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High temperature liquid metal corrosion and high temperature electrical conductivity of Y_2O_3

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Abstract

Yttrium sesquioxide has been proposed as a promising candidate material for collector electrodes used in the laser enrichment system of uranium-235. For this purpose, yttria is expected to be compatible with molten uranium and electrically conductive. A corrosion test of yttria with molten lanthanum as a simulating metal for uranium and a measurement of its electrical conductivity under extremely low oxygen pressure were performed. It was shown from the corrosion test that a yttria sample was considerably corroded by the molten lanthanum at 1513 K and the maximum corrosion depth for 5 Ms was 0.162 mm. The electrical conductivity of hypo-stoichiometric yttria reduced by titanium was higher than that of pure germanium at room temperature (2.1 S/m). The oxygen pressures equilibrated with the yttria specimens were estimated to discuss the relation to measured conductivities. © 1997 Elsevier Science B.V.

1. Introduction

The laser enrichment of uranium-235 using atomic vapor is considered to be a promising method. In this method, collector electrodes and a crucible for molten uranium are exposed to uranium vapor or its molten metal under the severe conditions of high temperature about 1500 K and extremely strong reducing atmosphere.

Yttrium sesquioxide (yttria) has been proposed as a promising candidate material for these parts [1]. Compatibility tests of several ceramics and metallic materials against molten uranium have been performed to check the applicability for a crucible or a casting mould for uranium [2–5] and it has been considered that yttria was one of the most appropriate material. On the other hand, the electrical conductivity of yttria has been measured in the oxygen pressure range about 10^{-12} to 10^{5} Pa [6]. It was shown that yttria was a p-type semiconductor at high temperature and has a minimum value at the stoichiometric composition for electrical conductivity. Because of short heating time or high oxygen pressure, however, these tests were not sufficient with regard to the postulated conditions of this work.

The aim of this study is to investigate the long term compatibility of yttria against molten lanthanum metal as a simulating metal for uranium and the electrical conductivity at high temperature and under extremely low oxygen pressure which is equilibrated with active metals such as vanadium and titanium.

2. Experimental

2.1. Procedure

In the corrosion test, lanthanum metal as a corrosion agent was selected because of its similarity to uranium in chemical reactivity and thermophysical properties. An yttria specimen having the size 15 × 15 × 1 mm (width × height × thickness) and lanthanum metal blocks were set in a molybdenum crucible of 18 × 20 mm (internal diameter × height) which was covered with a lid having a small hole. The crucible was then kept at the prescribed temperature in a vacuum furnace. Because the depth of molten lanthanum was about 5 mm, the yttria specimen was

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immersed by 1/3 of its height. The heating temperatures were 1273 and 1513 K and the duration time of heating was from 86.4 ks to 5 Ms. After being cooled down to room temperature, the specimen was cut together with the crucible into two pieces. The cross-section of the specimen was polished and analyzed with an electron probe microanalyzer (EPMA).

The conductivity measurement of yttria was performed under a condition simulating the presence of molten uranium. Because of an extremely low oxygen pressure in the U–UO_2 system, such a condition was locally realized by placing yttria specimens between plates of titanium or vanadium at high temperatures. The specimens were previously reduced to hypo-stoichiometry by titanium or vanadium plates at 1600 K for 2.5 Ms in vacuo and were coated with titanium or vanadium on both sides by vapor deposition for the formation of electrodes. The electrical conductivity measurement was performed by the ac four-probe method at the temperature range of about 900 to 1600 K and the frequency range of 60 Hz to 30 kHz.

2.2. Specimen

The yttria specimens, 15 × 15 × 1 mm, were mainly prepared by hot-pressing of the yttria powder having a purity better than 99.9% and a density of 98.5% of the theoretical one. The purity of lanthanum metal used as a corrosion agent was over 99.9%.

Titanium used for the reducing agent was a commercial pure plate having a thickness of 1 mm and its oxygen concentration was 0.106 mass%. Vanadium, similarly, was a plate rolled from a vanadium ingot made by electron beam melting and its oxygen concentration was 0.04 mass%.

3. Results and discussion

3.1. Corrosion test

Although yttria specimens were initially white, all yttria specimens corroded at 1513 K by lanthanum metal changed to black. On the other hand, the yttria specimens corroded at 1273 K changed gradually from brown to black with time. This suggests that the reduction rate to hypo-stoichiometry at 1273 K is considerably slower than that at 1513 K.

The compositional images of the specimens corroded at 1513 K for the typical duration time are shown in Fig. 1. The upper part of the yttria surfaces, for instance the top part of the 0.93 Ms figure, did not contact the molten metal and were not corroded except for reduction, while the lower part immersed in molten lanthanum was apparently corroded and the interface between the yttria and corroded layer was moved inward from the initial surface with time. On the position of the initial yttria surface, the dark corrosion product layer was observed. The enlarged images of the corroded area are shown in Fig. 2. The outer layer of the specimen corroded for 86.4 ks was composed of lanthanum oxide (lanthana) containing about 5% yttria. Its internal zone consisted of yttria containing about 5% lanthanum oxide and lanthanum metal. On the other hand, the outer layer of the specimen corroded for the range of 0.25 to 5 Ms was commonly yttria saturated with lanthana. Its inner area was the fairly compact and equimolar complex oxide of $LaYO_3$, in which yttria particles were included. Between the inner layer and the yttria matrix of the specimen corroded for 5 Ms, the white and thin penetrant, which is metallic lanthanum, was observed. Except for the specimen corroded for a short time, these layer structures and the compositions of corrosion products are almost similar for all specimens. The amount of lanthanum components in the uncorroded yttria and yttrium components in metallic lanthanum after the corrosion test were less than the analytical limit by EPMA.

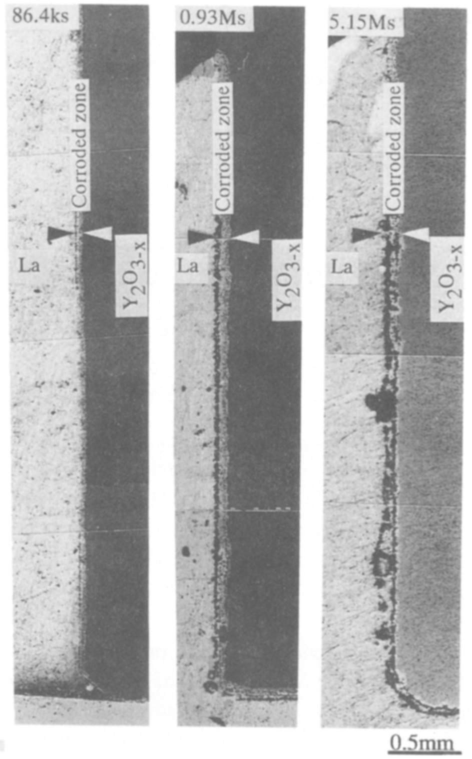

Fig. 1. Comparison of corrosion behavior on time dependence by EPMA compositional images. T: 1513 K.

The relation of corrosion depth and duration time is shown in Fig. 3. The corrosion rate at 1513 K was initially high and suddenly slowed down at about 0.25 Ms. The maximum corrosion depth of the specimens corroded for 5 Ms was 0.162 mm. The corrosion depth at 1273 K was about 1/3 of that at 1513 K.

The corrosion mechanism was considered as shown in

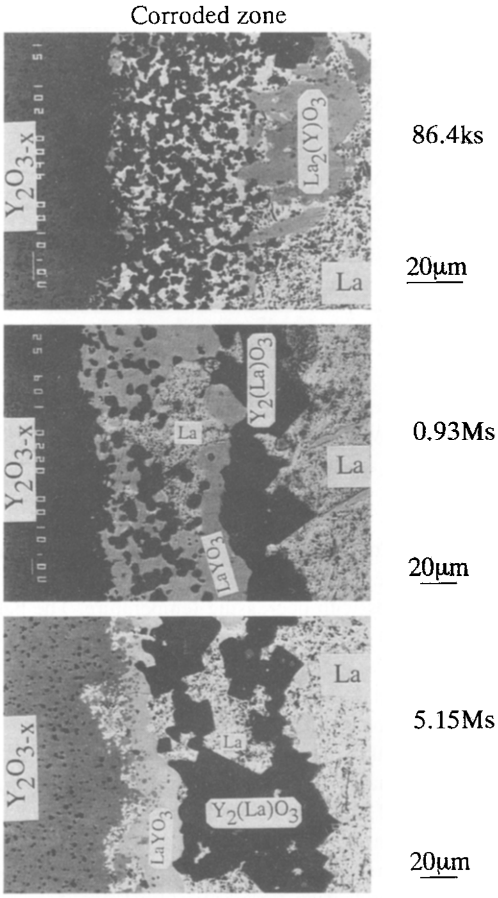

Fig. 2. Comparison of microstructure change of corrosion zones. *T*: 1513 K.

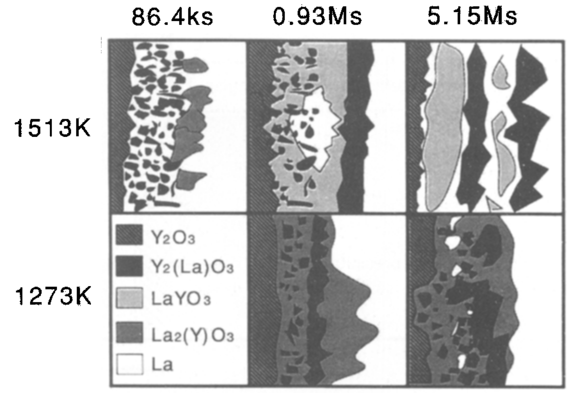

Fig. 4. Schematic drawing of corrosion of yttria by molten lanthanum.

Fig. 4: Molten lanthanum initially reduces yttria to a hypo-stoichiometric composition and is simultaneously oxidized to form lanthanum oxide. The lanthanum oxide subsequently reacts with yttria and forms the complex oxide. The density of this complex oxide is considerably higher than that estimated from the densities of yttria and lanthana. It suggests that the complex oxide is chemically or thermodynamically more stable than its own component oxides. Once the complex oxide layer is formed, therefore, it seems to show the corrosion resistance against molten lanthanum metal. This mechanism seems to cause the rapid slowdown on corrosion rate. Although the complex oxide layer is stable, this compact layer is also corroded with time at defects like cracks or grain boundaries in itself. Then the molten lanthanum, eventually, penetrates the yttria surface and locally corrodes the yttria matrix.

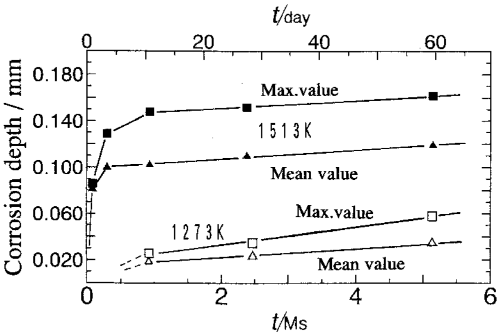

Fig. 3. Relation of corrosion depth and time.

3.2. Electrical conductivity measurement

The electrical conductivity of the hypo-stoichiometric yttria reduced by titanium is shown in Fig. 5. It is seen that the specimen was considerably conductive in the range of about 300 to 1650 K and the electrical conductivity was higher than that of pure germanium at room temperature (2.1 S/m). This specimen showed, further, characteristic behavior in the temperature dependence of conductivity; the conductivity was semiconductor-like in the range of 1400 to 1600 K, while it had a minimum at about 1250 K and again increased below this temperature, followed by appearance of a maximum at about 1000 K. This behavior

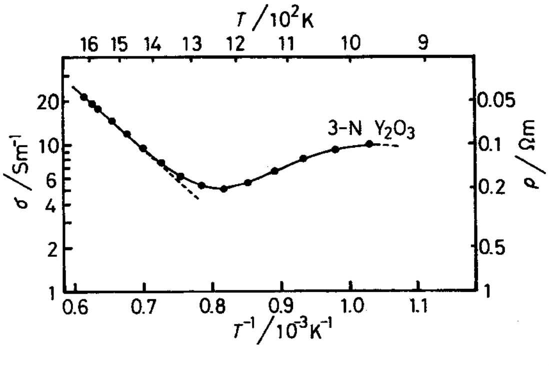

Fig. 5. Electrical conductivity of hypo-stoichiometric yttria specimen reduced by titanium. Reduction condition: 1600 K, 2.5 Ms.

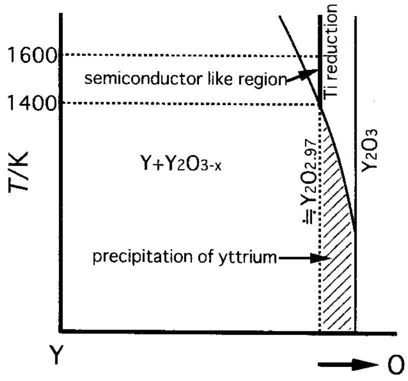

Fig. 6. Schematic phase diagram of $Y-Y_2O_3$ system.

could be explained as follows: As described later, the oxygen concentration in the titanium plate using reduction of yttria was about 0.2 mass%. Near the reduction temperature of 1600 K, the oxygen activity in yttria, being a phase boundary of the $Y-Y_2O_3$ system, is estimated to be slightly lower than that of titanium containing about 0.2% oxygen from the thermochemical consideration [7,8]. Then, the composition of the hypo-stoichiometric yttria reduced by titanium is considerably close to that of the yttria-side phase boundary in the $Y-Y_2O_3$ system (shown in schematic phase diagram of Fig. 6) at 1600 K, that is reduction temperature. At the high temperature range of 1400 to 1600 K, yttria is in a single phase. At a lower temperature than about 1400 K, however, the nonstoichiometric width in composition of yttria decreases with decreasing temperature. The hypo-stoichiometric yttria reduced by titanium at this temperature range is, consequently, in the two phase region of yttrium and Y_2O_{3-x}. Metallic yttrium, as a result, precipitates at defects like grain boundaries and dislocations. The quantity of precipitated yttrium increases with decreasing temperature. Because the precipitated yttrium acts locally as short circuit paths for electrical conduction, the electrical conductivity of the yttria specimen should increase with decreasing temperature. On the other hand, the electrical conductivity of yttria matrix rapidly decreases with decreasing temperature. The behavior below 1200 K is probably caused by the balance of these effects. The electrical conductivity was independent on frequency. It indicates that the conduction carriers in yttria are electrons or electron holes.

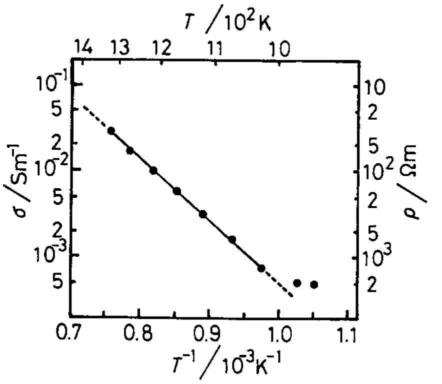

Fig. 7. Electrical conductivity of hypo-stoichiometric yttria specimen reduced by vanadium. Reduction condition: 1600 K, 2.5 Ms.

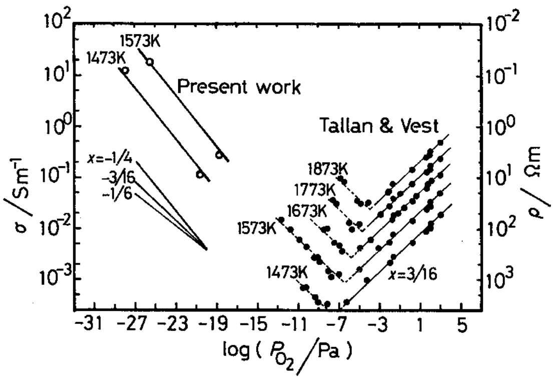

Fig. 8. Relation between oxygen pressure and measured electrical conductivity of hypo-stoichiometric yttria together with Tallan's data.

The electrical conductivity of hypo-stoichiometric yttria reduced by vanadium is shown in Fig. 7. The electrical conductivity of hypo-stoichiometric yttria reduced by vanadium is considerably low compared with that reduced by titanium. The electrical conductivity of this specimen was also independent on frequency.

In order to determine the relation of electrical conductivity and oxygen pressure, the oxygen concentrations of the metal plates equilibrated with yttria specimens were analyzed. The oxygen concentrations in the titanium and the vanadium plates were 0.238 and 0.060 mass%, respectively. The oxygen pressures equilibrated with the yttria specimens can be calculated from these oxygen concentrations [7,9]. The relation between the measured electrical conductivity of hypo-stoichiometric yttria and oxygen pressure is shown in Fig. 8 together with Tallan's data. The extrapolated two straight lines through our measured points, respectively, go by stoichiometric positions at the same temperatures in Tallan's data, which means that our result is valid. The electrical conductivity of yttria in the range of about 10^{-17} to 10^{-27} Pa can be, approximately, regarded to be proportional to the minus one-fourth power of oxygen pressure. In this case, the main defect species in yttria is estimated to be singly charged oxygen interstitials. Finally, the electrical conductivity under extremely low oxygen pressure is expressed by the following equation:

$$\ln(\sigma/\mathrm{S\,m^{-1}}) = 13 + (-1/4)\ln\left(P_{O_2}/1.01325\times10^5\ \mathrm{Pa}\right) + (-376\ \mathrm{kJ/RT}).$$

4. Conclusion

From the corrosion test, it was found that polycrystal yttria was considerably corroded by molten lanthanum as a simulating metal of uranium at 1513 K. Its corrosion rate was initially high and changed to be appreciably low. The maximum corrosion depth of the specimens corroded for 5 Ms was 0.162 mm. The corrosion depth at 1273 K was reduced to about 1/3 of that at 1513 K.

The electrical conductivity of hypo-stoichiometric yttria reduced by titanium was higher than that of pure germanium at room temperature (2.1 S/m). Its electrical conductivity in the range of 1400 to 1600 K showed semiconductor-like behavior. The conduction carriers in hypo-stoichiometric yttria were estimated to be electrons or electron holes. The oxygen pressures equilibrated with the yttria specimens were estimated to discuss a relationship with the measured conductivities.

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