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FY–22 MSR Milestone M3AT-22OR0702011 Corrosion of 316H Stainless Steel Specimens in Two FLiBe (LiF-BeF$_2$) Salt Batches

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FY22 ART Milestone M3AT-22OR0702011

Corrosion of 316H Stainless Steel Specimens in Two FLiBe (LiF-BeF_2) Salt Batches

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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 fluoride salts. To complete the milestone, commercial FLiBe was compared to a batch of FLiBe produced by the conventional hydrofluorination process. However, the batch was stopped early due to an HF leak and the salt did not undergo the final H_2 sparging. Subsequent static compatibility testing of 316H specimens in 316H capsules resulted in small mass losses for the commercial FLiBe and much larger mass losses for the 2nd batch of FLiBe.

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 developed during the 1950's and 1960's [8]. To study compatibility of materials, such as type 316H stainless steel, in molten salt environments, impurities need to be removed by adequate salt treatment. However, standards for salt purity and purification conditions do not exist which can lead to large variability in reported mass loss and corrosion rates. Various characterization techniques are being studied and some results are reported. Static capsule experiments were selected as the primary metric for comparing the two different batches of FLiBe salt. Results are presented for 1000 h capsule experiments at 650°C where 316H specimens were exposed in 316H capsules.

Experimental

316H stainless-steel specimens measuring approximately 1.25 cm x 0.65 cm x 0.20 cm were cut, polished to 600-grit finish and weighed to ±0.04 mg accuracy using a Mettler Toledo model XP205 balance. Stainless-steel 316 capsules measuring 25.4mm in diameter and 76 mm in length were cleaned and 316H specimens were attached to one endcap of each capsule into which ~30 g of solid FLiBe salt was filled in an Ar-filled glovebox. While still in the glovebox, the capsules were welded shut to create a gas-tight seal. The stainless-steel inner capsules were sealed within stainless steel outer capsules for safety and secondary containment before heating in a box furnace. Figure 1 shows a photograph of welded inner capsules and a schematic of a filled capsule on the right. A similar procedure has been used in previous studies [9-13].

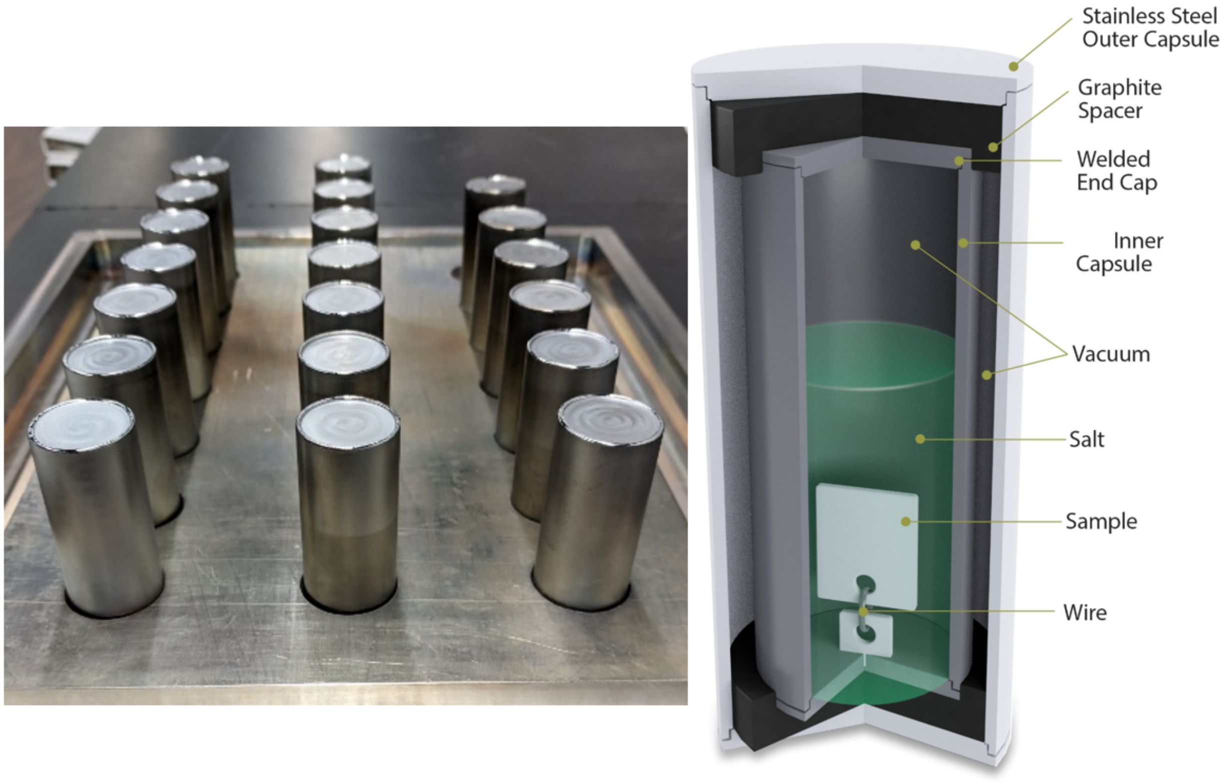

Figure 1. Welded capsules (left) and a diagram showing the capsule components for molten salt corrosion tests (right)

One batch of salt was donated by a commercial partner and is labeled batch #1. The second batch of FLiBe salt was prepared by melting a mixture of LiF and BeF_2 in a 2:1 molar ratio (melting point ~455°C). The typical procedure requires two sparging steps in H_2-HF and then in H_2 to remove moisture and impurities [8,14,15]. The second batch, labeled batch #2, was produced by the hydrofluorination process but without the final H_2 sparge. The omission of this step likely left the salt with a high fluorine potential from unreacted fluorine species remaining in the salt. Each salt was handled similarly inside an Ar-filled glovebox and broken into pieces for loading into capsules.

Capsules were heated in a programmable box furnace at 650°C for 1000 h. After 1000h, the capsules were taken out of the furnace and were inverted to allow the salt to drain away from the specimens. Samples were removed from the capsules and cleaned by ultrasonic vibration in warm water to remove remaining salt from the samples. After cleaning, the samples were tested for beryllium contamination before being weighed for mass change. After weighing, the samples were metallographically cross-sectioned for further examination.

Results

Results of glow discharge mass spectroscopy (GDMS) analysis for FLiBe #1 and FLiBe #2 before 316H specimen exposures are shown in Table 1. Only major impurities are shown in the table. The laboratory batch #2 actually had lower impurities than the commercial batch #1, which may be a result of the starting feedstocks.

Table 1. Elemental analysis by glow discharge mass spectrometry (GDMS) for FLiBe salts showing major impurity elements present before and after 316H specimen exposures at 650°C, 1000-hour tests.

	Na	**Mg**	**Al**	**Si**	**K**	**Ca**	**Cr**	**Mn**	**Fe**	**Ni**	**Sr**
FLiBe #2 before exposure	140	7.5	4.7	< 0.5	6.2	10	2.1	0.49	1.3	< 1	< 0.5
FLiBe #1 before exposure	700	9.4	6.5	< 0.5	42	23	3.9	1.8	21	< 1	1
FLiBe #1 after exposure	490	20	8.1	3.6	52	14	100	7.8	110	8.8	0.83
Values are in parts per million by weight (μg/g)											

The capsule experiments were conducted in triplicate and a direct comparison of the mass change data for the two salt batches is shown in Figure 2. Specimens in the interrupted batch #2 showed more than 200 times greater mass loss than specimens exposed in the commercial FLiBe, batch #1. Results of the triplicate exposures suggest high repeatability for the two conditions.

Table 1 also shows results of batch #1 after the capsule exposure. Other elements were below the detectability limit of 0.5 μg/g level. A dramatic increase in the Cr and Fe contents in the salt were observed as well as minor increases in Mn and Ni. These results were presented in a previous report [16]. Similar salt measurements for this salt have not been performed.

Metallographic cross-section images of the batch #1 specimens were shown in a previous report [16]. Figure 3 shows example cross-sections for the batch #2 specimens. Surprisingly, there was no evidence of deep grain boundary attack or void formation. This may reflect uniform dissolution in this salt. Because of the significant attack, no further characterization was conducted.

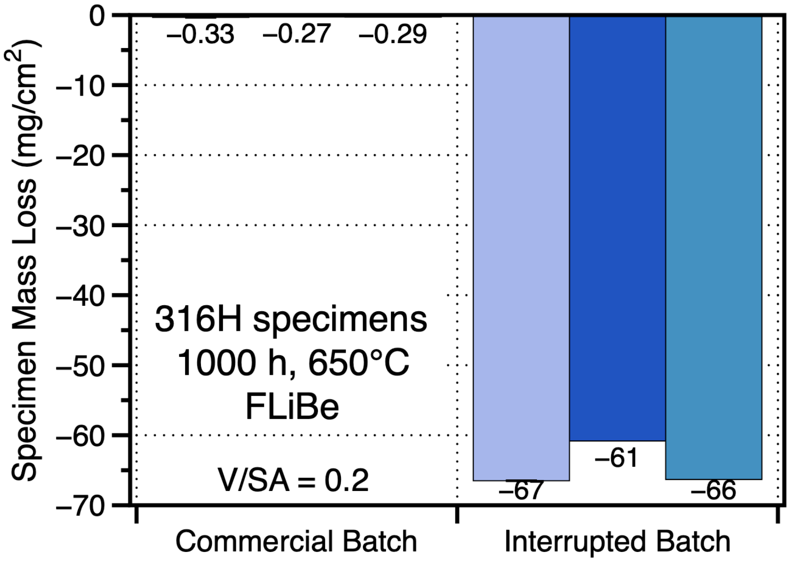

Figure 2. Mass loss for 316H specimens in two FLiBe salt batches at 650°C for 1000 h in 316H capsules.

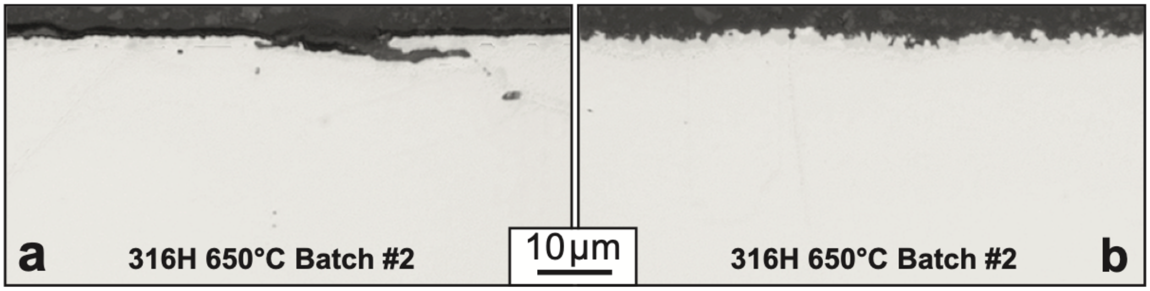

Figure 3. Light microscopy of polished cross-sections of two alloy 316 specimens after exposure to the 2nd batch of FLiBe for 1000 h at 650°C in a 316H capsule.

Discussion

Direct comparison between the two FLiBe batches from Figure 2 shows drastically different mass change data. FLiBe #2 (the laboratory interrupted batch) salt appears to be highly corrosive to 316H specimens exposed at 650°C for 1000 h as evidenced by greater than 60 mg/cm^2 mass loss while specimens exposed in commercial, FLiBe #1, showed only minor mass loss with an average mass loss of ~0.29 mg/cm^2. This large difference in corrosivity between the two batches of FLiBe can be explained by the presence of unreacted fluorinating specie remaining in FLiBe #2 because of the omission of the hydrogen sparge step as shown in the reaction below:

$$O^{2-} + 2HF \rightarrow H_2O + 2F^-$$

The unreacted fluorinating specie can react with common alloying elements such as Cr and Fe to form salt-soluble corrosion products, MF_2, as shown below:

$$2F^- + M \rightarrow MF_2 + 2e^- \quad M = alloying\ elements$$

The analysis shown in Table 1 can be misleading because of the lower initial elemental impurities present in FLiBe #2 vs. FLiBe #1. However, water and other corrosive fluorine species were not measured by GDMS. Techniques to measure water and other corrosive impurities were not readily available for a Be-containing salt. Comparison of elemental impurities before and after specimen exposures in FLiBe #1 clearly show a change in salt composition with increases in Cr, Fe, Ni and Mn after exposure.

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