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CORROSION PRODUCT DEPOSITION IN MOLTEN FLUORIDE SALT SYSTEMS*

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ABSTRACT

Hastelloy N (Ni-16% Mo-7% Cr-5% Fe) is quite compatible with pure fluoride salts and corrosion is difficult to detect. However, when impurities are present both metal fluoride and metal corrosion products may deposit as the result of the interaction of molten fluoride salts and alloys in a temperature gradient system. We have studied both types of deposits as they have occurred in iron-base and nickel-base thermal convection loops operating in the range of 460 to 605°C. In the iron-base loop, metal deposits consisting mainly of iron resulted from extreme changes in the equilibrium constant of the corrosion reaction with changes in temperature and from the highly oxidizing conditions of the salt. Metal-fluoride deposits also caused plugging in both the iron-base and a nickel-base loop and were mainly chromium fluorides. These were precipitated from the saturated salt. Under steady-state (low corrosion rate) conditions, more of the least stable fluoride corrosion products (such as iron and nickel) deposited than the more stable chromium fluorides. The amount of deposition in the cold leg was a function of the overall corrosion rate and varied only a small amount with temperature. Examination of the steady-state deposits with the scanning electron microscope showed several interesting features including possible growth steps with cubic symmetry.

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INTRODUCTION

The success of a molten-salt nuclear reactor system is strongly dependent on the compatibility of fluoride salts with the materials of construction comprising the primary and secondary circuits of the reactor.

A number of factors contribute to molten-salt corrosion. The tendency for a reaction to occur is measured in terms of the chemical potentials of the reactants and the products. The reaction kinetics will be influenced by the temperature, pressure, concentration of impurities, nobility of the salt constituents and metal constituents, solubility effects of the corrosion products, viscosity of the melts, and flow rate. A large part of the experimental work to date has been devoted to understanding and separating the effects of these and related parameters on the corrosion.

Many types of alloys have been considered for use in a molten-salt environment, but the nickel-based alloys, especially Hastelloy N, have proved to be the most corrosion resistant. Of the major constituents of Hastelloy N, chromium is much more readily oxidized in fluoride salts than iron, nickel, or molybdenum. Accordingly, attack in our system is normally manifested by the selective removal of chromium from the Hastelloy N. Several oxidizing reactions may occur depending on the salt composition and impurity content, but among the most important reactants causing oxidation are UF_4 , FeF_2 , and HF . The fluoride salts of interest to us are classed as fuel (containing UF_4 for fission) and coolant (used as a heat transfer medium). Fluorides such as LiF , BeF_2 , and NaF are commonly used as base melts.

Because our experimental systems are not isothermal, temperature gradient mass transfer effects are quite important. Conventionally, we observe weight losses in the hotter regions of our loops and weight gains in the colder sections. When the salts are chemically pure, corrosion

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is very small. As the salts become progressively more impure, the corrosion rate increases and amount of material being transferred from the hotter to cooler regions increases.

While most of our attention has been focused on the corrosion in high-temperature regions, the companion deposition process in the colder regions is very important because of the possibility of plugging. The study of the deposition process, through identification of the material (composition and structure) deposited in a flowing nonisothermal molten-salt system, is undertaken to determine the mechanisms of the corrosion and deposition processes (in particular, the rate-controlling steps), the predominant species involved in the mass transfer process, and the morphology of the deposit. The experiments described contained a coolant-type salt based on sodium fluoroborate. The NaBF_4 -8 mole % NaF mixture is the current favored coolant salt for a Molten-Salt Breeder Reactor due to its low melting point and low cost. Fuel-type salts are mentioned in the discussion.

Experimental Apparatus

The test systems that will be discussed are thermal convection loops of the types shown in Figs. 1 and 2. In these systems, the flow results from the difference in density of the salt in the hot and cold portions of the loops. The thermal convection loops shown in Fig. 1 had but one surge tank and no removable corrosion specimens, while the newer thermal convection loops represented by Fig. 2 had surge tanks atop each leg and a double ball valve arrangement which allowed corrosion specimen removal and insertion during operation.

The corrosion product deposition study discussed in this paper was made in five systems which are described in Table 1. Included were four Hastelloy N loops and one iron-based Croloy 9M system. The alloy compositions are given in Table 2. The analysis of the deposits was made by optical microscopy, electron microprobe, scanning electron microscopy, and x-ray fluorescence in the scanning electron microscope.

Results and Discussion

In the first example, loop 12, a Croloy 9M loop containing a sodium fluoroborate salt, flow stoppage occurred after 1440 hr operation. When this loop was sectioned for examination, a dark gray plug that completely filled the cross-sectional area for a vertical distance of 1 in. was found in the cold leg (Fig. 3). Also small, green crystals were seen in the drain line, and a metallic layer was found against the inside of the tubing in the cold section and in the salt.

The thin metallic layer about 2.5 mils thick was deposited on the inside of the tubing in the entire cold-leg section (over one-half the loop). In some places, the material had become detached from the tubing and was found in the frozen salt. The metallic layer represented about 4% of the total mass of the material (mostly salt) removed (by mechanical means) from the loop. Chemical analysis revealed the layer to be 90 wt % Fe and 10 wt % Cr metal.

The dark-gray plug located in the coldest part of the loop was composed of dendritic crystals. We found similar crystals adhering to specimens in the cold leg (Fig. 4). Chemical analysis showed that the crystals were essentially pure iron with less than 1% of other elements. The analysis of the green deposit showed that it consisted mainly of chromium and iron fluorides mixed with the salt.

In the second example, a Hastelloy N loop (loop 10) was operated with a fluoroborate salt for a year and was then shut down. Examination showed that a partial plug in the lower part of the cold leg (Fig. 5) had closed approximately 75% of the cross-sectional area of the pipe. Analysis showed this emerald-green plug to be single crystals of Na_3CrF_6 . Smaller amounts of two complex iron fluorides, Na_3FeF_6 and NaFeF_4 , were also identified in the cold leg.

Our next examples are from loops in which no plugs formed. The deposits in these loops apparently were produced under steady-state dissolution-deposition conditions. Figure 6 shows optical and scanning electron micrographs of a specimen which was exposed to NaBF_4 -8 mole % NaF for 4180 hr at 476°C in the cold leg of loop 13. During this time period the hot-leg specimen at the highest temperature lost 4.3 mg/cm^2 and the cold-leg specimen gained 3.2 mg/cm^2 . The scanning electron micrograph of the surface in Fig. 6 shows that the cold-leg specimen was coated with a discontinuous deposit which was analyzed as essentially Hastelloy N enriched with nickel and molybdenum.

Figure 7 shows optical and scanning electron micrographs of a cold-leg specimen which was exposed to NaBF_4 -8 mole % NaF at 500°C for 10,050 hr from loop 17. After 1050 hr, steam was injected into the loop and the specimen then remained in the loop for an additional 9000 hr. The total weight loss of the hot-leg specimen at the highest temperature was 40.9 mg/cm^2 , and the weight gain of the cold-leg specimen was 16.0 mg/cm^2 . Figure 7(a) shows a dark deposit on the cold-leg specimen, and the deposit exhibits a layered structure when viewed from above [Fig. 7(b)] with the scanning electron microscope.

Our final example is a cold-leg specimen which was exposed to NaBF_4 -8 mole % NaF for 19,300 hr at 460°C in loop 20. The hot-leg specimen at the highest temperature lost 14.4 mg/cm^2 while the cold-leg specimen gained 2.8 mg/cm^2 . The scanning electron micrographs of the cold-leg

specimen suggest that there has been both dissolution and deposition on the surface. The plateaus seen in Fig. 8 have a flat truncated appearance suggesting that they were part of the original specimen surface and that the lower areas had been attacked. The stereo pairs in Fig. 9 show that the rest of the specimen surface is lower than this plateau. There is also evidence that there was deposition on the surface. Many of the grains appear to have cubic symmetry, and Fig. 10 shows possible growth steps with cubic symmetry. The chemical composition in this area is 65% Ni-25% Fe-0.5% Cr-11% Mo.

Thermodynamics of System Corrosion

The cycle of mass transfer initiated by the corrosion of metals by fluoride salts is known to begin in the hotter regions of a loop system with the oxidation of loop wall constituents to form metal fluorides that are soluble in the salt. The equilibrium constant for this oxidation reaction increases with increasing temperature; thus in a nonisothermal system the dissolution of metal fluorides at the hottest temperature ultimately sets up a redox condition with decomposition of the metal fluoride in colder regions. Accordingly in a multicomponent alloy the concentration of the attacked constituent, M , will decrease at loop surfaces at high temperature (weight loss) and increase at surfaces at lower temperatures (weight gains). At some intermediate temperature, the initial surface composition of the structural alloy will be in equilibrium with the fused salt and no weight change will result.

In some fluoride salt melts (e.g., NaF-LiF-KF-UF_4) the equilibrium constant of the reaction changes sufficiently with temperature to support the deposition of pure metal in the cold zone.¹ A condition similar to this probably existed in the iron-based loop 12, which was first discussed. Even though chromium is less noble than iron, the iron did form the metallic deposit probably because of the oxidizing conditions present and the fact that the iron was available in greater quantity in the alloy. In other melts (e.g., $\text{LiF-BeF}_2\text{-UF}_4$) the temperature dependence of the corrosion equilibrium is small, and the equilibrium is satisfied at all useful temperatures without the deposition of pure metal in the cold zone.¹ In the $\text{LiF-BeF}_2\text{-UF}_4$ system the rate of chromium reduction in the salt at cold-leg regions is dependent on the rate at which chromium can diffuse into the cold-leg wall. If the chromium concentration gradient tends to be small, or if the bulk of the cold-leg surface is held at a relatively low temperature, the corrosion rate is almost negligible.

¹Molten-Salt Reactor Progr. Semiann. Prog. Rept. July 31, 1964, ORNL-3708, pp. 241-44.

Conditions may also exist where the corrosion product fluoride exceeds its solubility in the cold leg and deposits as the fluoride. This was the case with the Hastelloy N loop 10 that plugged. The large amount of corrosion product fluoride implies that highly oxidizing conditions existed in salt during this test.

In our Hastelloy N loops where no plugs were formed (13, 17, and 20), the corrosion was selective with preferential removal of the least noble component chromium. Iron was removed next, followed by nickel and molybdenum. The deposits in these loops consist mainly of iron and nickel with the more stable chromium fluoride remaining in the salt. It also appears, from weight change data such as that seen in Fig. 11 where we plotted weight change versus the position of the corrosion specimen in the loop, that deposition in the cold leg is not entirely a function of temperature. It is noted that, unlike the weight losses in the hot leg, the weight gains throughout the cold leg vary only a small amount. Thus, the deposits are functions of nucleation sites and perhaps flow patterns along with temperature.

CONCLUSIONS

1. The corrosion rate of alloys such as Hastelloy N by fluoride salts is quite low when the salts are pure. As the purity decreases, increasing quantities of both metal fluoride and metal corrosion products may deposit in a flowing molten fluoride salt loop system under a temperature gradient.
2. The metal deposits resulted from extreme changes in the equilibrium constant of the corrosion reaction with changes in temperature and from the highly oxidizing conditions of the salt.
3. The metal fluoride deposits were produced by precipitation of the corrosion products (large amounts of which were produced by highly oxidizing conditions of the salt) from the saturated molten salt.
4. In the steady-state deposits, the least stable fluoride corrosion products (such as iron and nickel) deposited in more quantity than the more stable chromium fluorides.
5. The deposition in the cold leg was not entirely a function of temperature as the weight gains throughout the cold leg vary only a small amount.

Table 1. Five Systems Which Operated at 605°C Maximum Temperature and 460°C Minimum Temperature from Which Deposition Study Was Made

Loop No.	Loop Material	Molten Salt	Time (hr)	Remarks
12	Croloy 9M	$\text{NaBF}_4\text{-NaF-KBF}_4^a$	1440	Cross section completely plugged
10	Hastelloy N	$\text{NaBF}_4\text{-NaF-KBF}_4^a$	8760	Cross section 3/4 plugged
17	Hastelloy N	$\text{NaBF}_4\text{-NaF}^b$ (steam addition)	10,000	Deposits on cold-leg specimens
13	Hastelloy N	$\text{NaBF}_4\text{-NaF}^b$	4180	Deposits on cold-leg specimens
20	Hastelloy N	$\text{NaBF}_4\text{-NaF}^b$	20,000	Deposits on cold-leg specimens

^a90-4-6 mole %.

^b92-8 mole %.

Table 2. Chemical Composition of Alloy Test Materials

Alloy	Composition (wt %)								
	Ni	Cr	Mo	Fe	C	Mn	S	P	Si
Hastelloy N	70.8	7.47	15.59	4.01	0.07	0.54	0.005		0.64
Croloy 9M		8.87	0.98	89.00	0.09	0.48	0.012	0.010	0.47

LIST OF FIGURES

Fig. 1. Schematic of MSRP Natural Circulation Loop.

Fig. 2. MSRP Natural Circulation Loop and Salt Sampler.

Fig. 3. Iron Dendrite Plug in Coldest Section (460°C) of Croloy 9M Loop 12 Operated in Fluoroborate Salt for 1440 hr at a Maximum Temperature of 605°C and a Temperature Difference of 145°C .

Fig. 4. Pure Iron Crystals from Croloy 9M Loop 12 Which Operated for 1440 hr in Fluoroborate Salt at a Maximum Temperature of 605°C and a Temperature Difference of 145°C . $10\times$. Reduced 12%. (a) Crystals adhering to specimen, and (b) crystals removed from specimen for photographing.

Fig. 5. Plug Formed in Hastelloy N Loop 10 Containing NaBF_4 - NaF - KBF_4 (90-4-6 Mole %) After 8760 hr at a Maximum Temperature of 605°C and Temperature Difference of 145°C . $8\times$. Reduced 40%.

Fig. 6. Hastelloy N Specimen from Loop 13 Exposed to NaBF_4 - NaF (92-8 Mole %) at 476°C for 4180 hr. Weight gain 3.2 mg/cm^2 . (a) Optical micrograph of cross section, $500\times$. Etchant, glyceresia. (b) Scanning electron micrograph of surface, $1000\times$.

Fig. 7. Hastelloy N Specimen from Loop 17 Exposed to NaBF_4 - NaF (92-8 Mole %) at 500°C for 10054 (1054 hr before steam addition). Weight gain, $+16.0\text{ mg/cm}^2$. (a) Optical micrograph of cross section, $500\times$. (b) Scanning electron micrograph of surface, $1000\times$.

Fig. 8. Scanning Electron Micrographs of Hastelloy N Exposed to NaBF_4 -8 Mole % NaF in Loop 20 at 460°C for 19,300 hr. (a) $5000\times$. (b) $2000\times$.

Fig. 9. Scanning Electron Micrograph Stereo Pairs of Hastelloy N Exposed to NaBF_4 -8 Mole % NaF in Loop 20 at 460°C for 19,300 hr. $1000\times$.

Fig. 10. Scanning Electron Micrograph of Hastelloy N Exposed to NaBF_4 -8 Mole % NaF in Loop 20 at 460°C for 19,300 hr. $5000\times$.

Fig. 11. Weight Changes from Hastelloy N Specimens Exposed to NaBF_4 -8 Mole % NaF as a Function of Position and Time.

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(a)

(b)

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 (b) Scanning electron micrograph of surface, 1000 $\times$.

(a)

(b)

Fig. 7. Hastelloy N Specimen from Loop 17 Exposed to $\text{NaBF}_4\text{-NaF}$ (92-8 mole %) at 500°C for 10054 hr (1054 hr before steam addition). Weight gain, $+16.0 \text{ mg/cm}^2$. (a) Optical micrograph of cross section, $500\times$. (b) Scanning electron micrograph of surface, $1000\times$.

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