HOT CORROSION OF HEAT-RESISTANT ALLOYS INDUCED BY MOLten FLuORIDE MIXTUREs

Masahiro Kawakami, Masato Kawabe*1, Masaru Okuyama*2 and Koin Ito
Toyohashi University of Technology
Hibarigaoka, Tempaku-cho, Toyohashi 440 JAPAN

ABSTRACT

Heat resistant alloys have been heated with the coating of molten fluoride mixture at 500 - 700 °C, either in air or in Ar. The weight change was monitored with a thermogravimetric balance for 20 hrs. The air oxidation of Hastelloy-N, Inconel 625 and N-155 was accelerated significantly with NaBF₄-NaF coating. The electrochemical polarization revealed that the corrosion current corresponded well to the rate of accelerated oxidation. With LiF-BeF₂ coating, some volatile materials are formed, and oxidation is accelerated.

INTRODUCTION

It is well known that high temperature oxidation of heat resistant alloys are accelerated by the adhesion of molten salts(1,2). The accelerated oxidation of nickel base alloys by molten Na₂SO₄ has been investigated extensively by many researchers (3-6). Those by molten Na₂CO₃, NaNO₃(7-9) and NaCl-KCl(10) have also been reported. But it is not known whether molten fluorides do induce the accelerated oxidation of alloys. Molten fluoride mixtures, such as NaBF₄-NaF and LiF-BeF₂, are considered as candidates for heat transfer media in molten salt reactors. Therefore, it might be of some interest to examine the hot corrosion of alloys induced by such salts, although the accelerated oxidation can be avoided in the practical reactor design even if it happens.

In the present work, hot corrosion (including accelerated oxidation) of several heat resistant alloys have been investigated with coating of the above fluoride mixtures. The experimental methods are thermogravimetric measurements and electrochemical polarization measurements.

Present address; *1 Suzuki Motor Co. Ltd., Sototakatsuka, Hamamatsu 432-29 JAPAN, *2 Oyama National College of Technology, 771 Nakaguki, Oyama 323 JAPAN.
EXPERIMENTALS

(1) Materials
Composition of the fluoride mixtures are 92mol%NaBF$_4$-8mol%NaF and 66mol%LiF-34mol%BeF$_2$, which are considered as the heat transfer media in the secondary cooling loop of molten salt reactors. The heat resistant alloys are commercial Hastelloy-N(M.M.), home-made Hastelloy-N(h.m.), commercial Inconel 625 and commercial N-155. Compositions of the alloys are shown in Table 1.

Table 1. Composition of the alloys.(wt%)

| Elements | Cr  | Fe  | Co | Mo  | Si  | Mn | Ni |
|----------|-----|-----|----|-----|-----|----|----|
| Hastelloy-N (M.M.) | 7.0 | 4.0 | -- | 16.7 | 0.3 | 0.5 | Bal. |
| Hastelloy-N (h.m.) | 7.1 | --  | -- | 16.7 | 0.3 | 0.4 | Bal. |
| Inconel 625    | 23.9| 3.5 | -- | 11.7 | 0.5 | --  | Bal. |
| N-155          | 22.0| 30.5| 19.3| 3.7 | 1.9 | --  | 19.8 |

(2) Thermogravimetric measurements
Test pieces of 5mmx10mmx1mm were cut out from the alloy stock and polished with dry abrasive paper of #1000. The fluoride mixtures were pre-fused in Ar. The test piece coated with the salt mixture was set in a thermogravimetric balance, and heated up to the desired temperature either in air or in Ar. The weight of the test piece was continuously measured for 20 hrs. After the measurement, the scale formed on the test piece was examined by EPMA.

(3) Electrochemical polarization measurements
Figure 1 shows the schematic diagram of experimental apparatus. The working electrode was cut out from the alloy stock and graphite rod in the form of plate or cylinder. The reference electrode was a kind of Ag-AgF electrode. The counter electrode was made of platinum net. NaBF$_4$ and NaF powders of reagent grade were mixed in the composition shown above and kept in a dry box for 24 hrs. before the experiment. The salt mixture was put in a high alumina crucible, fused at 400 °C and dehydrated with Ar for 10 min.; then, the salt mixture was heated up to the experimental temperature. Three electrodes were dipped into the fused salt. The rest potential of the working electrode was measured with a potentiometer. After getting a stable rest potential, the working electrode was polarized in noble direction down to -1.6 V in order to reduce oxide film on the electrode surface. Then, polarization in less-noble direction was carried out. The potential was raised 25 mV every 30 sec up to +2.0 V.
RESULTS AND DISCUSSION

(1) Thermogravimetric measurements with NaBF$_4$-NaF mixture

(1)-1 Decomposition of the salt mixture

Figure 2 shows the heating pattern and the weight change with time. The test piece of Hastelloy-N(M.M.) was heated with 43.3 mg/cm$^2$ of the salt mixture in Ar. Temperature was raised linearly up to 700 °C for 30 min., and kept constant. When the temperature reached 400 °C, the weight began to decrease remarkably. The weight change per unit surface area, $\Delta W/S$, reached down to $-2.17.1$ mg/cm$^2$ for 40 min. and $-20.2$ mg/cm$^2$ for 1200 min.. No change was observed in the appearance of test piece. Thus, the weight loss was attributed to the decomposition of NaBF$_4$ to NaF and BF$_3$ which had very high vapor pressure. Assuming that the whole weight loss should correspond to the amount of evaporated BF$_3$, the composition of salt mixture changed to 31mol%NaBF$_4$-69mol%NaF, after 1200 min. Referring to the phase diagram, this composition was in solid-liquid two phase region at 700 °C. The fractions of weight loss during heating in Ar were nearly the same in all experiments. Thus, the salt mixture was considered to be in solid-liquid co-existing state in all oxidation experiments. The rate of weight loss after 40 min. was not high and could be negligible, compared with the oxidation rate as will be shown later. Thus, the air was introduced at 40 min. from the beginning of heating to start the oxidation experiment.

(1)-2 Oxidation curve of alloys

Figure 3 shows the oxidation curves of Hastelloy-N(M.M.) with and without salt coating at 700 °C. The air oxidation was very much accelerated with the salt coating. The accelerated oxidation curve could be divided into three time periods, namely, an incubation period in which the oxidation was very slow, a catastrophic period and a moderate acceleration period. With larger amount of salt coating, the catastrophic oxidation started later and lasted longer. But, the rate of oxidation in the moderate acceleration period was the same, regardless of the amount of salt coating.

Figure 4 shows the oxidation curves of Hastelloy-N(h.m.) at different temperatures. The oxidation was very much accelerated by the salt coating at 700 °C. The shape of oxidation curve with the salt coating was similar to that shown in Figure 3. At 600 °C, the weight decreased initially due to the salt decomposition and increased after 800 min.. At 500 °C, the weight decreased monotonously. From microscopic observation of the test piece heated at 500 °C, no oxide film could be found on the surface. From these, it can be said that the oxidation was significantly accelerated at 700 °C, but no accelerated oxidation was observed at a temperature lower than 600 °C. Figure 5 shows the effect of amount of salt coating on the oxidation curve. The amount of oxidation was larger with larger amount of salt coating.
coating, although crossover was observed with the curve of 6.8 and 4.8 mg/cm² from 500 to 800 min.

Figure 6 shows the curves of Inconel 625 with and without salt coating at different temperatures. The accelerated oxidation did occur from 600 °C. The amount of accelerated oxidation was larger at higher temperature. The shape of accelerated oxidation was different from those of Hastelloy-N. Neither incubation nor catastrophic periods were observed, although the initial oxidation rate was very fast.

Figure 7 shows the oxidation curves of N-155 at different temperatures. The accelerated oxidation was observed at every temperature. The shape of the oxidation curves are nearly the same as those of Inconel 625.

(1)—3 Comparison of the accelerated oxidation behavior among alloys

The amount of oxidation is sometimes expressed as the following function of time,

\[ \Delta W/S = a t^b \]

where, \( t \) is time, \( a \) and \( b \) are parameters. In figure 8, the accelerated oxidation curves of alloys at 700 °C are replotted in log-log form. From the slope of lines, the value of \( b \) was estimated. The oxidation is called "catastrophic", when \( b \) is larger than unity, and "moderate acceleration", when \( b \) is less than unity. In the cases of Hastelloy-N(M.M.) and Hastelloy-N(h.m.), \( b \) was about 2 in an early period of time and 0.36-0.4 in later period. But the absolute amount of oxidation was larger in Hastelloy-N(M.M.) than in Hastelloy-N(h.m.). In the case of Inconel 625, \( b \) was slightly less than unity initially and almost constant at 0.1 in later periods. This small value of \( b=0.1 \) shows very slow oxidation and is favorable from the view point of hot corrosion resistance. In the case of N-155, \( b \) changed from 0.7 in early periods to 0.4 in later periods. It can be said from the figure that Hastelloy-N(h.m.) should be the best with respect to hot corrosion resistance, among the present alloys.

The effect of chromium content on the accelerated oxidation can be seen by comparing the result of Hastelloy-N(M.M.) to that of Inconel 625, because compositions of the two alloys are similar to each other, but chromium content in Inconel 625 is more than 3 times larger than in Hastelloy-N(M.M.). Significant differences can be seen in later periods. The value of \( b \) in Inconel 625 was very small. Thus, chromium can be considered effective for hot corrosion resistance. The effect of iron content can be seen by comparing the result of Hastelloy-N(M.M.) to that of Hastelloy-N(h.m.). The amount of oxidation of Hastelloy-N(M.M.) was always larger than that of Hastelloy-N(h.m.). Since Hastelloy-N(h.m.) contains no iron, iron can be considered detrimental with respect to hot corrosion resistance. This detrimental effect can also be seen by comparing
the result of Inconel 625 to that of N-155. Protective effect of chromium seen in Inconel 625 was cancelled by the detrimental effect of iron in N-155, because the latter contained a much larger amount of iron.

(1) Morphology of the scale formed by accelerated oxidation

Photo. 1 shows microscopic picture of the scale formed on Hastelloy-N(M.M.) at 700 °C and distribution map of elements. The scale was of 500 um thickness and had a kind of multi-lamellar structure. Map of elements shows that the scale was mainly composed of nickel oxide and contained some amounts of iron, chromium and molybdenum oxides uniformly. Sodium was concentrated in the outer layer. Thus, the outer layer might be a mixture of oxides and salt. No concentration gradient of elements was observed in the alloy phase, showing no preferential oxidation. The feature of scale formed by the accelerated oxidation with NaBF₄-NaF mixture was similar to that shown in Photo. 1, in all alloys.

(2) Thermogravimetric measurements with LiF-BeF₂ mixture

(2)-1 Vaporization of salt and hot corrosion of Hastelloy-N(h.m.)

Triangles in Figure 9 show the weight loss of salt coated on platinum net. The vaporization of the salt occurred during heating at 700 °C, but its rate was not so fast. Circles in the figure show the weight change of Hastelloy-N(h.m.) with the salt coating heated in air. The weight decreased till 1000 min. and increased later. Squares in the figure show the weight change when the alloy with the salt coating was heated in Ar. The weight decreased faster in the initial period of time than heated in air and continued to decrease throughout the heating time. Therefore, it can be said that two kinds of reaction occurred simultaneously, when the alloy was coated with LiF-BeF₂ and heated in air. The one might be the formation of some volatile material, and the other is the accelerated oxidation.

(2)-2 Weight change of Inconel 625 and N-155

Figure 10 shows the weight change of Inconel 625 with the salt coating heated in air at different temperature. The weight decreased initially and increased later. The formation of some volatile material and the accelerated oxidation occurred simultaneously, also in the case of Inconel 625. The rate of both reactions were faster at higher temperature.

Figure 11 shows the weight change of N-155 with the salt coating heated in air at different temperature. No weight loss was observed, contrary to the other two alloys. The oxidation was significantly accelerated. The amount of oxidation was larger at higher temperature. The oxidation curve was not smooth but stepwise.
(2) Morphology of the scale

Photo. 2 shows the microscopic picture of the scale formed on Inconel 625 with the salt coating heated in air at 700 °C. The feature of scale was globular and very different from that in the case of NaBF₄-NaF mixture. Although the weight change was negative at the end of experiment, oxide phase was found in the scale. Oxide phase was composed of chromium and iron oxides with a small amount of molybdenum oxide. Nickel oxide was scarcely found in the oxide phase. Porous layer was found in the alloy phase, just beneath the salt-alloy interface. The layer was deficient in chromium and iron contents. Outside of the layer, some precipitates were found, which might be the intermetallic compound of nickel and molybdenum. The morphology of the scale on the other alloys was nearly the same as that shown in Photo. 2.

(3) Electrochemical polarization measurement in NaBF₄-NaF

Figure 12 shows polarization curves of Inconel 625 and N-155 in Ar at 600 °C. Iₐ and Iₐ are anodic and cathodic currents, respectively. The polarization curves were similar to each other, although the anodic current of Inconel 625 was smaller in higher potential region than that of N-155. The anodic current had an active dissolution peak at -0.3V and showed the passivation around 0 V. Figure 13 shows polarization curves of a graphite electrode at 600 °C, in air and in Ar. The cathodic current in air was larger than that in Ar. Thus, the cathodic current can be attributed to the reduction of dissolved oxygen in the salt, in the potential range from -0.4 to 0.3 V.

\[ O_2 + 4 \text{e}^- = 2 \text{O}_2^- \] ..............................(2)

This potential range coincided with that where active dissolution of alloy electrode occured, as shown in Figure 12.

\[ M = M^{n+} + n \text{e}^- \] ..............................(3)

Thus, it can be postulated that the accelerated oxidation might occur electrochemically by the coupling of reactions (2) and (3).

Figure 14 shows polarization curves of the alloys at 700 °C. The anodic current of Hastelloy-N(h.m.) was much smaller than those of others, in the above potential range. This accorded with the result of thermogravimetric measurement, where the amount of accelerated oxidation of Hastelloy-N(h.m.) was the smallest among the alloys. Figure 15 shows the polarization curve of Hastelloy-N(h.m.) in air at 700 °C. The corrosion current was estimated as 1.32 mA/cm² by extrapolating cathodic and anodic currents with the aid of the Tafel relation. The rate of accelerated oxidation of Hastelloy-N(h.m.) was estimated from the slope of the curve shown in Figure 4, between 400 and 1000 min., and converted to the current density of 1.7 mA/cm², assuming di-valent electrode reaction and the mean atomic weight of
These two current densities seem to be in accordance with each other.

CONCLUSION

The air oxidation of the present alloys is significantly accelerated by the adhesion of NaBF$_4$-NaF. The amount of accelerated oxidation is larger with larger amount of the salt mixture and at higher temperature. The result of electrochemical polarization measurement indicates that the electrochemical mechanism, in which the anodic dissolution of metallic element is coupled with the cathodic reduction of oxygen, plays an important role. When the nickel based alloys are heated with LiF-BeF$_2$ coating in air, the weight decreased initially and increased later. Thus, it is seen that some kind of volatile material might be formed simultaneously with the accelerated oxidation.

ACKNOWLEDGEMENT

The present work is financially supported by Grant-in Aid for Energy Research, The Ministry of Education, Science and Culture, Japan.

REFERENCES

1. M. Kawakami, K.S. Goto and R.A. Rapp, Trans. ISIJ, 20, 646(1980).
2. J. Stringer, Annual Reviews of Materials Science, 477 (1977).
3. E.L. Simons et al., Corrosion NACE, 11, 505 (1955).
4. C. Tedmon and A.U. Seybolt, Corros. Sci., 8, 125 (1968).
5. J.A. Goebel et al., Met. Trans., 4, 261 (1973).
6. R.A. Rapp and K.S. Goto, Proc. Symp. Fused Salt, Oct. (1978).
7. N.S. Bornstein and M.A. DeCresente, Trans. AIME, 245, 1947(1969).
8. N.S. Bornstein and M.A. DeCresente, Corrosion, 26, 209 (1970).
9. N.S. Bornstein and M.A. DeCresente, Met. Trans., 2, 2875 (1971).
10. M. Kawakami et al., Proc. JIMIS-3; High temperature Corrosion, 279 (1983).
11. M.W. Rosenthal et al., "The Developmental States of Molten-Salt Breeder Reactors", ORML-4812, (1972).
12. M.W. Rosenthal et al., JAERI-M, 5181 (1973).
Figure 1. Schematic diagram of the apparatus in electrochemical polarization experiment.

Figure 2. Weight change of Hastelloy-N(M.M.) heated in Ar.

Figure 3. Oxidation curves of Hastelloy-N(M.M.) with and without NaBF₄-NaF coating at 700°C.

Figure 4. Oxidation curves of Hastelloy-N(h.m.) with and without NaBF₄-NaF coating at different temperature.

Figure 5. Effect of the amount of NaBF₄-NaF on the oxidation curve of Hastelloy-N(h.m.) at 700°C.
Figure 6. Oxidation curves of Inconel 625 with and without NaBF₄-NaF coating at different temperature.

Figure 8. Comparison of accelerated oxidation among alloys.

Figure 7. Oxidation curves of N-155 with NaBF₄-NaF coating at different temperature.

Figure 9. Weight change of Pt net and Hastelloy-N(h.m.) with LiF-BeF₂ coating in Ar and air.

Figure 11. Weight change of N-155 heated in air with LiF-BeF₂ coating.

Figure 10. Weight change of Inconel 625 heated in air with LiF-BeF₂ coating.
Figure 12. Polarization curve of alloys in NaBF₄-NaF at 700°C.

Figure 13. Polarization curve of oxygen in NaBF₄-NaF at 600°C.

Figure 14. Polarization curve of alloys in NaBF₄-NaF at 700°C.

Figure 15. Polarization curve of Hastelloy-N(h.m.) in NaBF₄-NaF at 700°C in air flow.
Photo. 1  Microscopic picture of the scale formed on Hastelloy-N(M.M) with NaBF$_4$-NaF coating at 700 °C, and map of elements.

Photo. 2  Microscopic picture of the scale formed on Inconel 625 with LiF-BeF$_2$ coating at 700 °C, and map of elements.