CORROSION RESISTANCE OF SOME NICKEL-BASE ALLOYS TO MOLTEN FLUORIDE SALTS CONTAINING UF₆ AND TELLURIUM

J. R. Keiser, D. L. Manning,† and R. E. Clausing
Metals and Ceramics Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Selection of a material for the primary containment vessel of a Molten-Salt Breeder Reactor has required the development of an alloy to resist corrosion by both the UF₆ and the fission product tellurium contained in the fuel salt. Thermal convection loop corrosion studies have been performed to establish the time and concentration dependence of chromium mass transfer and to determine the corrosion rate of niobium-modified Hastelloy N. Voltammetry was used to measure the oxidation potential and corrosion product concentration of the salt. Two types of tensile specimens designed for conventional tensile testing and for testing in an Auger electron spectroscopy apparatus have been exposed to tellurium-containing salt systems to determine both the penetration rate of tellurium and the effect on cracking behavior of niobium additions to Hastelloy N. Results indicate that Hastelloy N modified by the addition of 1 wt % Nb has improved resistance to tellurium cracking while maintaining UF₆ corrosion resistance when compared with the unmodified alloy.

INTRODUCTION

The corrosion investigations which are the subject of this report are part of the technology development program for the Molten-Salt Breeder Reactor. The MSBR is a fluid-fueled thermal breeder reactor. As such, the MSBR offers several potential advantages over other breeder reactors being developed, such as on-site fuel reprocessing and a relatively low fast-neutron fluence.

A schematic diagram of a Molten-Salt Breeder Reactor is shown in Fig. 1.1 This reactor has a graphite core for moderating the neutrons, a chemical reprocessing plant for removing fission products from the

*Research sponsored by the Energy Research and Development Administration under contract with the Union Carbide Corporation.
†Analytical Chemistry Division.

315
salt, and a liquid fuel containing both fertile and fissile components. The liquid fuel, a 72-16-11.7-0.3 mole % mixture of LiF, BeF₂, ThF₄, and UF₆, leaves the reactor core at 704°C, passes through the primary heat exchanger, and then returns to the core at about 565°C. Hastelloy N, a nickel-base alloy developed at Oak Ridge National Laboratory, was used as the primary containment material for the Molten-Salt Reactor Experiment, a test reactor which was successfully operated from 1965 to 1969. The composition of Hastelloy N is given in Table 1.

Although this alloy performed satisfactorily in the MSRE, two potential problems were noted: embrittlement because of neutron irradiation and intergranular cracking associated with intergranular penetration by fission product tellurium. Based on these observations, testing of Hastelloy N was continued to improve both the radiation and fission product resistance of the alloy.

Other researchers have found that the neutron irradiation problem can be alleviated by the addition of an alloying component to create a fine dispersion of carbide particles which trap the helium atoms produced during irradiation.² By trapping the helium in this manner, large bubbles are avoided and embrittlement is minimized.

Several approaches existed for seeking a solution to the intergranular cracking problems associated with pickup of tellurium. The most promising approach was to modify the composition of the containment material to reduce the entry of tellurium. The potential containment materials considered included compositional modifications of Hastelloy N, other nickel-base alloys, and some iron-base alloys. Besides determining the resistance of these alloys to grain boundary cracking by tellurium, it was also necessary to measure their resistance to corrosion by molten fluoride salt.

A considerable amount of work has been reported on the measurement of the corrosion of Hastelloy N by molten fluoride salt containing UF₆.³,⁴ On the other hand, little or nothing has been reported on the grain boundary embrittlement of nickel-base alloys by tellurium, although sulfur embrittlement of copper,⁵ iron,⁶ nickel,⁷ and nickel-base alloys,⁸ and tellurium embrittlement of copper⁹ have been reported.

The corrosion of Hastelloy N by salts of the type used as fuel for a molten-salt reactor, that is, containing UF₆, has been attributed to temperature gradient mass transfer of the most active constituent of the alloy — chromium.³ When UF₆-containing salt is added to a Hastelloy N system, the reaction

\[ 2\text{UF}_6 + \text{Cr} \rightarrow \text{CrF}_2 + 2\text{UF}_3 \]  

(1)

316
is expected to occur. The extent of this reaction is controlled by the activity of chromium in the alloy, the UF₄/UF₃ ratio in the salt, and the CrF₂ concentration in the salt. If this Hastelloy N—salt system has a temperature gradient imposed on it, the temperature dependence of the equilibrium constant for reaction 1 allows equilibrium to be reached in the colder portions of the system first. Reaction 1 will continue to proceed to the right in the hotter portion of the system, but as the salt circulates around the system, reaction 1 will move to the left in the colder regions and deposition of chromium will occur. After a relatively short time, a steady-state condition will be reached where the amount of chromium being returned to the wall in the cooler regions exactly balances the amount of chromium being removed from the wall in the hotter regions. The amount of chromium, ∆M, removed from a unit area of surface can be shown to be

\[ ∆M = BC₀ \sqrt{D} \]  

(2)

where B is a temperature-dependent constant, C₀ is the initial concentration of chromium in the alloy, and D is the diffusivity of chromium in the alloy. In this model the diffusion of chromium in the Hastelloy N is the limiting step for mass transfer. If strong fluoride formers such as Ti, Nb, and Al are added to Hastelloy N, mass transfer of these elements would be expected to occur by the same mechanism as discussed above.

For the case of tellurium corrosion of Hastelloy N, no clearly defined model exists. As in the case of sulfur embrittlement of some metals, segregation of the detrimental material to the grain boundaries is apparently the cause of embrittlement, but neither the reaction by which tellurium enters the Hastelloy N nor the exact cause of embrittlement is known. Also unexplained is why, and in what manner, some alloying additions significantly affect embrittlement.

Experimental Methods

Two types of experimental assemblies were used for these corrosion measurements. Metal vessels filled with salt and containing some chemical form of tellurium have been used for exposing test specimens in order to measure their resistance to grain boundary cracking. The salt used in these experiments was the designated MSBR fuel salt mixture, except that UF₄ was excluded because of a potential problem in voltammetrically detecting tellurium in the presence of UF₄. The tellurium was added to the salt as chromium telluride, most often Cr₃Te₆. Selection of this telluride was based on the similarity of the depth and frequency of grain boundary cracks in specimens exposed to a salt-Cr₃Te₆ mixture to that observed in the MSRE. The exposure temperature was 700°C, because this was the maximum operating
temperature proposed for an MSBR, and because, in combination with 
Cr$_3$Te$_4$, relatively short exposure times (25–1000 hr) were required to 
simulate the results found in the MSRE.

Two types of specimens have been tested in these experiments. 
Cylindrical tensile specimens about 5 cm long and with a gage diameter 
of about 3 mm have been used to make comparisons of various alloys. 
Specimens of this type were exposed to the salt-telluride mixture, 
tensile tested to failure, then examined metallographically. The 
number and depth of cracks in the gage length were used as a measure of 
susceptibility to grain boundary cracking.

The other type of specimen was designed to be examined by Auger 
electron spectroscopy (AES). Examination of these specimens has pro­
vided data on the identity and penetration rate of the material that 
causes the grain boundary embrittlement, as well as some indication of 
the manner by which niobium affects the cracking resistance of 
Hastelloy N.

The other types of experimental equipment used for corrosion mea­
surements was a thermal convection loop system which circulated the 
MSBR-type fuel salt. A schematic drawing of a loop system is shown in 
Fig. 2. The loop portion of the assembly is constructed of Hastelloy N 
tubing and is heated on the bottom and the left vertical side. By 
cooling the other two sides, the molten salt in the tubing can be made 
to flow by density difference, thus approximating the temperature and 
circulation characteristics of an MSBR. The velocity of the salt in a 
loop is about 1 m/min. Other important features of the loop are 
removable corrosion specimens and ports which permit insertion of 
electrodes for voltammetric examination of the salt. Sixteen corrosion 
specimens are used, with eight inserted in the hot leg (heated vertical 
section) and eight in the cold leg (cooled vertical section). These 
specimens are removed from the loop every 500 hr for weighing and 
examination. When the exposures of a particular set of specimens were 
completed, several of the specimens were examined metallographically 
and, if warranted, with the electron microprobe. From these results 
the temperature dependence of the weight gains or losses was determined, 
and from the microprobe examination it was determined which components 
of the specimen material had been transported.

The present tests represent the first time that controlled­
potential voltammetry has been applied to our molten-salt corrosion 
studies. Voltammetry is an electrochemical technique which can be 
used to determine some of the species present in a high-temperature 
salt system. For these measurements the electrodes consist of the 
loop itself, which serves as the counter electrode, and two iridium 
electrodes which comprise the quasi-reference and working electrodes 
respectively. The iridium electrodes are typically 1-in. lengths of 
18-gauge wire welded to 1/8-in.-OD nickel risers. The electrode area

318
exposed to the melt was about 0.1 to 0.2 cm². Voltammograms (current-voltage curves) were recorded with the iridium quasi-reference electrode (Ir QRE) poised at the equilibrium potential \( E^{\text{eq}} \) of the melt as the reference. In this manner, on-line measurements of relative changes in the "oxidation potential" of the salt and of the concentration of certain impurities and corrosion products can be made. The "oxidation potential" of the salt is a measurement of the tendency of the melt to react with oxidizable materials which it contacts. For melts which are poised by a redox buffer such as U(IV)/U(III) [where the concentration of U(IV) > U(III)], current-voltage curves are recorded for the U(IV) + U(III) electrode reaction vs an Ir QRE which is poised at the equilibrium potential of the melt. This potential, in turn, depends on the U(IV)/U(III) ratio. The reference potential is the voltammetric equivalent of the standard electrode potential \( E^0 \), that is, the potential at which the U(IV)/U(III) ratio is unity at the electrode surface. Theoretically, \( E^0 \) is the potential which corresponds to the current value at 85% of the peak current. This holds true for a reversible couple where both oxidized and reduced forms are soluble and the concentration of the reduced form in the bulk melt is smaller than the oxidized form. It follows from the Nernst equation,

\[
E_{\text{eq}} - E^0 = \Delta E = \frac{RT}{nF} \ln \frac{\text{U(IV)}}{\text{U(III)}}
\]

that the difference between \( E_{\text{eq}} \) and \( E^0 \) is a measure of the U(IV)/U(III) ratio. The voltammetric method is particularly useful in nonaqueous solvents where reference electrodes are frequently not available or the standard potentials may not be known.

**Experimental Results**

The use of voltammetry to provide on-line measurements of the oxidation potential and corrosion product concentrations of the salt is illustrated in Fig. 3, in which both the current-voltage curve and its derivative are included. The large peak on the derivative curve is due to the U(IV) + U(III) reaction, while the narrower peak located on the left side of the uranium peak is due to the Cr(II) + Cr(0) reaction. The voltage associated with the peak current of the uranium wave is used to determine the oxidation potential of the salt.

Figure 4 shows the measured relationship between the U(IV)/U(III) ratio and time for one of the thermal convection loops. This loop had the highest oxidation potential \([\text{U(IV)}/\text{U(III)}] \) ratio of the tests from this study. Some perturbations occurred when specimens were inserted, due to an inadvertent addition of moisture at the same time. All fluctuations were considered to be small enough that they did not affect corrosion measurements.
The corrosion measurements made with this loop were conducted to
determine the effect of time on thermal gradient mass transfer. If
mass transfer of a given alloying element is diffusion limited, then
the weight loss should decrease as the square root of exposure time, as
indicated in Eq. (2). As shown in Fig. 5, the weight change of a
specimen exposed to MSBR fuel salt at 690°C does show a change
proportional to the square root of time.

The effect of chromium concentration on the mass transfer rate of
Hastelloy N exposed to MSBR fuel salt was determined from the 1000-hr
weight change results of 7, 10, and 12% chromium-modified Hastelloy N
alloys exposed to salt in thermal convection loops. As shown in
Fig. 6, it was found that the mass transfer rate was approximately a
linear function of the chromium concentration, as would be expected
according to Eq. (2).

To study the grain boundary embrittlement problem, some of the
initial AES work was directed toward confirming the identity of the
fission product responsible for intergranular cracking of specimens
from the MSRE. A sample of Hastelloy N foil from the MSRE was frac­
tured in the Auger spectrometer. The sample was 0.004 in. thick and
had been exposed to molten fluoride salt for about 6000 hr at 650°C,
but for only 3000 hr of this time was the material exposed to salt
containing fission products. Figure 7 shows scanning electron
microscopy images of the fracture surfaces. There is no evidence of
macroscopic deformation. The fractures are completely along grain
boundaries filled with carbide particles. The carbide particles did
not fracture, but seemed to separate from the matrix cleanly along the
matrix–carbide interface. Figure 8 shows (a) an absorbed sample
current image of the region shown in Fig. 7, and elemental maps of this
region for (b) tellurium, (c) nickel, and (d) molybdenum obtained
using Auger electron images. These images show that the composition
of the fracture surface is quite uniform; that is, there are no marked
differences in tellurium concentration from the center to the near­
surface regions. Analyses of the sample at the spots designated 1, 2,
and 3 on the absorbed sample current images [Fig. 8(a)] are given in
Table 2. Spot 4 is a nearby area not in this field of view. No other
fission products or embrittling agents were found on this fracture
surface, and (as we shall show below) the tellurium concentration is
much higher than is required to cause brittle intergranular fracture.

In order to determine the thickness of the tellurium-enriched
layer in the grain boundary, the samples were sputtered with 1000-eV
argon ions. Figure 9 shows the relative changes in the concentration
of Te, Cr, C, and Mo as a function of sputtering time (or depth below
the original fracture surface) for spot 4 in Table 2. Note that
tellurium decreases to less than 5% of its original concentration
when five atom layers are sputtered from the fracture surface,
indicating that the tellurium is present as a very thin layer on the
grain boundary.
After it was established that tellurium was the material responsible for intergranular cracking of Hastelloy N in the MSRE, the next problem was to learn more about the mechanism of embrittlement. In order to determine the penetration rate of tellurium, a series of Hastelloy N specimens were exposed to LiF-BeF$_2$-ThF$_4$ salt containing Cr$_3$Te$_4$ at 700°C for times from 24 to 500 hr. Penetration depth increased as a function of time as expected, but there appeared to be considerable dependence of penetration on the structure of the boundary and relative grain orientations, so that there was quite a variation in penetration depth on each sample. For these relatively short-time exposures, penetration varied with $t^{1/2}$ or $t^{1/3}$ as shown in Fig. 10. If tellurium penetration is controlled by bulk diffusion or grain boundary diffusion with no bulk solubility, a time dependence of $t^{1/2}$ would be expected.* Figure 11 is a composite showing an absorbed sample current image and AES elemental maps for tellurium.† The analyses of spots 1 through 4 are given in Table 3. The embrittled region of this sample contained much less tellurium than did the MSRE sample.

For all tellurium-salt experiments an attempt was made to measure the concentration of tellurium in the salt by both voltammetry and analytical methods. No evidence of tellurium solubility was found at a detection limit of about 5 ppm; nevertheless, tellurium was transported through the salt to the specimens.

Additions of elements that produce finely dispersed carbides in Hastelloy N were found to be effective in reducing radiation embrittlement. Therefore we felt one way to alleviate the intergranular cracking problem was to make an alloying modification to Hastelloy N that would alter the type or distribution of the phase containing tellurium. Modifications involved additions of titanium, niobium, and several of the rare earths. Tensile specimens made from each of the experimental alloys were exposed to a salt-Cr$_3$Te$_4$ mixture and then were tensile tested which produced cracks at the points where tellurium had penetrated. By means of metallographic techniques, the number and depth of cracks in each specimen were determined, and it was found that the addition of niobium to Hastelloy N markedly affected intergranular cracking. As shown in Fig. 12, for specimens exposed for 250 hr the effect of niobium was optimized when the addition was 1 to 2 wt %.

Since addition of niobium to Hastelloy N significantly improved the cracking resistance of the alloy, it was considered important to

---

*If tellurium has some solubility in the bulk, a time dependence of $t^{1/4}$ would be expected.

†Also shown is an SEM image of one area of a sample exposed to the salt-Cr$_3$Te$_4$ mixture for 101 hr.
measure its resistance to corrosion by UF₆. Consequently, specimens of 1% Nb-modified Hastelloy N have been put into a thermal convection loop for evaluation. Measurements made after 1000 hr exposure showed no difference in weight change for 1% Nb-modified Hastelloy N compared with standard Hastelloy N.

Since a niobium-modified Hastelloy N may prove to have the desired corrosion resistance, it is of interest to learn how niobium acts to reduce the grain boundary cracking caused by tellurium. Specimens of the niobium-modified alloy have been exposed to the salt-Cr₃Te₄ mixture and examined with AES. Preliminary results indicate that tellurium is distributed throughout the alloy rather than being segregated in a thin continuous film along the grain boundaries.

CONCLUSIONS

The most significant conclusions which can be drawn from this work with the nickel-base alloy, Hastelloy N, and the MSBR fuel salt, LiF-BeF₂-ThF₄-UF₆, are:
1. voltammetry can provide on-line measurement of the oxidation potential and impurity concentrations of the salt;
2. chromium is the primary material reacting with fluoride salts containing UF₆;
3. time and chromium concentration dependence of mass transfer is as given in Eq. (1);
4. fission product tellurium was the cause of intergranular cracking of Hastelloy N in the MSRE;
5. addition of limited amounts of niobium to Hastelloy N can significantly improve its resistance to tellurium-induced intergranular cracking;
6. addition of 1 wt % Nb to Hastelloy N does not significantly change its resistance to salt corrosion.
REFERENCES

1. The Development Status of Molten-Salt Breeder Reactors, ORNL-4812 (August 1972).

2. M. W. Rosenthal et al., "Recent Progress in Molten-Salt Reactor Development," At. Energy Rev. IX: 601 (1971).

3. J. H. DeVan, M.S. Thesis (University of Tennessee, 1960).

4. J. W. Koger, Alloy Compatibility with LiF-BeF$_2$ Salts Containing ThF$_4$ and UF$_4$, ORNL-TM-4286 (December 1972).

5. S. P. Clough and D. F. Stein, Scr. Metall. 9: 1163 (1975).

6. E. D. Hondros and M. P. Seah, Scr. Metall. 6: 1007 (1972).

7. K. M. Olsen, C. F. Larkin, and P. H. Schmitt, ASM Trans. Q. 53: 349 (1961).

8. K. N. Strafford, G. R. Winstanley, and J. M. Harrison, Werkst. Korros. 25: 487 (1974).
Table 1. Composition of Hastelloy N (wt %)

| Mo | Cr | Fe | Mn | Si | C  | Ni |
|----|----|----|----|----|----|----|
| 12 | 7  | 0.5 max | 0.2 | 0.1 max | 0.05 | Balance |

Table 2. Analysis of MSRE foil sample\(^a\) by Auger electron spectroscopy

| Spot No. | Analysis (at. %) |
|----------|------------------|
|          | Te   | Mo   | Ni   | Cr  | C   |
| 1        | 12.6 | 32.5 | 29.8 | 4.4 | 20.7|
| 2        | 9.0  | 17.5 | 46.8 | 5.9 | 20.7|
| 3        | 10.6 | 18.2 | 43.8 | 5.1 | 22.4|
| 4        | 12.3 | 6.8  | 54.6 | 5.8 | 20.5|

\(^a\) Grain boundary regions exposed by fracture in AES system.

Table 3. AES analysis of Hastelloy N tensile specimen exposed to salt + Cr\(_3\)Te\(_4\) for 101 hr

| Spot No. | Analysis (at. %) |
|----------|------------------|
|          | Te   | Mo   | Ni   | Cr  | C   | O   |
| 1        | 12.7 | 66   | 12.3 | 6.6 | 0.6 |
| 2        | 4.0  | 8.2  | 47.9 | 7.6 | 27.4| 4.5 |
| 3        | 6.6  | 6.8  | 59.1 | 8.3 | 15.3| 3.9 |
| 4        | 9.1  | 2.9  | 42.2 | 6.2 | 35.0| 4.6 |
Fig. 1. Molten Salt Breeder Reactor Schematic.

Fig. 2. Thermal Convection Loop Schematic.

Fig. 3. Typical Voltamogram for MSBR Fuel Salt.

Fig. 4. Log(U⁴⁺/U³⁺) vs Elapsed Time from Voltammetric Measurements of Thermal Convection Loop.
Fig. 5. Weight Change vs Square Root of Exposure Time for Hastelloy N Specimen Exposed to MSBR Fuel Salt at 690°C.

Fig. 6. Effect of Chromium Concentration in Modified Hastelloy N on Weight Change After 1000 hr in MSBR Fuel Salt.

Fig. 7. Scanning Electron Micrographs of Fracture Surface of MSRE Foil Fractured and Examined in Auger Apparatus.
Fig. 8. Elemental Displays from MSRE Foil.

Fig. 9. Variation of Selected Constituents in MSRE Specimen vs Depth from Grain Boundary Fracture Surface (Sputtering Removes Approximately 1 Atom Layer Per Minute).

Fig. 10. Tellurium Penetration vs Exposure Time for Hastelloy N in Salt + Cr₃Te₄.
Fig. 11. AES Absorbed Current Images and Tellurium Elemental Maps of Hastelloy N Exposed to Salt + Cr$_3$Te$_6$ for 101 hr.

Fig. 12. Effect of Niobium in Modified Hastelloy N on Grain Boundary Cracking when Exposed in Salt-Cr$_3$Te$_6$ + Cr$_5$Te$_6$ for 250 hr at 700°C.