CORROSION BEHAVIORS OF MATERIALS USED IN URANIUM METAL PRODUCTION

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ABSTRACT

Corrosion behaviors of materials used in molten uranium or fluoride were studied in order to predict life spans of the materials and know contamination levels of uranium by the materials. By means of compatibility tests, materials, such as Y$_2$O$_3$ to molten uranium, graphite and W also to molten uranium to some extent, graphite and Mo to molten fluoride, are proved to be corrosion resistance materials, and their corrosion behaviors are discussed. Furthermore, the materials were used in electrolysis operation, and evaluated by comparing their corrosion behaviors with those observed in the compatibility tests. The result is that each material shows quite similar corrosion behavior in both cases.

INTRODUCTION

There is a process which electrolyze uranium oxides directly to metal in fluoride electrolyte among the electrolysis processes. In this process, uranium metal electrodeposited is dealt with in liquid phase because of its high electrolysis temperature (around 1200°C). Both molten uranium and fluoride are so corrosive that it is important to find corrosion resistance materials to select apparatus materials. Furthermore, it is important to know life spans of the materials and contamination of uranium from the materials by making their corrosion behaviors clear.

Though studies on corrosion resistance materials to molten uranium or fluoride were, if anything, done energetically so far$^{(1)-(25)}$, they are not always available for the selection of apparatus materials for mass production. There are many things which have not been revealed yet, for example, long-term corrosion resistance at high temperature
around 1200°C, corrosion behaviors in electrolysis apparatus, effects of degradation in density of materials for higher cost performance etc.

From such background, first, candidate materials listed in Table 1 were chosen by means of literature review (1)-(23). In choosing them, workability and possibility of mass production, etc., were taken account of as well as corrosion resistance. Properties of the candidate materials were also shown in Table 1. Then, compatibility tests were carried out on those materials. On the basis of results of the compatibility tests, corrosion resistance materials were selected. The corrosion behaviors of those materials were also investigated by both the compatibility tests and electrolysis operation.

EXPERIMENT

Compatibility Tests

Selection of corrosion resistance materials. Preliminary compatibility test were carried out between the candidate materials, and molten uranium or fluoride. Each material was formed to a crucible shape whose outer diameter and height were about 30mm by machining, sintering and plasma spray. Fifty grams of uranium metal or 7 grams of fluoride (74wt%BaF2-11wt%LiF-15wt%UF4) was then filled in the material crucibles. Uranium metal was pickled and fluoride was dried at 100°C in advance. Chemical compositions of uranium metal and fluoride used in the tests were shown in Table 2. The material crucibles filled with uranium metal or fluoride were placed in a furnace, and heated on the conditions listed in Table 3. After heating, the outside appearances of material crucibles were observed, then the material crucibles were cut for analyses. Cross sections of the interfaces between materials and uranium metal or fluoride were also observed and analyzed, using XRD, EPMA, etc.

Long-term compatibility test. Compatibility test extended to from 96 hours to 936 hours were carried out on materials which showed good corrosion resistance in the test within 32 hours. Heating temperature was mainly set to 1240°C, here. Some of the materials needed covers on the crucibles in order to prevent molten uranium or fluoride creeping out because of their high wettabilities.

Corrosion evaluation of Materials in Electrolysis Operation

The materials which showed good corrosion resistance in the compatibility tests (including exceptional materials) were used in apparatuses of electrolysis or related experiments, and checked their corrosion behaviors. Details of the electrolysis and related experiments are described in the another paper of this proceedings volume. Each material was used repeatedly at around 1200°C in the experiments. Total use times of the materials changed from several hours to several tens of hours according to parts of apparatuses where the materials were used. Every material, except a few materials, experienced heat
cycles between room temperature and around 1200°C more than 5 times. After the experiments, components of the apparatuses were taken apart, and specimens for analyses were sampled. The specimens were analyzed by the same methods as the compatibility tests.

Corrosion behaviors of materials in the electrolysis process were evaluated by comparing results obtained with those of the compatibility tests.

RESULTS AND DISCUSSION

Compatibility Tests

Selection of corrosion resistance materials. Result of the preliminary compatibility test is summarized in Table 4. Yttrium oxide showed good corrosion resistance to molten uranium regardless of the decrease in density, the difference between sintered body and plasma-splayed one. Tungsten, graphite, \( \text{UO}_2 \) and \( \text{CaAl}_4\text{O}_7 \) showed corrosion resistance to molten uranium to some extent. On the other hand, graphite (regardless of the degradation in both purity and density), amorphous carbon and Mo showed good corrosion resistance to molten fluoride. Tungsten and BN did not show any reaction with molten fluoride, but embrittlement by recrystallization in the case of W and infiltration of molten fluoride in the case of BN were observed.

Selected materials by the test were as follows. Materials for molten uranium were \( \text{Y}_2\text{O}_3 \), W and graphite (W and graphite were selected because of their functions as a conductor or corrosion resistance to molten fluoride). Materials for molten fluoride were graphite (including amorphous carbon) and Mo.

Long-term compatibility test. Result of the long-term compatibility test was qualitatively same as that of preliminary compatibility test but degree of the corrosion was greater except in the case of graphite to molten fluoride. Graphite to molten fluoride did not show any corrosion.

Corrosion behaviors of selected materials

Corrosion behaviors revealed by the compatibility tests were as follows.

\( \text{Y}_2\text{O}_3 \) to molten uranium. When the temperature was 1240°C, slight amount of \( \text{UO}_2 \) was formed at the interface between \( \text{Y}_2\text{O}_3 \) and molten uranium, and slight color change of \( \text{Y}_2\text{O}_3 \) was observed only in the vicinity of the interface even after 936 hours contact. On the other hand, when the temperature was 1400°C, remarkable color change of \( \text{Y}_2\text{O}_3 \) from white to black was observed after 96, 936 hours contact, and \( \text{UO}_2 \) layer was formed (\( \sim 100 \mu \text{m} \) thick after 96 hours). In every condition, Yttrium was not...
detected in uranium metal. The color change is considered to be those caused by oxygen defects because only Y₂O₃ can be the oxygen source of the UO₂ layer. Therefore, it is considered that the corrosion behaviors of Y₂O₃ are formation of the oxygen defects and the oxidation of molten uranium forming UO₂.

Graphite to molten uranium. It was observed that UC layer was formed at interface between graphite and molten uranium by reaction of C + U \rightarrow UC. Uranium Carbide was formed not only at the interface but in molten uranium region as UC dendrite. The UC dendrite soaked up molten uranium while growing up along the surface of graphite crucible, hence it was observed that molten uranium crept up on the inner wall of graphite crucible. Weight increases of UC, estimated from width of the UC layer and carbon content of uranium containing the UC dendrite, are plotted in Fig.1. The formation rate of UC decreases with time. The slope of line within 8 hours is in between 0.5 and 1.0. On the contrary, the slope of line over 8 hours is about 0.5 or less. This indicates that the rate determining step may change from reaction-diffusion to diffusion (or slower step than diffusion) with time. Therefore, it is suggested that the UC layer may be protective to some extent.

W to molten uranium. It was observed that grain boundaries of W were dissolved preferentially and some amounts of grains were floating in uranium metal. Tungsten contents in uranium metal after the test at 1240°C are shown in Fig.2. The W contents are almost constant regardless of their heating time. Figure 2 indicates that W dissolves quickly in molten uranium and no more dissolution do not occur after W content reaches its solubility (within 3 hours). The grains of W grew up by recrystallization with the heating time, and W embrittled remarkably especially in the case of 936 hours. Wettability of W with molten uranium also increased with the heating time, and molten uranium crept out from the W crucible in the case of 936 hours. This creeping is considered to be caused by the coarse surface of recrystallized W and its capillarity.

Graphite to molten fluoride. Graphite heated with molten fluoride did not show any corrosion, and no increase of carbon content in fluoride was observed. The carbon content changes with time were also shown in Fig.2. Hence, it can be said that graphite is a good corrosion resistance material to molten fluoride. The only change observed in the compatibility tests was slight infiltration of molten fluoride when graphite was degraded in purity and density.

Mo to molten fluoride. Molybdenum recrystallized with time but its embrittlement was slight compared to W. Neither reaction layer nor increase of Mo content in fluoride was observed. Therefore, Molybdenum is good corrosion resistance material to molten fluoride. However, it was suggested that the Mo content in fluoride was effected by moisture content of fluoride before heating. When Mo was heated with fluoride which had experienced premelting, Molybdenum was not detected in fluoride. On the contrary, when Mo was heated with fluoride powder which was only dried at 100°C, Molybdenum was
detected. This results indicate that Mo is corroded only when moisture exists in the fluoride.

Y₂O₃ to molten fluoride. Yttrium oxide is not a corrosion resistance material to molten fluoride but it is so good corrosion resistance material to molten uranium that its compatibility with molten fluoride is tested. As the result, existence of Y₂O₃ + UF₄ → YOF + UO₂ + YF₃ reaction was suggested. This reaction progressed quickly and UO₂ layer was formed at the interface while a part of Y₂O₃ changed to YOF. Many cracks were introduced both in area of YOF (including remaining Y₂O₃) and UO₂ layer. Yttrium was detected in fluoride by analysis.

Corrosion evaluation of Materials in Electrolysis Operation

Result of corrosion evaluation of materials is summarized in Table5. Part names of apparatus where materials were used and their histories are also written in Table 5. Every material functioned normally as a corrosion resistance material during its service. Especially Y₂O₃ to molten uranium, and graphite to molten fluoride showed similar results to the compatibility tests even though they were heat cycled at least 5 times. Graphite and W to molten uranium were cracked at the vicinity of the interface between graphite and uranium. Those cracks are considered to be caused by stronger effects of differences of thermal expansion between materials and uranium metal when their size become bigger. Therefore, it is desirable that graphite and W do not experience any heat recycling when they are used as corrosion resistance materials to molten uranium. It was clear that Mo corroded in electrolyte initially because Mo was detected in electrolyte contacted with Mo parts. However, the corrosion considered to be that occurred by moisture initially included in raw fluoride because Mo content decrease drastically after the series of electrolysis experiments. Boron nitride was used as an insulator in the electrolyte, but infiltration of fluoride was observed in the same way with the compatibility test. Hence, possibility of electrical short was suggested in the long run.

CONCLUSION

Corrosion resistance material to molten uranium is Y₂O₃, and both graphite and tungsten show corrosion resistance to some extent. On the other hand, corrosion resistance materials to molten fluoride are graphite and Mo. Yttrium oxide corrodes slowly by molten uranium, and Mo also corrodes by molten fluoride in the presence of moisture content. Corrosion behaviors of these materials in electrolysis operation are similar to those observed in compatibility tests. However, introduction of cracks by heat cycling is recognized in the case of Graphite and W to molten uranium. These results are quite useful to design further experiments for prediction of life spans of the materials and contamination of uranium by the materials in the electrolysis process for uranium metal production.
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Table 1 List of candidates for corrosion resistance materials to molten uranium or fluoride chosen by literature review

| Candidates | Properties | Candidates | Properties |
|------------|------------|------------|------------|
| W          | W>99.95%, 99.6%TD | W          | W>99.95%, 99.6%TD |
| Ta         | Ta>99.83%, 100.0%TD | Ta         | Ta>99.83%, 100.0%TD |
| Graphite   | a. Ash<0.01%, 82.3%TD b. Ash<0.1%, 77.8%TD | Mo         | Mo>99.93%, 98.7%TD |
| YfO3       | a. YfO3>99.9%, 100.3%TD b. YfO3>99.9%, 70.0%TD c. Plasma-sprayed | Graphite   | a. Ash<0.01%, 82.3%TD b. Ash<0.1%, 77.8%TD |
| UO2        | UO2>99.9%, 97.7%TD | Carbon**   | Ash<0.5%, 1.48g/cm³ |
| ZrO₂*      | ZrO₂:92.76%, 5.96g/cm³ | YfO3       | YfO₃>99.9%, 100.3%TD |
| ZrSiO₄     | ZrO₂:65.87%, SiO₂:32.58%, 3.79g/cm³ | AIN        | AIN>99.4%, 100.9%TD |
| CaAlO₄      | Al₂O₃:80.0%, CaO:19.5%, 2.14g/cm³ | BN         | BN>99.5%, 83.8%TD |

ZrO₂*: partially stabilized by 4.60wt%YfO₃
Carbon**: amorphous carbon

Table 2 Uranium and fluoride used in the compatibility tests

| Uranium | Elements | Contents | Elements | Contents | Elements | Contents |
|---------|----------|----------|----------|----------|----------|----------|
| ppm     |          |          |          |          |          |          |
| Al      | < 10     | In       | < 1      | Ti       | < 4      |
| B       | < 0.4    | Mg       | < 1      | V        | < 1      |
| Ba      | < 1      | Mn       | 9        | W        | < 50     |
| Ca      | < 5      | Mo       | 5        | Zn       | < 10     |
| Cd      | 0.5      | Na       | < 1      |          |          |
| Co      | < 2      | Ni       | 28       | C        | 686      |
| Cr      | 5        | Pb       | < 1      | Cl       | < 10     |
| Cu      | 12       | Sn       | < 1      | F        | < 5      |
| Fe      | 78       |          |          |          |          |

| Fluide   | Constituents | Purities | Compositions |
|----------|--------------|----------|--------------|
| ppm      | BaF₂         | > 98     | 74           |
|          | LiF          | > 98     | 11           |
|          | UF₄          | > 99     | 15           |

Table 3 Conditions of compatibility tests

| Items       | Tests            | Selection of corrosion resistance materials | Long-term compatibility test |
|-------------|------------------|---------------------------------------------|-------------------------------|
| Atmosphere  | Ar gas, 1 atm    | Ar gas, 1 atm                                |                               |
| Temperature | 1240°C, 1400°C   | 1240°C (Y2O3:1400°C)                        |                               |
| Time        | 3, 8, 32 hrs     | 96, 936 hrs                                 |                               |
| Heating and cooling rate | 300°C/min        | 300°C/min                                   |                               |

Table 4 Result of preliminary compatibility test

| Corrosives Uranium | Candidates | Remarks | Compatibility | Corrosion behaviors |
|--------------------|------------|---------|---------------|---------------------|
| W                  | Fair       | Solution of grain boundary, Embrittlement by recrystallization |
| Ta                 | Poor       | Solution of grain boundary |
| Graphite           | Fair       | Formation of UC layer |
| YfO₃               | Good       | Formation of very thin UO₂ layer |
| UO₂                | Fair       | Formation of thin UO₂ layer |
| ZrO₂               | Poor       | Formation of UO₂ layer |
| ZrSiO₄             | Poor       | Formation of UO₂+USi₅ layer and porous ZrO₂ layer |
| CaAlO₄             | Fair       | Formation of thin UO₂ layer |
| BN                 | Fair       | Embrittlement by recrystallization |
| Mo                 | Good       | Fluorination |
| Graphite           | a, b table1| Fair     | Formation of UC layer |
| YfO₃               | a-c table1 | Good    | Formation of very thin UO₂ layer |
| UO₂                | Fair       | Formation of thin UO₂ layer |
| ZrO₂               | Poor       | Formation of UO₂ layer |
| ZrSiO₄             | Poor       | Formation of UO₂+USi₅ layer and porous ZrO₂ layer |
| CaAlO₄             | Fair       | Formation of thin UO₂ layer |
| BN                 | Fair       | Embrittlement by recrystallization |
| Carbon             | Good       | Slight infiltration |
| YfO₃               | Poor       | Embrittlement, Formation of YOF and UO₂ layer |
| AIN                | Poor       | Embrittlement, Formation of U-rich layer |
| BN                 | Fair       | Infiltration |
Fig. 1 Weight increase of UC estimated from width of UC layer and carbon content of uranium containing UC dendrite at 1240°C

Fig. 2 Tungsten content of uranium contacted with W crucible, and C content of fluoride contacted with graphite crucible at 1240°C

Table 5 Corrosion evaluation of materials by using them in electrolysis operation

| Corrosives | Materials | Part names of apparatus (Experiment) | Histories of use | Differences from the compatibility tests, Heat cycle resistances |
|------------|-----------|--------------------------------------|------------------|---------------------------------------------------------------|
| Molten uranium | Y2O3 | Stopper rod (Transport experiment of molten uranium) | a. 1220-1260°C b. 4 hrs c. 5 | No difference |
| | | | | Show heat cycle resistance |
| Graphite | Container of molten uranium (Electrolysis experiment) | a. 1150°C b. 6 hrs c. 1 | Small difference |
| | | | | Crack was introduced by cooling |
| W | Cathode (Electrolysis experiment) | a. 1100-1300°C b. 68 hrs c. 15 | Small difference |
| | | | | Crack was introduced by heat cycles |
| Molten fluoride | Graphite | Electrolytic cell (Electrolysis experiment) | a. 1100-1190°C b. 27 hrs c. 5 | No difference |
| | | | | Show heat cycle resistance |
| Mo | Purge tube of stirrer gas (Electrolysis experiment) | a. 1100-1190°C b. 27 hrs c. 5 | No difference |
| | | | | Show heat cycle resistance |
| BN | Insulator in electrolyte (Electrolysis experiment) | a. 1150°C b. 6 hrs c. 1 | No difference |