 shows the morphological SEM images of four Ni-based alloys and TZM after 300 h of corrosion tests at 600 °C with moisture content of 3.19%. Hastelloy-N and Haynes-242 experienced exhibited intergranular attack during the corrosion tests. It is believed that the formation of carbides near the grain boundary regions leads to the selective corrosion on the boundaries [19]. Meanwhile, the effect of intergranular corrosion was more pronounced for Haynes-242. Haynes-263 also exhibited intergranular corrosion pattern after a test period of 300 h. Due to a relatively larger amount of Cr (20 wt.%) content in the Haynes-263 sample and the more negative Gibbs free energy of formation of chromium fluoride [16], the dissolution rate of this alloying component was comparatively high, especially for regions near the grain boundaries, leading to the serious intergranular attack. For Hastelloy-B3, in addition to grain boundaries, grains were also attacked by the corrosive medium. As compared the corrosion patterns between Hastelloy-B3 (1.5% Cr) and other tested Ni-based alloys in this study, the Ni-based alloys containing lower Cr contents tends to suffer more general corrosion than intergranular corrosion. Furthermore, because TZM alloys possessed metallurgically and compositionally uniform and lacked of passivating elements, the corrosion pattern tended to be general corrosion, leading to the relatively uniform reduction of thickness over the surface (Fig 5e).

Fig. 6 shows the morphological SEM images of Hastelloy-N after 100 and 200 h of corrosion tests at 700 °C with different moisture contents. It is noted that intergranular corrosion was still the dominant corrosion pattern, which is consistent to what we have

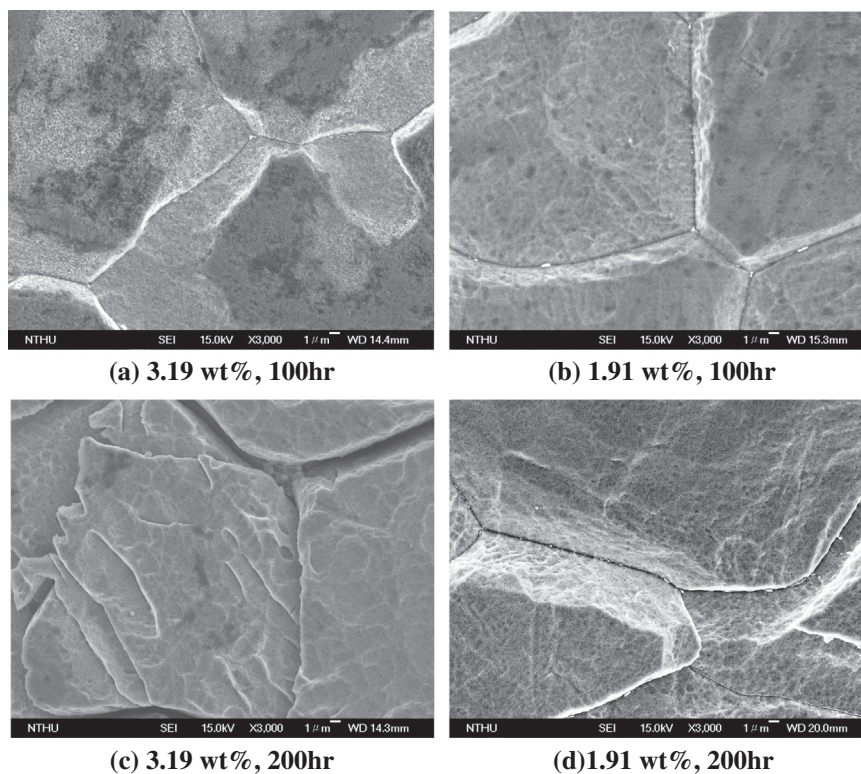


Fig. 7. The morphological SEM images of Hastelloy-B3 after (a) 100 h with moisture content of 3.19 wt.%, (b) 100 h with moisture content of 1.91 wt.%, (c) 200 h with moisture content of 3.19 wt.% and (d) 200 h with moisture content of 1.91 wt.%, of corrosion tests at 700 °C.

observed at 600 °C. In addition to intergranular corrosion, pitting was also observed for Hastelloy-N. It can be found that the scale of pitting on the samples is more serious in the FLiNaK salts with moisture content of 3.19 wt.%. This is likely that higher moisture content of FLiNaK salt exacerbated the extent of pitting on the samples, further generating higher mass loss of tested alloys. Fig. 7 shows the morphological SEM images of Hastelloys-B3 after 100 and 200 h of corrosion tests at 700 °C with different moisture contents. Similar to the SEM results at 600 h, Hastelloys-B3 experienced more general corrosion than intergranular corrosion. It is noted that the general corrosion is more severe on the samples in the FLiNaK salts with moisture content of 3.19 wt.%. Additionally, the attacked grain boundary in the sample with higher moisture content is deeper and wider than that at lower moisture content. These above results suggested that, when higher moisture content is present in the FLiNaK salts, more aggressive corrosion attack happened on the tested alloys, which agreed well with the measured mass loss of Hastelloy-N and Hastelloys-B3 after corrosion tests.

4. Conclusions

The corrosion characteristics on several Ni-based alloys and TZM at 600 and 700 °C with moisture content of 3.19 wt.% and 1.91 wt.% in FLiNaK molten salts were studied. Hastelloys-N and Hastelloys-B3 exhibited relatively better corrosion resistances, while Haynes 263 showed the poorest corrosion resistance. When the residual moisture is present in the FLiNaK salts, the mass loss of the test alloys no longer increased linearly with increasing Cr contents, instead; the mass losses of the tested alloys varied linearly with original Cr content plus one-third of Mo content (Cr wt.% + 1/3 Mo wt.%). Additionally, we find that the mass loss of the tested alloys is primarily determined by the purity of FLiNaK salts. However, once a minor amount of H₂O is present in the FLiNaK salts, the effect of temperature becomes more significant

on the mass loss of the tested alloys. The results of structural characterization revealed that lower Cr content in the Ni-based alloys would suffer more general corrosion than intergranular corrosion. Additionally, the samples in the FLiNaK salts with higher moisture content would aggravate intergranular corrosion and pitting.

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