

Formation Mechanisms of the Needle-shaped Crystals of Ruthenium Dioxide during Vitrification of Nitric Acid Solution Containing Nitrosyl Ruthenium Nitrate - 11265

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ABSTRACT

Laboratory scale experiments were performed to investigate the chemical mechanisms of the formation of needle-shaped ruthenium dioxide crystals in borosilicate glass. Nonradioactive nitric acid solutions containing nitrosyl ruthenium nitrate were used to conduct the experimentation. First, Na_3RuO_4 was formed by reactive dissolution of molten NaNO_3 and RuO_2 . The RuO_2 was formed from the decomposition of the nitrosyl ruthenium solution followed by the formation of volatile RuO_4 . The formation of RuO_4 was confirmed by mass spectrometry under an atmosphere of 20 volume percent O_2 at a temperature of greater than 1000 °C. It was postulated that the RuO_4 formation may be an intermediate step of the resulting needle-shaped crystals of ruthenium dioxide found in the glass. Upon analysis of the glass, needle-shaped crystals of RuO_2 were formed in both the calcine layer and in the borosilicate glass near the calcine layer / glass interface.

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 with a Joule heating system is in operation. Recently, the process has been temporarily halted due to technical trouble arising from sedimentation of platinum group metals in a liquid-fed ceramic melter (LFCM). In the LFCM, a liquid aqueous solution containing HLW is first calcinated to get the mass. The calcined material is then mixed with glass beads heated above its fusion temperature. In the course of analyzing origin of the temporal ceasing, the formation of RuO_2 was confirmed by X-Ray Diffraction (XRD) analysis of the sediment in the melter as a result of a given sampling protocol for this case, but the detail mechanisms of RuO_2 formation was not clear. RuO_2 crystals can impact melter operations by increasing the viscosity of molten glass as well as excess electrical conduction through glass which may cause electrical energy loss and significant local damage of the internal structure of the glass melter.

We performed laboratory-scale experiments using non-radioactive Ru and obtained fundamental scientific data which might lead to an explanation how ruthenium dioxide is formed during the vitrification of HLW. We have already reported in Waste Management Symposia in 2009 that RuO₂ of reagent grade reactively dissolved in molten salt of sodium nitrate with a significant solubility of greater than 6% in mass in the temperature range of more than 600 °C. The chemical form of ruthenium in the molten salt was determined as Na₃RuO₄ by XRD measurement. We also confirmed that the needle-shaped crystals formed near the interface between the molten salt and borosilicate glass contained the ruthenium species of concern. Additionally, some leaching experiments were performed using a glass specimen containing needle-shaped crystals of RuO₂, and no enhancement effect on leachability of the glass was observed due to the existence of RuO₂. This fact showed that HLW vitrification is still appropriate for this waste stream even if the sedimentation of significant amount of RuO₂ occurred in the glass melter in the reprocessing plant. However the detail chemical mechanisms of the formation of the needle-shaped crystals of RuO₂ were not understood at that time. Now, in the present study, we will report the more detail mechanisms of forming needle-shaped crystals of RuO₂ during the vitrification process. In the experimental work, we performed thermal analyses of Na₃RuO₄(which was obtained by the reaction between NaNO₃ and RuO₂ with applying XRD), thermal gravimetry, and gas measurement with using a mass spectrometer under the two conditions of 100% Ar and 80% Ar + 20% O₂ from room temperature through 1150 °C.

REACTIVE DISSOLUTION OF RUTHENIUM DIOXIDE IN SODIUM NITRATE

Detail of experimental results as well as methods and chemicals used were previously reported [4]. In the quenched specimen obtained after the reaction of RuO₂ and NaNO₃, existence of stable Na₃RuO₄ was confirmed to exist by XRD analysis (Mini Flex, Rigaku, Japan). So, it is expected that first nitrosyl ruthenium is converted into Na₃RuO₄ in a calcine layer onto borosilicate glass melt in the LFCM system.

SUBSEQUENT CHEMICAL REACTIONS OF Na₃RuO₄

In the following sections of the paper, we will discuss the subsequent chemical reactions of Na₃RuO₄ in the calcine layer by contact with gas and solid phases. The chemical reaction with gaseous phase was studied first. As a gaseous phase, we assumed atmospheric air in the cell where the LFCM system is installed in the reprocessing plant. Thus, a gas mixture of 80% N₂ and 20% O₂ on volume basis was assumed for the experiments. Future experiments have been planned to look at the case concerning the decomposed gas from nitrate salts. The gas mixture of 80% N₂ and 20% O₂ on volume basis was an example of oxidizing

circumstances, thus the chemical reactions with borosilicate glass melt was studied from the stand point of Reduction – Oxidation (REDOX) reactions of Ru chemical species.

DECOMPOSITION OF SODIUM RUTHENATE AT TWO DIFFERENT GASEOUS CONDITIONS

Experimental

Starting chemicals of Na_3RuO_4 was prepared by a method described in a previous paper[4] using nitrosyl ruthenium purchased from Rare Metallic Co., Japan of purity >99% as well as NaNO_3 of Wako Special Grade purchased from Wako Pure Chemical Industries, Ltd. The purity of synthesized Na_3RuO_4 was checked by using XRD (Rigaku, Miniflex, Japan). The two different gaseous conditions for decomposition of the starting materials were prepared by mixing gases of technical grade, Ar and O_2 fed into a thermal gravimetric device (Shimadzu TGA-50H, Japan) through mass flow controllers. The gases of G1 grade (purity >99.999%) used in the experiment were obtained from Taiyo Nippon Sanso, Japan. The temperature of the specimen was controlled and recorded with the thermal gravimetric device. The gaseous effluent from the thermal gravimetric device (i.e. the reaction gas product) flowed through a continuous leak valve and was analyzed by a mass spectrometer (CANON-ANELVA M-200QA-M, Japan).

Results and discussion

The graph in **Fig. 1** shows a signal strength for a mass peak corresponding to the formula weight of RuO_4 i.e. 165, against temperature for decomposition of Na_3RuO_4 . For the case using the gas mixture of 20% O_2 and 80% Ar in volume, Na_3RuO_4 decomposed into RuO_4 at greater than 1000 °C, on the other hand with 100% Ar, RuO_4 was not detected. These results showed Na_3RuO_4 decomposed into RuO_4 under the atmospheric conditions of air at greater than 1000 °C. RuO_4 is known to be a yellow colored needle shaped crystalline solid with a high volatility[5]. Crystals with a needlelike morphology may be formed in the calcine layer, when the temperature of the calcine layer is elevated greater than 1000 °C. These experimental results imply that the temperature of the calcine layer is an important operational parameter in the LFCM for reducing/eliminating RuO_4 volatility as well as reducing/eliminating the formation of needle-shaped RuO_2 .

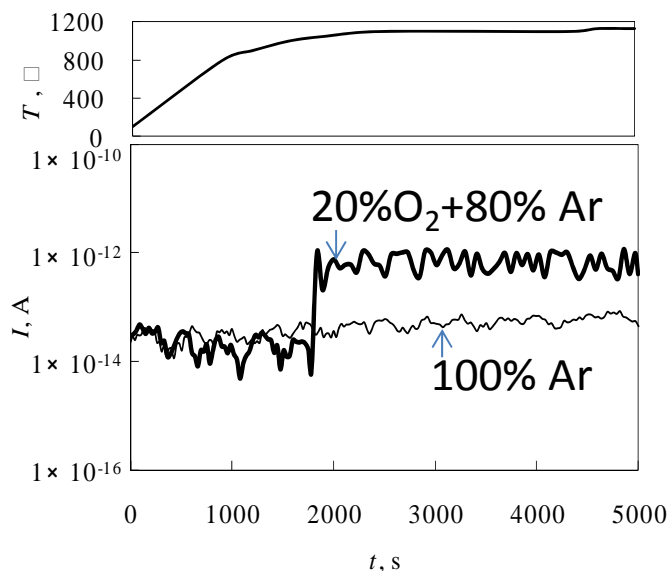


Fig. 1. Signal strength for a mass peak corresponding to the formula weight of RuO_4 observed by mass-spectrometry of the effluent gas from TGA-50H (bottom), and temperature for decomposition of Na_3RuO_4 (top).

FORMATION OF NEEDLE-SHAPED RUTHENIUM DIOXIDE IN CALCINE LAYER AND BOROSILICATE GLASS

Experimental

8 g of borosilicate glass solid purchased from Asahi Glass Co., Ltd. were placed in a long-body crucible of high pure aluminum oxide (SSA-H, Type T2, Nikkato Co. Ltd., Japan). As shown in Table 1, the chemical composition of the borosilicate glass was a typical one used for fixation of high level radioactive waste. The glass materials were heated at 1250 °C for half an hour and glass layer of 30 mm in deepness was formed in the crucible. A calcine mass containing 0.15 g of Na_3RuO_4 (prepared as described in the preceding section) was placed on the borosilicate glass layer and heated at 850°C for 5 hours in an electric furnace. This was completed to promote reactions and diffusive transport phenomena of chemical species near the interface between the two phases. Following a slow cooling of the materials in the crucible, the crucible was sectioned into two pieces so that microscopic observations and XRD analysis with Miniflex could be performed.

Table 1. Content of borosilicate glass used in the experiment.

	Content, %
Al ₂ O ₃	6.5 ±1.0
B ₂ O ₃	16.3 ±0.2
CaO	2.3 ±0.6
K ₂ O	0.6 ±0.1
Li ₂ O	3.33 ±0.05
Na ₂ O	0.48 ±0.04
SiO ₂	67.1 ±1.5
ZnO	3.4±0.5

Results and discussion

Figure 2 is a photograph of the cross section of the specimen. The interface between borosilicate glass and calcine layer moved 2 mm in the upward direction from its original position during the thermal treatment. This appears to be due to the migration of the sodium contained in the calcine layer into the borosilicate glass layer.

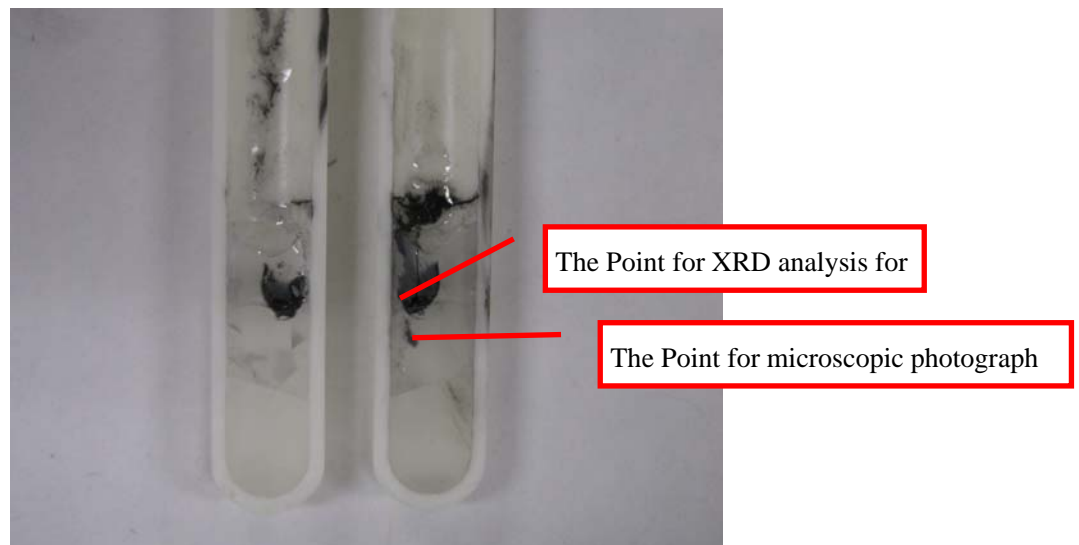


Fig. 2. A photograph taken for the cross-section of the specimen.

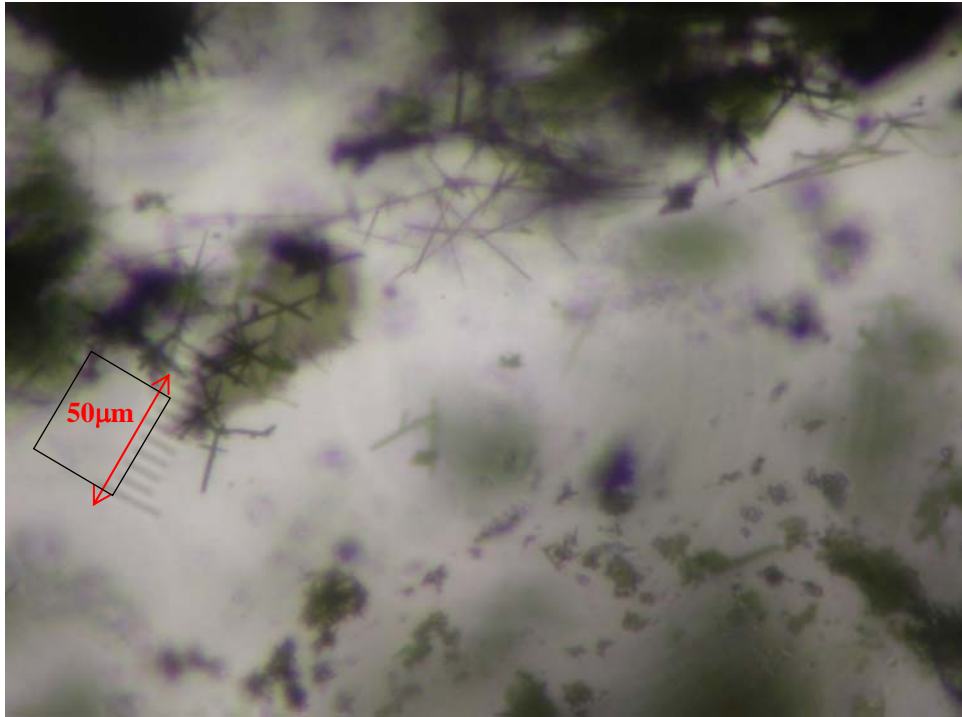


Fig. 3. A microscopic photograph of the specimen at the position shown in **Fig. 2**.

Figure 3 illustrates a sample of needle-shaped crystals observed in the heat treated specimen. The length of the needles ranged up to 50 or 100 μm . The XRD analysis showed these needle shaped crystals were assigned to RuO_2 as shown in **Fig. 4**. We obtained a microscopic photograph closer to the interface between the two phases as shown in Fig. 5 using a Scanning Electron Microscope (SEM) (JSM-6510, JEOL, Japan). According to this photograph, needle-shaped crystals of RuO_2 were found to be formed both in the calcine layer and in borosilicate glass near the interface. On average, the length of RuO_2 crystals observed in the calcine layer is much longer than that in the glass layer, and the latter seems oriented perpendicular to the interface. Therefore, RuO_2 found in the glass layer may be formed by some diffusive transportations of RuO_2 or its precursor from the calcine layer.

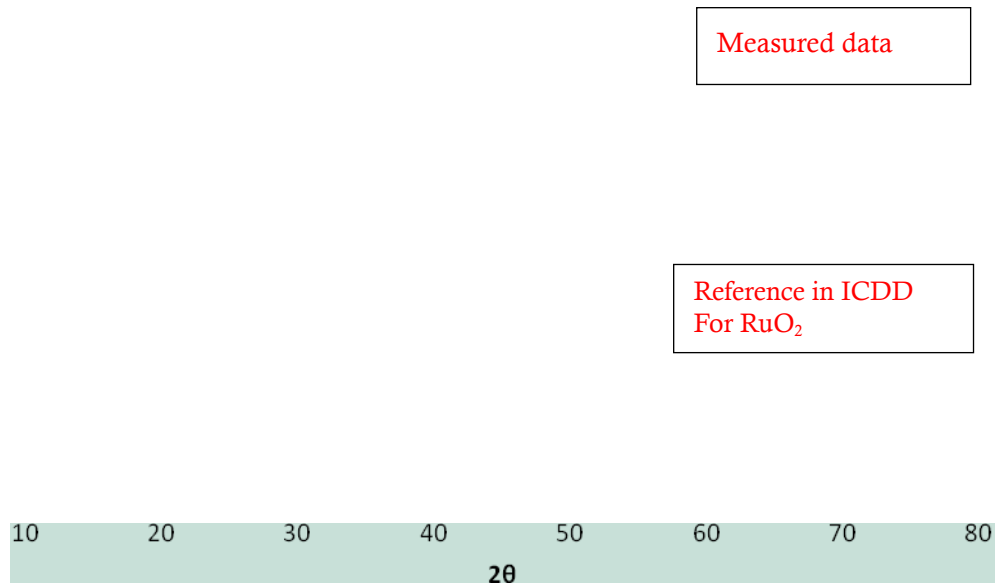


Fig. 4. Obtained diffraction data of the specimen at the position shown in **Fig. 2** compared with the data found in ICDD for RuO₂.

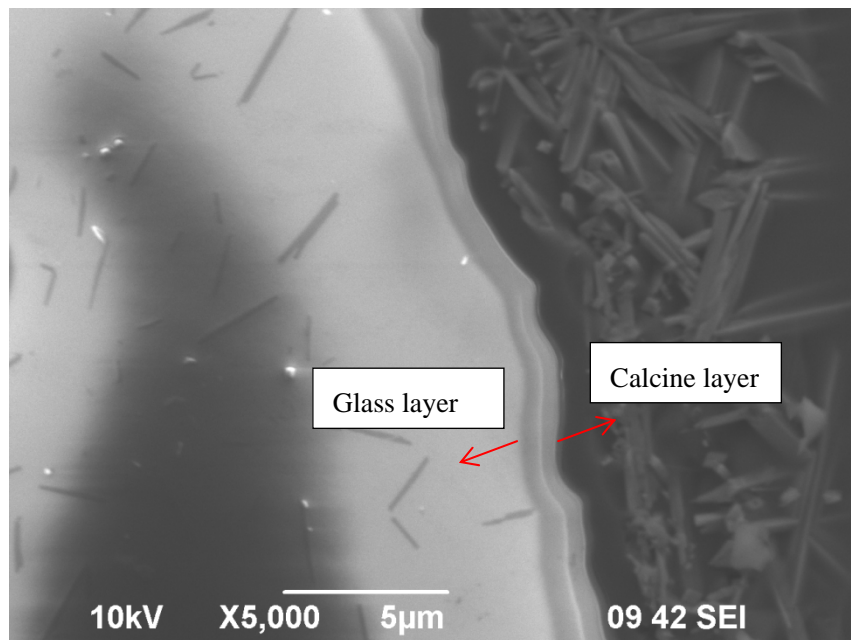


Fig. 5. Photograph taken for the specimen equivalent to that shown in Fig. 2 with a SEM.

CONCLUSIONS

We have investigated the formation of needle-shaped ruthenium dioxide using equivalent conditions seen during the vitrification of high level radioactive solutions containing nitrosyl ruthenium nitrate on a laboratory-scale. Na_3RuO_4 was formed by reactive dissolution of molten NaNO_3 and RuO_2 . The RuO_2 was formed from decomposition of nitrosyl ruthenium solution followed by formation of volatile RuO_4 . The formation of RuO_4 was confirmed by mass spectrometry under an atmosphere of 20% O_2 in volume at greater than 1000 °C. It is postulated that the RuO_4 formation may be an intermediate step of the resulting needle-shaped crystals of ruthenium dioxide. Additionally needle-shaped crystals of RuO_2 were found to be formed both in calcine layer and in borosilicate glass near their interface.

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