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FY–22 MSR Milestone M4RD-22OR0603034 Corrosion of 316H Stainless Steel Specimens in Flowing FLiBe (LiF-BeF$_2$)

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FY22 Milestone M4RD-22OR0603034

Corrosion of 316H Stainless Steel in Flowing FLiBe (LiF-BeF$_2$)

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Summary

This milestone was originally envisioned for completion in FY21 and was delayed due to the COVID-19 response and difficulties in fabricating/obtaining fluoride salts. A monometallic type 316H stainless steel thermal convection loop (TCL) was operated for 1000 h with flowing LiF-BeF$_2$ (i.e. FLiBe) salt and a peak temperature of 650°C. In general, the attack was minimal. However, classic mass transfer was not clearly observed with mass losses in both the hot and cold legs. There was an issue with cleaning the loop with water and specimens may have oxidized, which was not an issue with the previous FLiNaK TCL.

Introduction

Compatibility of type 316H stainless steel with molten fluoride salts has been identified as a key research area for molten salt reactor development [1]. The 1960's molten salt reactor experiment (MSRE) used Ni-based Hastelloy N (Ni-7Cr-16Mo) as a structural alloy [2] but current developers favor 316H because of its ready availability and ASME code qualification. Numerous studies have been conducted on steel compatibility in FLiBe with general agreement that Cr is selectively removed during FLiBe exposure [3-7]. The removal of Cr from the alloy is especially pronounced when the fluorine potential of the salt is high due to the presence of impurities such as free fluoride ions, water, oxides and hydroxides. Purity of the salt is reliant on purification methods which typically use the hydrofluorination process [8-10] developed during the 1950's and 1960's. Moving beyond static, isothermal compatibility experiments [5-7,11-13], flowing salt experiments in a thermal gradient are needed to study mass transfer, which is the major concern with potentially corrosive working fluids [13-15]. Historically, thermal convection loops (TCLs) [13-20] have been used as an initial assessment of compatibility before investing in a forced convection loop. Thus, this task conducted a monometallic TCL experiment with type 316H stainless steel tubing and 316H specimens with a peak temperature of 650°C and FLiBe salt provided by industry. Similar procedures were used so that these results could be compared to previous results in flowing FLiNaK salt [19].

Experimental

The purified, commercially produced Li_2BeF_4 (FLiBe) salt contained impurities shown in Table 1 with reported values similar to two batches of salt made at ORNL (listed as #1 & #2). Table 1 focuses on the elements that were changing in the salt, more extensive salt analyses have been reported elsewhere [21]. Typical procedures used to purify salt using H_2-HF have been presented elsewhere [8-10]. Flowing salt experiments were conducted using a harp-shaped (~0.75 m tall by 0.5 m wide) TCL, which is shown in Figure 1 and has been described in detail elsewhere [18,19]. All of the components in contact with salt were made from type 316H stainless steel including the 26.7 mm OD x 2.9 mm wall thickness tubing and the specimens in the hot leg (HL) and cold leg (CL) which consisted of small dogbone tensile specimens (25mm long with a 1.5 x 0.76 mm gage, designated SS-3) and coupons (1.8 x 19 x 25 mm). The coupons were made from the same heat with a composition of 68wt.%Fe-16.5Cr-10.4Ni-1.9Mo-1.5Mn-0.3Si-0.4Cu-0.034C (note this is <0.04C H specification) determined by combustion and plasma analyses. The specimens had a 600 grit finish. Identical chains of 20 specimens were suspended in the vertical HL and CL using 316L wire (1.6 mm diameter) and spanned the distance between the thermowells located in

Table 1. GDMS characterization of FLiBe salt before and after capsule testing

Salt	Cr (ppmw)	Fe (ppmw)	Mn (ppmw)	Ni (ppmw)
As-received commercial FLiBe	3.9	21	1.8	<1
Post-flowing test (1000 h/650°C)	208	14	32	1.2
Purified laboratory FLiBe #1	2.4	1.2	1	<1
Purified laboratory FLiBe #2	2.1	1.3	0.5	<1

the top, middle and bottom of each leg. At the middle and bottom of each chain a welded 316H spacer kept the chain centered in the flow path. Prior to loading with salt, the TCL was internally cleaned with water plus 20% nitric acid, followed by water and then acetone before evacuation and pre-heating to ~500°C using heat tape. The salt was melted in a type 316L SS pot above the HL prior to its introduction into the TCL using a SS valve, Figure 1a. The temperature of the flowing salt in the TCL was monitored primarily by type K thermocouples in 6 thermowells at the top, middle and bottom of the HL and CL that were inserted ~3 mm into the flow path. Three resistively heated furnaces heated the vertical HL and the bottom leg, Figure 1b. The TCL temperature was controlled at the top of the HL to 650±1°C for 1000 h and the bottom of the CL averaged 518°C. The top leg and CL were lightly insulated and not actively cooled. The temperature difference created a density gradient resulting in flow of ~2 cm/s determined by monitoring a "hot spot" created by a torch applied for 60 s to the bottom of the CL. After 1000 h, the salt was dumped into a similar SS pot by opening a SS valve below the CL [19].

Figure 1. Images of the 316H thermal convection loop (a) before furnace installation and insulation showing the fill tank at top and dump tank at bottom, (b) during operation and (c) water collection system. The loop flow path is approximately 1m tall and 0.5m wide [19].

The specimens were cleaned prior to exposure using acetone and methanol and after exposure by using deionized water sonication at 40°C for 1 h followed by cleaning in acetone. Prior to handling, specimens were tested to have <0.2μg Be/100cm^2. (Due to a clogged valve in the TCL water collection system (Figure 1c), the specimens were inadvertently exposed to room temperature water for >24 h.) Before and after exposure, the specimens were weighed using a Mettler Toledo model XP205 balance with an accuracy of ~±0.04 mg. The specimens were then sectioned and mounted in epoxy and polished for light microscopy, scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) (TESCAN model MIRA3) and glow discharge optical emission spectroscopy (GDOES) (Horiba model GD Profiler 2) to measure average composition through the reaction product(s). Using GDOES, depth profiles were acquired by sputtering the surfaces with an electric field-induced glow discharge plasma using 850 Pa of Ar and 50W of power with measurements made every 1 s and an anode diameter of 2 mm which defined the size of the region measured.

Results

After the 1000 h exposure to flowing commercial FLiBe and cleaning, Figure 2 compares the mass change for 316H specimens in the TCL experiment. The mass changes are plotted versus the estimated exposure temperatures. For the previously reported FLiNaK TCL specimens also shown in Figure 2 [19], specimen mass gains were observed on the CL, which suggested mass transfer from the HL to the CL. However, after exposure in FLiBe, mass losses were observed for most 316H specimens. The mass losses were higher than in the static capsule experiments (stars in Figure 2)[12] but are still relatively low.

Figure 3 shows light microscopy of several HL and CL specimens from the FLiBe TCL experiment. Consistent with the largest mass loss (3.0 mg/cm^2), the 316H specimen at the top of the HL showed indications at the surface of dissolution in the salt, Figure 3a. The surface was less convoluted with a mass loss of 1.5 mg/cm^2 at an estimated temperature of 636°C. At the other locations shown, there appears to be a reaction product on the surface. At the end of the

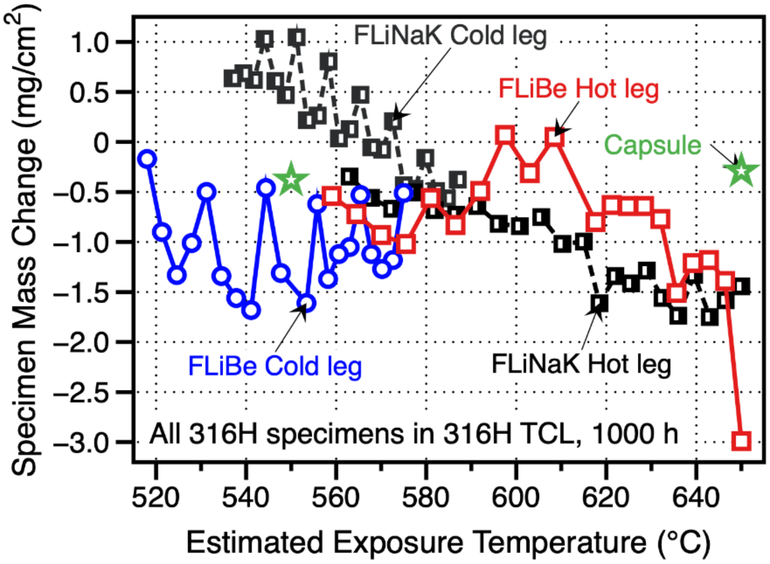

Figure 2. Specimen mass change of 316H specimens as a function of estimated exposure temperature in flowing FLiBe salt compared to values [14] for FLiNaK salt after 1,000 h. The capsule mass change values are shown as stars.

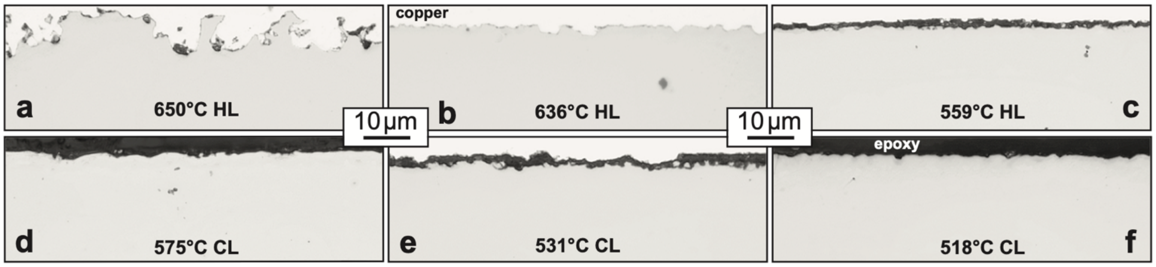

Figure 3: Light microscopy of polished cross-sections of alloy 316H specimens after 1000 h exposures to flowing FLiBe salt in the hot leg (HL) at (a) 650°C, (b) 636°C and (c) 559°C and in the cold leg (CL) at (d) 575°C, (e) 531°C and (f) 518°C.

FLiBe TCL experiment after the salt was drained, the TCL was filled with deionized water to remove residual salt from the specimens and tubing. However, FLiBe is less soluble than FLiNaK in water and the valve to the tank at the bottom of the CL designed to capture the Be-containing water (Figure 1c) clogged and the water remained in the TCL for >24 h at room temperature. During this period, the 316H surface may have oxidized, unlike the FLiNaK TCL experiment. This may have affected the mass change data as well, especially if material was removed during cleaning to remove any Be residue.

Figure 4 shows example GDOES sputter profiles with the quantification based on the alloy composition [22]. As expected, Cr and Mn were depleted at the specimen surfaces at both the top of the HL (Figure 4a) and the bottom of the CL (Figure 4b). This is consistent with the increased Cr and Mn detected in the salt after the flowing experiment was completed, Table 1. In both cases, C appears to be enriched in the near surface region. However, C is difficult to quantify and the presence of C (perhaps just as a surface impurity) needs to be further characterized. The C is mentioned because, based on the dark color of the as-received commercial FLiBe salt, it appeared to have a high C content but the salt C composition has not been quantified because of issues testing Be-containing salt using combustion analysis. In the CL, very little Ni enrichment was observed. In Figure 4c, the Cr profiles from several specimens suggests that the Cr depletion is similar on the TCL HL and CL with only a slight increase at the highest temperature. However, comparing Fe profiles suggests that Fe may be being transferred from the HL to the CL as Fe appears to be most enriched at the surface of the specimen from the bottom of the CL at 518°C, Figure 4d. While less pronounced than in the FLiNaK TCL such that specimen mass gains were not measured in the FLiBe TCL, Figure 2, both TCL experiments appeared to show evidence of Fe mass transfer. However, because of the inadvertent water exposure during cleaning of the FLiBe TCL and potential surface oxidation, it is not possible to compare the two experiments.

The GDOES results only provide an average composition in the sputtered area. To determine if there was deeper grain boundary attack, six specimens were examined by SEM/EDS. Figure 5 shows EDS maps from the specimen at the top of the HL with the most significant attack, Figure 3a. In this particular area analyzed, the Cu plating did not enter into the surface pores. There was no evidence of deeper penetrations or depletions under these conditions and the other specimens showed even less evidence of localized attack and are not shown. Two line profiles were measured on each specimen analyzed and those results are summarized in Figure 6. As expected, the deepest Cr depletion was observed at the hottest location in the loop (650°C) and the other locations showed less depletion, Figure 6a. Comparing the Fe profiles, the deepest Fe depletion was observed at the top of the hot leg, Figure 6b. However, Fe enrichment was not observed in the salt after the experiment, Table 1. The only other specimen to stand out was from near the bottom of the cold leg where Fe was enriched at the surface, similar to the GDOES result, Figure

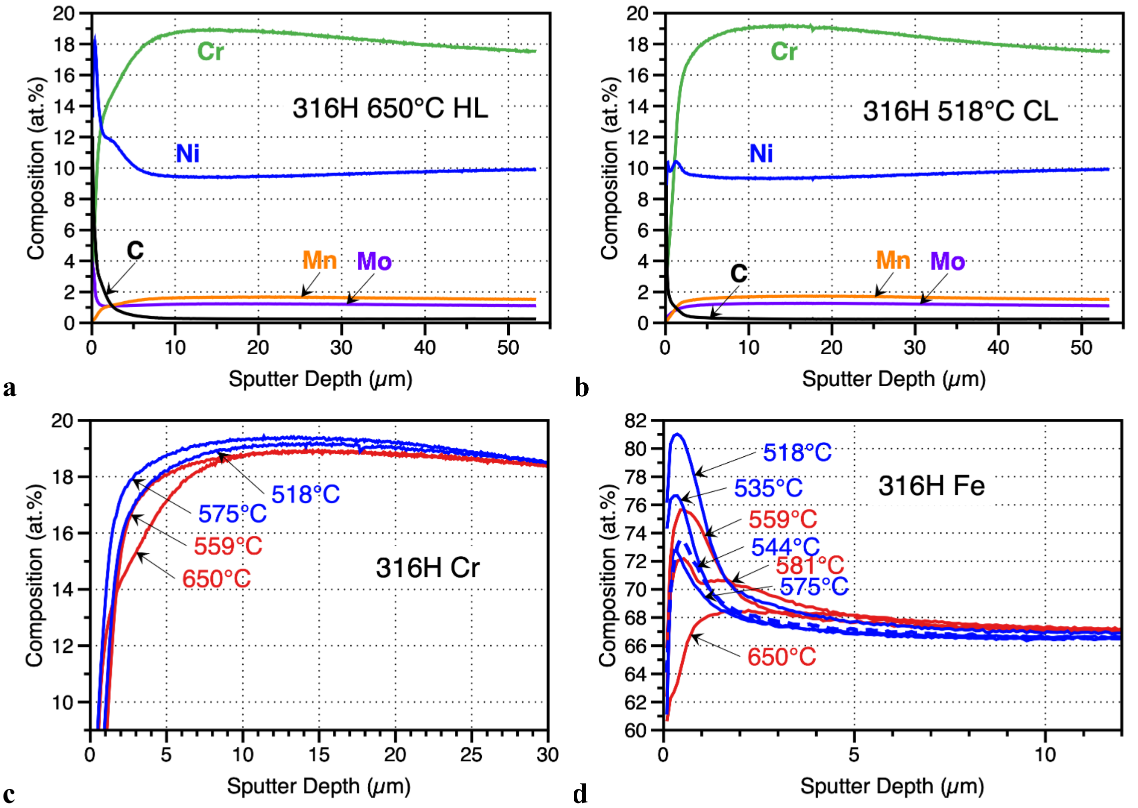

Figure 4: GDOES sputter depth profiles of 316H specimens after 1000 h exposures to flowing FLiBe salt at (a) 650°C in the hot leg and (b) 518°C in the cold leg. Compilations of profiles are shown for (c) Cr and (d) Fe.

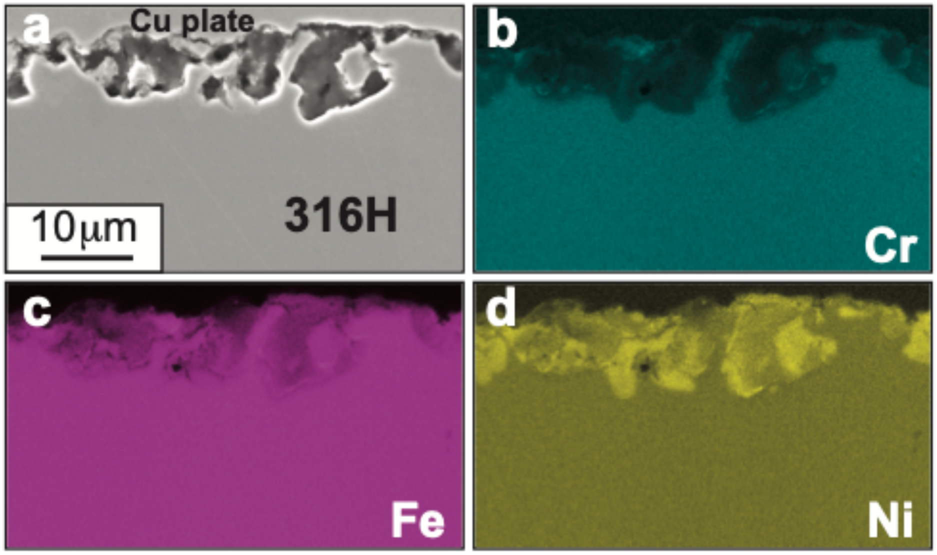

Figure 5: (a) SEM secondary electron image and (b-d) associated EDS maps of the same region.

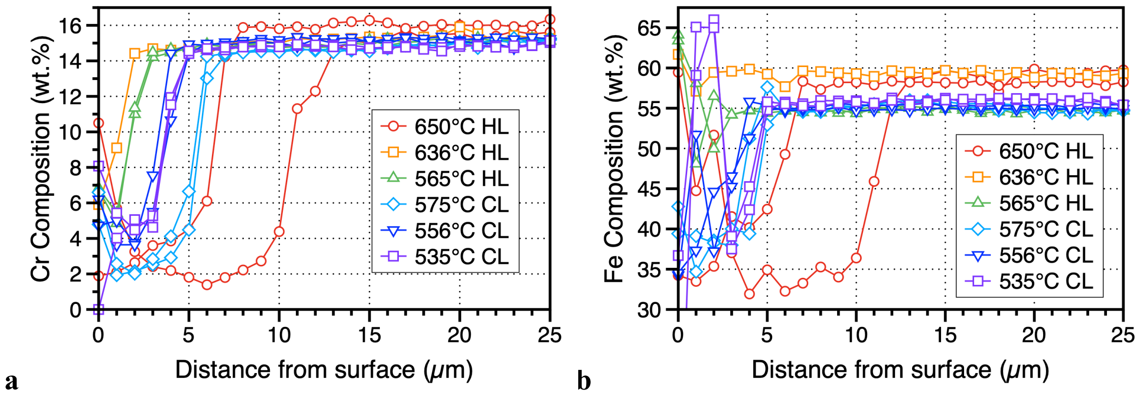

Figure 6: SEM EDS line profiles from selected hot leg (HL) and cold leg (CL) specimens (a) Cr contents and (b) Fe contents.

4d. These results confirm that the depletion was minimal under these conditions. Using dissolution data being collected, the next step will be to attempt to model these results based on the proposed framework [23].

Conclusions

An initial thermal convection loop experiment has been performed to assess the compatibility between FLiBe and type 316H stainless steel at 500°-650°C. Small mass changes were observed for 316H specimens exposed to purified, commercial FLiBe salt. The mass changes were similar to prior results for FLiNaK using nearly identical procedures. However, the results were not directly comparable because of an issue during cleaning of the FLiBe salt where the specimens may have been oxidized in room temperature water. Similar to the results in FLiNaK, the dissolution of both Fe and Cr was observed in FLiBe and, using GDOES characterization, there was evidence of mass transfer of Fe in both salts.

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