Crystallization of Ruthenium Dioxide during Vitrification of HLW, and its Effect on Leachability of the Glass - 9032

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ABSTRACT

Ruthenium (Ru) is one of the major fission products contained in the High-Level Radioactive Waste (HLW). During reprocessing spent nuclear fuel, Ru is immobilized with the other fission products in borosilicate glass matrix. Japan Nuclear Fuel Limited (JNFL) currently operates a nuclear reprocessing plant in Japan where HLW vitrification process is in operation. Recently, the process was temporarily stopped due to a trouble arising from sedimentation of platinum group metals in the glass melter. A crystallization of RuO_2 was confirmed by XRD analysis of the sediment in the melter, but the detail mechanisms of the crystallization have not been clarified. We performed a laboratory scale experiments using non-radioactive Ru and obtained fundamental data which might lead to an explanation how to form crystals of RuO_2 during vitrification of HLW. Additionally, some leaching experiments were performed with using a glass specimen containing the needle-like crystals of RuO_2. No enhancement of leachability of the glass was observed due to the existence of RuO_2 in the glass.

INTRODUCTION

Ruthenium (Ru) is one of the major fission products contained in the High-Level Radioactive Waste (HLW).[1] During reprocessing spent nuclear fuel, Ru is immobilized with the other fission products in borosilicate glass matrix. Japan Nuclear Fuel Limited (JNFL) currently operates a nuclear reprocessing plant where HLW vitrification process is in operation. Recently, the process was temporarily stopped due to a trouble arising from sedimentation of platinum group metals (PGMs) in the glass-melter [2]. The plant employs a glass-melter of ceramics walls with using a Joule-heating system and the sedimentation of PGMs lead to troubles of electric energy loss, local over-heating, high viscous glass formation and unexpected low production rate of the vitrification. These troubles are mainly caused by existence of needle like crystal of RuO_2[3], because it is electrically conductive and the size of the needlelike crystal is 1 to 10 micrometers in length. The sedimentation of the electric conductive materials actually leads to local heating phenomena which cases erosion of furnace wall bricks and the formation of the solids in the molten glass increases effective viscosity of the glass markedly.

Although an improvement of the vitrification process, especially removing RuO_2 from the molten glass would be possible by applying some proposals with the process modifications[4-5], it takes a long time to realize and demonstrate. In this paper, the authors will report on some results of experiments performed on a laboratory scale using non-radioactive Ru and obtained fundamental observations which might lead to an explanation how to form crystals of RuO_2 during the vitrification of HLW. Additionally, some leaching experiments were performed with using a glass specimen containing the needle-like crystals of RuO_2, because we should discuss and confirm safety aspect of the already produced HLW glasses in Japan.

SOLUBILITY OF RUTHENIUM DIOXIDE IN SODIUM NITRATE

In some reprocessing plants, high-level liquid wastes of aqueous nitric acid solution, which are the mixture of the raffinate stream from solvent extraction processes and solvent scrub waste stream and solid sludges from back washing and regeneration process from a centrifuge clarifier for fuel solution before feeding for solvent extraction processes, are directly introduced in to a glass melter and followed by being calcinated on molten glass in a glass melter. The major constituent in the mixture is sodium nitrate and the salt is contained in the calcine. Since the melting point of sodium nitrate is 581 K, it is probable that the sodium nitrate becomes fused into molten salt, where RuO_2 may dissolve in it if solubility is high enough. Unfortunately, the data of solubility of RuO_2 in the molten sodium nitrate is not found in the literature, and so we measured the solubility in the first place as follows.

Experimental

All chemicals are of reagent grade or higher, and purchased from Wako Pure Chemical Industries, Ltd. (Japan). An excess amount, i.e., 0.2 g of $Ru(NO)(NO_3)_3$ and 2.7 g of $NaNO_3$ was dissolved in 3 cm^3 of 1 mol dm^{-3} nitric acid and the solution was poured into a crucible made of Al_2O_3 and being followed by evaporating water at 523 K. At temperatures ranging from 773 to1073 the content of the crucible was kept at the constant temperature for 3 hours and made solid residue was settled out at the bottom of the crucible. A part of molten salt was sampled and dissolved in de-ionized water in a crucible made of Zirconium and evaporated water and being followed by fused with 200 mg KOH and 70mg KNO_3 for elemental determination. The fused content was dissolved with 1 mol dm^{-3} hydrochloric acid and the concentrations of ruthenium and sodium were determined using an ICP-AES (Shimadzu Co. ICPE-9000).

Results and discussion

Sampled specimens were slightly colored yellow just after taken from the crucible of Al_2O_3, but soon after being cooled black solid was observed in the specimens. The black solids were confirmed by using a microscope to be not needle-like-shape but granular.

The Solubilities measured are summarized in Table I. The solubility data in Table I shows a strong dependency on temperature. This implies that at the higher temperature more than 1000 K, RuO_2 dissolves well in the molten salt of sodium nitrate and when the molten salt is cooled down in some conditions; solid phase of RuO_2 appears separated in the molten or solid salt.

Table I. The measured values of Solubility of RuO2 in $NaNO_3$.

Temperature	Solubility g/ 100g
773 K	0.039
873 K	0.064
973 K	6.4
1073	>21[a]

[a] All the RuO_2 in the starting materials were dissolved in NaNO3, and the actual solubility is expected greater than the value shown here.

PREPARATION OF SIMULATED GLASS CONTAINING NEEDLE-LIKE CRYSTAL OF RUTHENIUM OXIDE

The authors have showed a possibility of RuO_2 being transferred into the calcine of HLW as is solved in molten salt such as $NaNO_3$. In our experiment, the RuO_2 crystallized from $NaNO_3$ was granular. The shape of RuO_2 appeared in the glass is, however, known as needle-like. This fact suggests the other mechanisms should be considered rather than solubility decrease of RuO_2 in the alkali salt by cooling of calcine made from HLW. Since the calcine of HLW is formed on the molten glass in the melter. It is probable that the salt in the calcine was easy to transport into the glass while RuO_2 dissolved in the salt is transport into the glass very slowly. In order to confirm this hypothesis, we perform an experiment of preparing a glass containing needle-like crystal of RuO_2 by placing molten salt solving RuO2 on a piece of borosilicate glass at a elevated temperature as follows.

Experimental

All chemicals are of reagent grade or higher, and purchased from Wako Pure Chemical Industries, Ltd.

(Japan). First of all, molten salt of $NaNO_3$ saturated with RuO_2 was prepared in the method described in the previous section at 773K. Borosilicate glass was prepared by fusing a mixture of SiO_2, B_2O_3 and Na_2SiO_3 in a platinum crucible at 1473 K The molten salt containing RuO_2 was powdered by a ball-mill (Pulverisette 7, Fritsch, Germany) at the room temperature and 53 mg of the powder was placed on the of borosilicate glass of 1 g in the platinum crucible. The content in the platinum crucible was heated and kept at 1073 K for half an hour in a electric furnace (KDF-80S, Koyo, Japan), and quenched at the room temperature.

Results and discussion

Ru crystals formed in the specimen was observed by a micro-analyzer and picture is illustrated in Fig.1 the crystals were needle-like shaped. As a technical remark, needle like crystal was formed by contacting the over saturated molten liquid of sodium nitrate with RuO_2 and borosilicate glass. This may be explained that sodium was transported into the glass, which was confirmed by an increase of sodium in the glass whose sample was taken and analyzed by the ICP-AES after being fused using a mixture of KOH and KNO_3 and neutralized and diluted with 1 mol dm^{-3} hydrochloric acid for elemental determination. There was no increase of Ru in the borosilicate glass so that RuO_2 migration rate from the phase of molten salt into the glass phase was low enough to form the crystal of RuO_2.

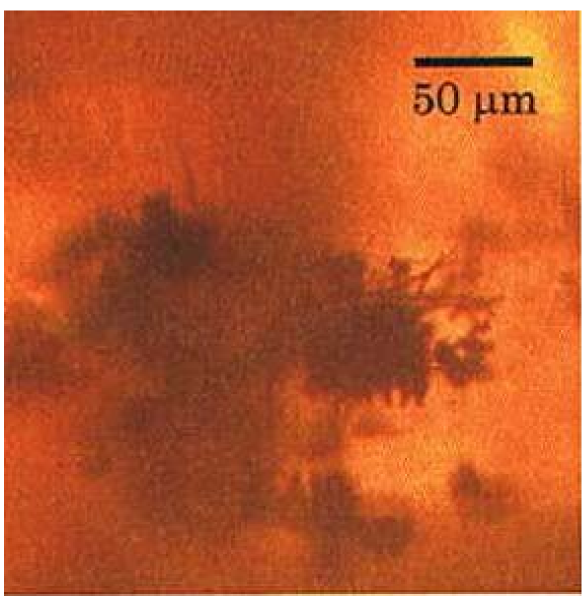

Fig.1 Photograph of ruthenium crystals appeared in the glass specimen.

LEACHING TEST OF THE SIMULATED GLASS SPECIMEN

Since a leaching rate of the waste matrix is one of characteristics of its safety performance, the authors experimentally measured a leaching rate from a borosilicate glass specimen which contains needle-like shaped RuO_2 as well as some elements simulating fission products, and compared the values with those obtained for a specimen without containing the crystal of RuO_2.

Experimental

A simulating HLW waste was prepared with the same method as described in a previous papers.[4-5] A series of leaching tests were performed based on MCC-I method using a powdered specimen[6]. The fused and quenched glass samples were ball milled into powder whose average sizes were 110±30 μm in Feret's diameter. The specific surface area was evaluated 0.021 m^2 g^{-1} The chemical composition of the glass was as same as of SON68 glass in the literature.[7] We prepared four specimens for leaching tests. One is the glass containing needle-like-shaped crystal of RuO_2, which was prepared by the same method described in the preceding section in this paper. The other three are typical SON68 glass specimens and these are used for obtaining referenced values of elemental leaching rates of simulating elements of fission products. The sodium and Ru contents in the sample containing the RuO_2 crystals were 8.5 % and 1.6 % in weight respectively, whereas 11.2% and 0% in the other samples without RuO_2 crystals. The leaching tests were performed at 363 K for 5 days with 40 mL of deionized water.

Results and Discussion

The elemental leaching rates from the four samples are shown in Table II. The experimental results show elemental leaching rates for the SON68 glass specimens containing the needle-like-shaped RuO_2 crystals were not greater than those for the SON68 glass specimens without RuO_2 in all elements. This is partially explained by the fact that the sodium content of the former glass was smaller than the latter ones.

Table II. Results of leaching tests for specimens of SON68 glass with the RuO_2 crystals.

	Leaching rate, g $m^{-2}d^{-1}$	
Elements	without RuO_2 crystal	With RuO_2 crystal
Si	0.078±0.003[a]	0.047

Li	0.0042±0.0002	0.0038
B	0.018±0.001	0.010
Na	0.029±0.001	0.020
Ca	0.0074±0.0002	0.0062
Fe	0.0004±0.0001	0.00032
Zn	0.0006±0.0001	0.00049
Sr	0.00052±0.00002	0.00049
Mo	0.0048±0.0002	0.0022

[a] the values after± show standard deviations of the leaching rates measured for the three samples.

CONCLUSIONS

We have successfully prepared a simulated high-level nuclear glass containing crystals of needle-like-shaped RuO_2 by contacting molten sodium nitrate saturated with RuO_2 on borosilicate glass of the SON68 glass. Additionally, some leaching experiments were performed with using a glass specimen containing the needle-like crystals of RuO_2. No enhancement of leachability of the glass was observed due to the existence of RuO_2 in the glass.

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