The Countermeasure for the Noble Metal in the HLW Vitrification - the Behavior of the Needle Shape Ruthenium Particle - 16107

Kunihiko Nakano*, Shunichiro Ueno*, Hiromichi Maekawa*,
Takayuki Nagai**, Yasuo Ayame**
*IHI Corporation (1, Shin-Nakahara-Cho, Isogo-ku, Yokohama, Japan)
** JAEA (4-33, Muramatsu, Tokai, Naka, Ibaraki, Japan)

ABSTRACT

In this study, we investigated the generation factors and the influences for the glass fluidity of the needle shape ruthenium particles. We report the results described below. (1) About the influence of the ruthenium addition form for the generation of the needle shape ruthenium particles, we compared two forms which were the nitric acid nitrosyl ruthenium (III) solution and the powdered RuO_2. As a result, the needle shape ruthenium particles were formed from the nitric acid nitrosyl ruthenium (III) solution, but they were not formed from the RuO_2. (2) The needle shape ruthenium particles were formed, only the condition of the glass beads, the sodium nitrate and the nitric acid nitrosyl ruthenium (III) solution. (3) Rh and Pd which were the noble metal elements and Mo such as the coexistence elements did not have the influence for the needle shape ruthenium particles growth. (4) As the result of the generation examination of the needle shape ruthenium particles in the range of 700-1150 degrees Celsius, the generation temperature of the needle shape ruthenium particles were approximately 800 degrees Celsius. (5)Retention time in melting affected for the generation of the needle shape ruthenium particles, but cooling rate did not influence them. (6) As the result of comparing the fluidity between the nitric acid nitrosyl ruthenium (III) solution and the powdered RuO_2 as ruthenium, the glass which added the ruthenium with the nitric acid nitrosyl ruthenium (III) solution was inferior to the fluidity.

INTRODUCTION

The high-level radioactive waste which is separated by spent nuclear fuel reprocessing is melted with the borosilicate glass beads for the vitrifying radioactive waste, in Japan. LFCM (Liquid Fed Joule-heated Ceramic Melter) is used for the high-level radioactive waste vitrification. This type melter is heated by passing an electric current for the molten glass, but the noble metal particle sediment in the melter which increases the

glass viscosity and is high conductivity negatively affects such as the drop of heating defectiveness and the glass fluidity for the melter operation. And the induction heat melter also has the same issue about the glass fluidity lowering caused by the noble metal. Therefore, the various countermeasures including the physical approach such as the melter shape modification for LFCM have been performed for the issue of the noble metal. But the induction heat melter cannot be applied the physical approach. This study was performed for the resolutions of the noble metal by the chemical approach.

For the stable melter operation, it is very important to understand the behavior of the noble metal particles in the molten glass. In particular, ruthenium is the most quantity in the noble metal elements and has much influence for the glass fluidity. Then we focused the ruthenium behavior in the molten glass.

In the molten glass, ruthenium exists such as two type shape particles which are grained shape and needle shape. In particular, the needle shape ruthenium particles comparing with the grained shape ruthenium particles are thought as affecting the molten glass fluidity lower. Therefor it is necessary to research the generation conditions of the needle shape ruthenium particles for the melter operation.

Influence of coexistence elements for the needle ruthenium generation

There are reports that the needle shape ruthenium particles are only generated by the ruthenium from the nitric acid nitrosyl ruthenium and are grown by the molybdenum, but there are reports to deny these [1, 2]. Therefore we investigated the influence of the addition forms (nitric acid nitrosyl ruthenium and RuO_2) and the coexistence elements (rhodium, palladium, molybdenum) for the needle shape ruthenium particles generation.

TABLE I shows the examination conditions. The glass beads were the borosilicate glass containing 4wt% Na_2O and diameter 2mm. We used the reagents which were $NaNO_3$, RuO_2 powder, the nitric acid nitrosyl ruthenium (III) solution, $Rh(NO_3)_3$, $Pd(NO_3)_2$, and $Na_2MoO_4 \cdot 2H_2O$. We added the glass beads and reagents were total 15g into the alumina crucible and melted them in the electric furnace. Then we observed the examination samples by SEM-EDX.

TABLE I. The examination conditions

Exam No.	1	2	3	4
Glass beads	Base	Base	Base	Base
Ru type [a)]	n-Ru	RuO_2	n-Ru	n-Ru
RuO_2(wt%)	0.67	0.67	0.67	0.67
Rh_2O_3(wt%)	—	—	0.15	—
PdO(wt%)	—	—	0.48	—
Na_2O(wt%)	10	10	10	10
MoO_3(wt%)	—	—	—	1.14
Temperature(^oC)	1150	1150	1150	1150
Retention time(h)	4	4	4	4

[a] n-Ru: nitric acid nitrosyl ruthenium (III) solution, RuO_2:RuO_2 powder

Fig. 1(a)-(d) show the results of SEM-EDX observation. Fig. 1(a) and (b) show the results of the exam No.1 and No.2 which were the conditions of addition $NaNO_3$ and Ru to the glass beads. We could find the needle and grainy shape ruthenium particles under the exam No. 1 which was added Ru in the nitric acid nitrosyl ruthenium (III) solution, but only the grainy shape ruthenium under the exam No.2 which was added in the RuO_2 powder. Therefore, the needle shape ruthenium particles are generated from adding $NaNO_3$ and the nitric acid nitrosyl ruthenium to the glass beads, and not generated from the RuO_2. These results accord with the former report [3].

Fig. 1(c) shows the result of the exam No.3 which was the conditions of addition $NaNO_3$, Ru, Rh, and Pd to the glass beads. We could find the needle shape ruthenium particles under the exam No.3. But, the difference that was more remarkable than the exam No. 1 not to include Rh, Pd about the size of the generated needle shape ruthenium particles were almost nothing. Therefore, Rh and Pd hardly have the influence for the growth of the needle shape ruthenium particles.

Fig. 1(d) shows the result of the exam No.4 which was the conditions of addition $NaNO_3$, Ru, and Mo to the glass beads. The degree of the needle shape ruthenium particles generation was almost same as the result of the exam No. 1. From this exam result, as for the growth effect of the needle shape ruthenium particles generation about Mo reported in a past study [4], we could not find it.

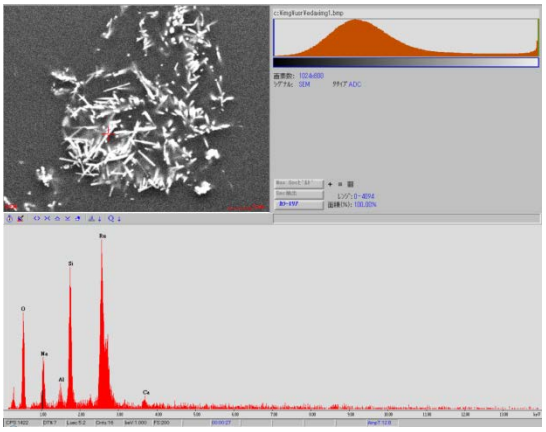

Fig. 1(a) Photo of SEM-EDX (Exam No.1) (Nitric acid nitrosyl Ru)

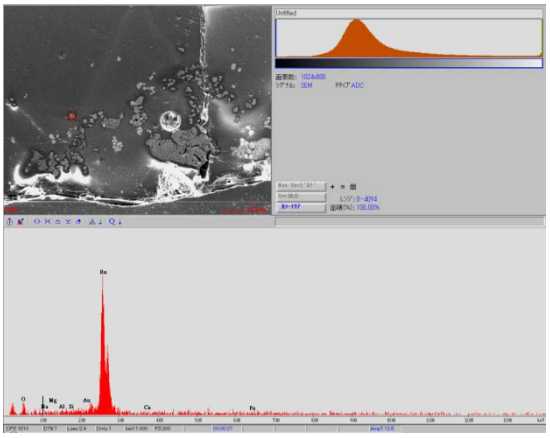

Fig. 1(b) Photo of SEM-EDX (Exam No.2) (RuO_2)

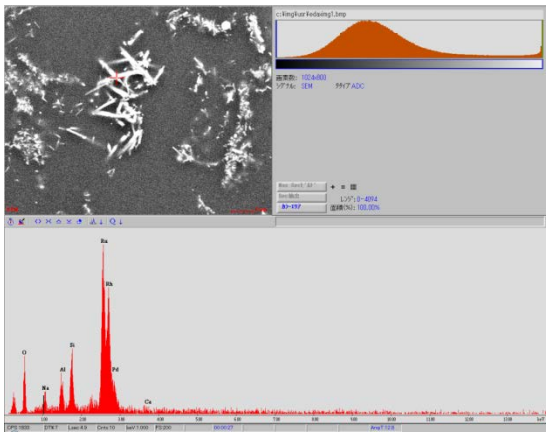

Fig. 1(c) Photo of SEM-EDX (Exam No.3) (Nitric acid nitrosyl Ru + Rh + Pd)

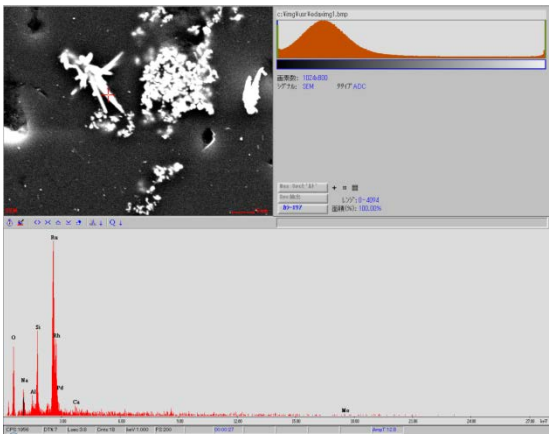

Fig. 1(d) Photo of SEM-EDX (Exam No.4) (Nitric acid nitrosyl Ru + Mo)

Influence of the temperature for the needle ruthenium generation

It turned out that the needle shape ruthenium particles generated from the glass beads, $NaNO_3$, the nitric acid nitrosyl ruthenium (III) solution by our previous tests. Next, we carried out the examinations to take in the generation temperature of the needle shape ruthenium particles.

TABLE II shows the examination conditions. The glass beads were the borosilicate glass containing 4wt% Na_2O and diameter 2mm. We used the reagents which were $NaNO_3$ and the nitric acid nitrosyl ruthenium (III) solution. We added the glass beads and reagents were total 15g into the alumina crucible and melted them in the electric furnace. Then we observed the examination samples by SEM-EDX.

TABLE II. The examination conditions

Exam No.	1	2	3	4	5	6	7
Glass beads	Base	Base	Base	Base	Base	Base	Base
RuO_2(wt%)	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Na_2O(wt%)	10	10	10	10	10	10	10
Temperature(^oC)	700	800	900	1000	1100	1150	800
Retention time(h)	0	0	0	0	0	0	4

Fig. 2(a) – (g) show the results of SEM-EDX observation. Fig. 2(a) shows the results of the exam No.1 which was at 700^{o}C. The glass beads did not melt enough, and Ru was not included in them. In addition, only the crystal of the molten sodium salt was observed in the circumference of the glass beads, and we could not find the needle shape ruthenium particles. Fig. 2(b) shows the results of the exam No.2 was at 800^{o}C. The glass beads became melting, and the ruthenium came to exist in glass. But the ruthenium particles existed only with the grainy shape, and we could not observe the needle shape ruthenium particles. Fig. 2(c) shows the results of the exam No.3 was at 900^{o}C. We were able to find the existence of the needle shape ruthenium particles at 900^{0}C. We estimated that it was necessary for the generation of the needle shape ruthenium particles that the ruthenium became incorporated into the melted glass beads by the results of the 700 - 900 ^{o}C examinations. Fig. 2(d) – (f) show the results from the exam No.4 to No.6 at the temperature range of 1000 – 1150^{o}C. In the conditions more than 1000^{o}C, we also could find the needle shape ruthenium particles. However, it was nothing that the quantity of the needle shape ruthenium particles increased and they were grown with the temperature rise.

The generation temperature range of the needle shape ruthenium particles was proved to be within 800 – 900^{o}C from the results of the exam No.1 - No.6. However, these tests finished after the examination temperature arrival without the retention time and were not considered it about the influence of the retention time for the generation of the needle shape ruthenium particles. Therefore we carried out the exam No.7 which was the conditions of retention time 4h at 800^{o}C. Fig. 2(g) shows the result of the exam No.7. We could find the needle shape ruthenium particles. From this result, although the glass viscosity is relatively high, if it has enough time to become incorporated to the melted glass beads for the ruthenium and to generate the

needle shape ruthenium particles, they are generated.

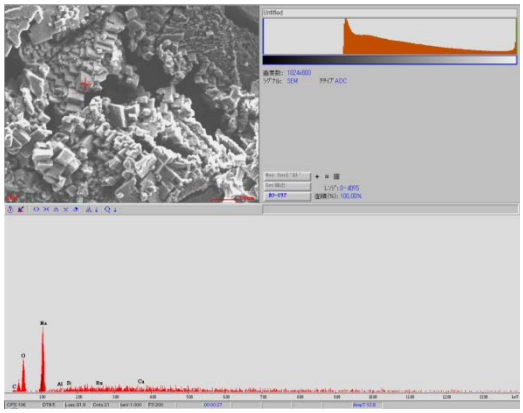

Fig. 2(a) Photo of SEM-EDX (Exam No.1) (700°C)

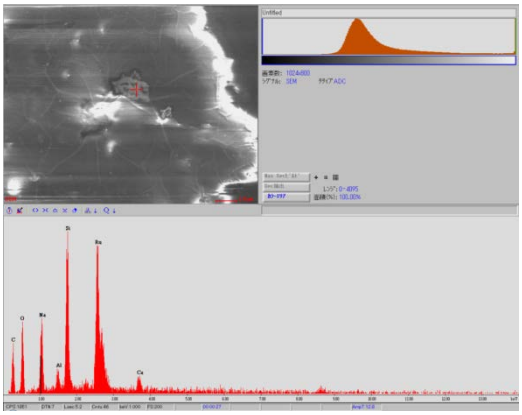

Fig. 2(b) Photo of SEM-EDX (Exam No.2) (800°C)

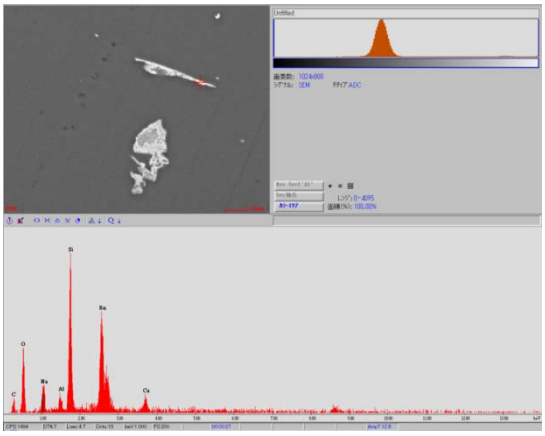

Fig. 2(c) Photo of SEM-EDX (Exam No.3) (900°C)

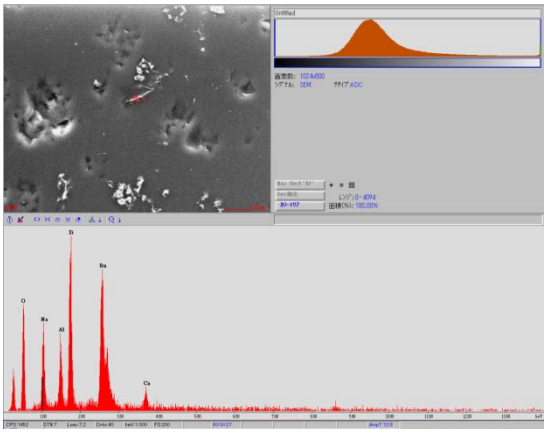

Fig. 2(d) Photo of SEM-EDX (Exam No.4) (1000°C)

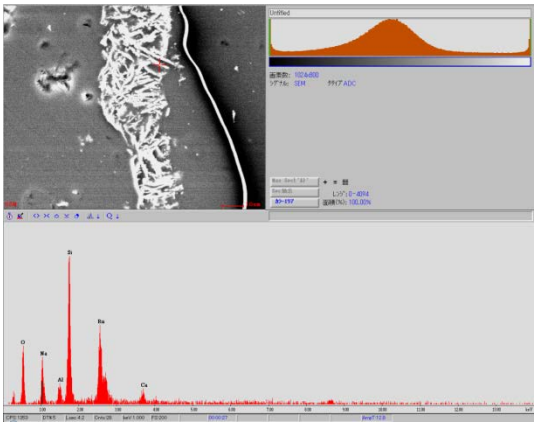

Fig. 2(e) Photo of SEM-EDX (Test No.5) (1100°C)

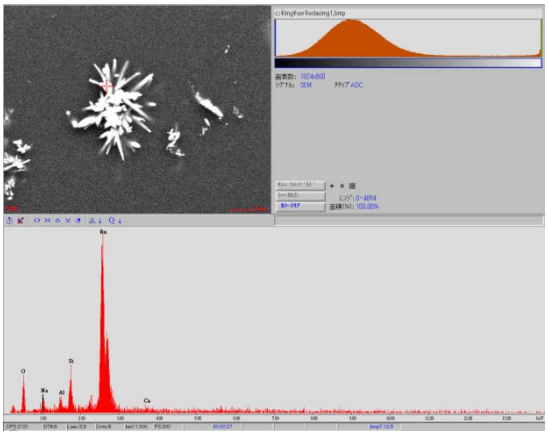

Fig. 2(f) Photo of SEM-EDX (Test No.6) (1150°C)

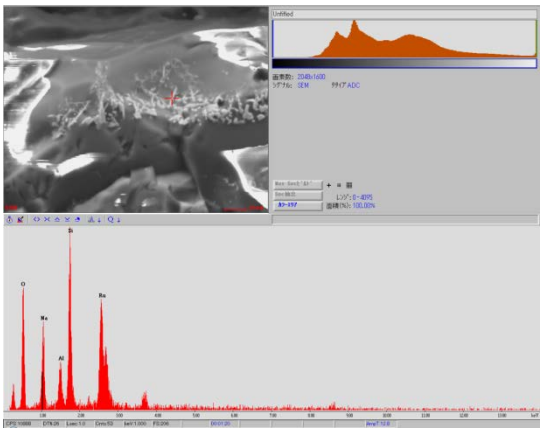

Fig. 2(g) Photo of SEM-EDX (Exam No.7)
(800°C, Retention time 4h)

Influence of the cooling rate for the needle ruthenium generation

We carried out the examinations to understand the influence of the glass cooling rate for the generation and growth of the needle shape ruthenium particles.

TABLE III shows the examination conditions. The glass beads were the borosilicate glass containing 4wt% Na_2O and diameter 2mm. We used the reagents which were $NaNO_3$, and the nitric acid nitrosyl ruthenium (III) solution. We added the glass beads and reagents were total into the alumina crucible and melted them in the electric furnace. Then we observed the examination samples by SEM-EDX.

TABLE III. Examination conditions

Exam No.	1	2
Glass beads	Base	
RuO_2(wt%)	0.67	
Na_2O(wt%)	10	
Temperature(°C)	1150	
Retention time(h)	4	
Cooling rate	Rapidly cooling by water	1°C/min

Fig. 3 shows the definition method of the ruthenium particle size. The shapes of the ruthenium particles have grainy and needle and it is necessary to define them about the particle size individually to greatly vary in the particle shapes. Therefore, we

measured the length and breadth of the particles and defined the oblong geometric mean value as the particle size about the grainy shape particles. Furthermore we measured the maximum length of the particles and defined it as the particle size about the needle shape particles.

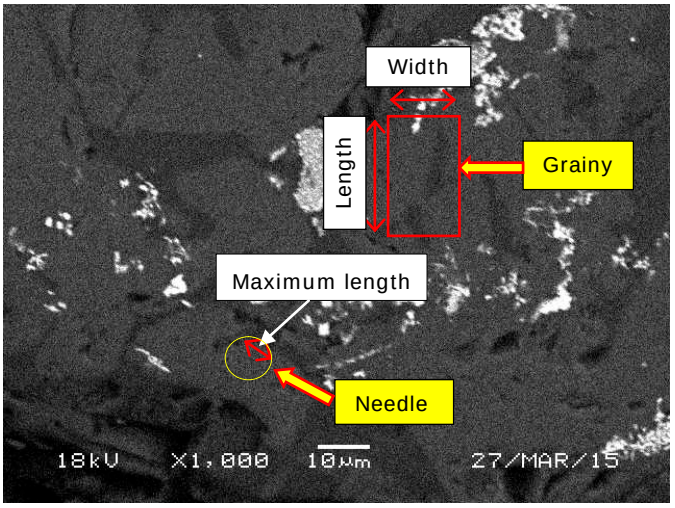

Fig. 3 The definition of the ruthenium particle size

The grainy shape particles: Particle size = $[(\text{Length})\text{x}(\text{Width})]^{0.5}$
The needle shape particles: Particle size = Maximum length

Fig. 4(a) – (d) show the examination results. In addition, the numbers of particles which we measured were 50 in both samples. From the SEM observation, we found the grainy shape ruthenium particles, the needle shape ruthenium ones and the aggregate of the needle shape ruthenium ones (Fig. 4(a)). The needle shape ruthenium particles, the aggregate ones and the grainy shape ruthenium particles existed in both samples. The particle size distributions were similar (Fig. 4(b), (c)). Besides the existence ratio of the grainy shape particles, the needle shape particles and the aggregate of the needle particles were similar in both samples, and the existence ratio of the needle shape particle and the aggregate ones for all particles was approximately 35% (Fig. 4(d)). Therefore, it is estimated that the generation of the needle shape ruthenium particles is not influenced by the cooling rate.

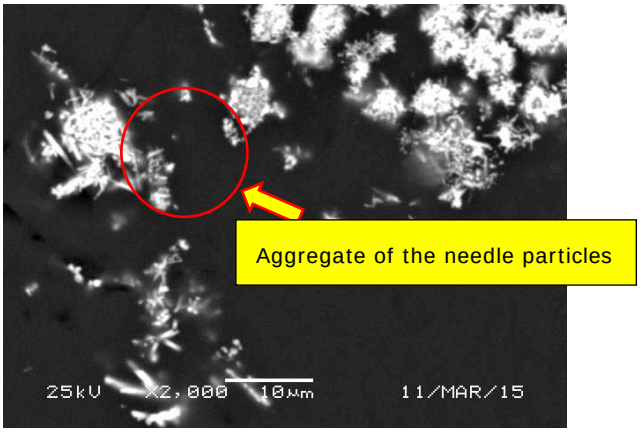

Fig. 4(a) The aggregate of the needle shape ruthenium particles

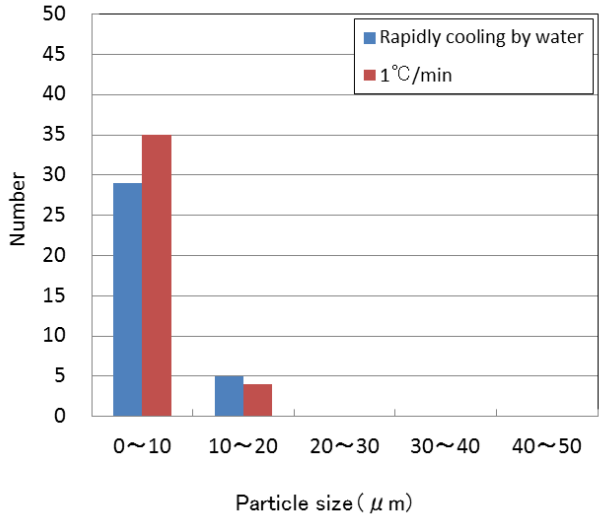

Fig. 4(b) The distribution of particle size
(Grainy particles + Aggregate of the needle particles)

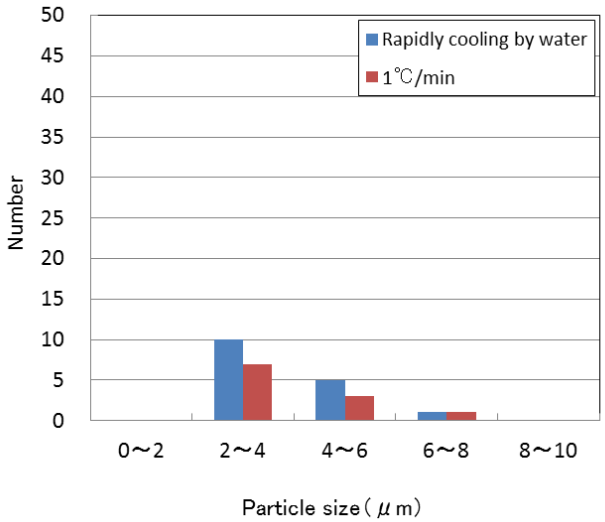

Fig. 4(c) The distribution of particle size
(The needle shape particles)

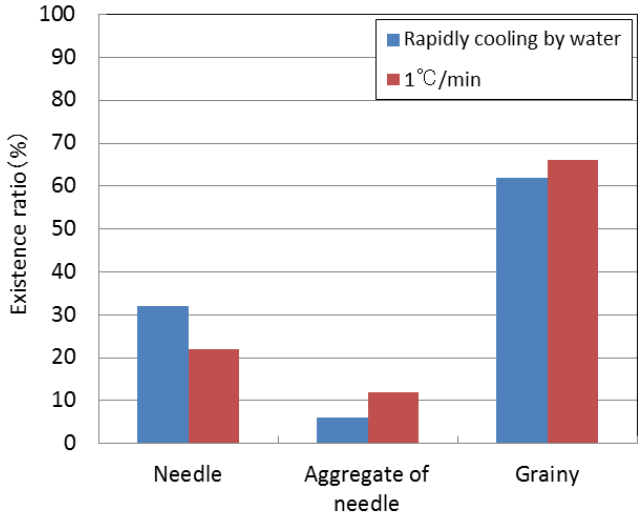

Fig. 4(d) The existence ratio for the particle shapes

Glass fluidity comparison

The glass containing the needle shape ruthenium particles may has the characteristic that its glass fluidity is worse than the glass containing the grainy shape ruthenium particles with the difference of the particle shape. However, it was nothing that the examination to understand the difference of the glass fluidity about the glass containing the needle shape ruthenium particles and the grainy shape ruthenium particles was carried out. Therefore we made the nitric acid nitrosyl ruthenium (III) solution addition glass which generated the needle shape ruthenium particles and the RuO_2 powder addition glass which did not generate them and carried out the examinations to estimate the influence that having the needle shape ruthenium particles or not gave the glass fluidity.

TABLE IV. shows the conditions of glass samples making. The glass beads were the borosilicate glass containing 4wt% Na_2O and diameter 2mm. We used the reagents which were $NaNO_3$, RuO_2 powder, the nitric acid nitrosyl ruthenium (III) solution. We added the glass beads and reagents into the alumina crucible and melted them in the electric furnace. After cooling and crushing the glass samples, we put 1.5g of them on the alumina combustion board and solidified them on 800^{o}C and retention time 1h. We used these samples for the fluidity examinations.

TABLE IV. The conditions of glass samples making

Sample No.	1	2	3	4
Glass beads	Base	Base	Base	Base
Ru type [b)]	n-Ru	RuO_2	n-Ru	RuO_2
RuO_2(wt%)	0.67	0.67	10	10
Na_2O(wt%)	10	10	10	10
Temperature(^oC)	1150	1150	1150	1150
Retention time(h)	4	4	4	4

[b] n-Ru: nitric acid nitrosyl ruthenium (III) solution, RuO_2:RuO_2 powder

Fig. 5 shows the samples which were installed in the electric furnace before the fluidity examination. And TABLE V. and Fig. 6(a) – (h) show the examination conditions and results.

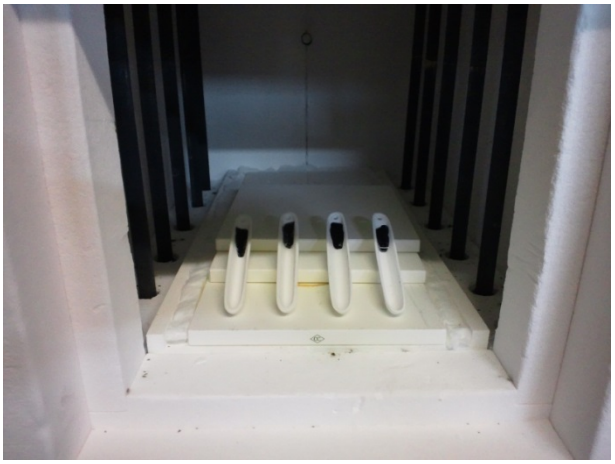

Fig. 5 The sample before the fluidity examination

TABLE V. The examination conditions and results

Sample No.	1	2	3	4
Ru type [c)]	n-Ru	RuO_2	n-Ru	RuO_2
RuO_2(wt%)	0.67	0.67	10	10
Temperature(^oC)	1000	1000	1000	1000
Inclination angle(^{o})	15	15	15	15
Retention time(min)	15	15	30	30
Flow distance(mm)	53	50	34	36

[c] n-Ru: nitric acid nitrosyl ruthenium (III) solution, RuO_2:RuO_2 powder

The influence of the RuO_2 concentration for the glass fluidity was remarkable (when RuO_2 concentration rose, fluidity decreased). But we could not find the influence of the additional ruthenium type for the glass fluidity. Because the quantity of the formed needle shape ruthenium particles might be very low in retention time 4h for glass samples making, the difference of the glass fluidity might not appear. Therefore we made the glass samples with retention time 40h and carried out the examinations about these samples.

Fig. 6(a) Sample No.1 before the exam (Nitric acid nitrosyl Ru, RuO_2 0.67wt%)

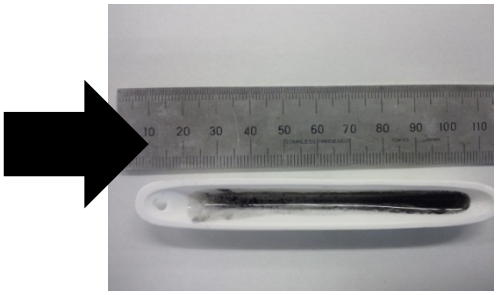

Fig. 6(b) Sample No.1 after the exam (Nitric acid nitrosyl Ru, RuO_2 0.67wt%)

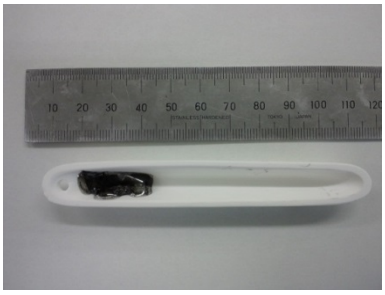

Fig. 6(c) Sample No.2 before the exam (RuO_2, RuO_2 0.67wt%)

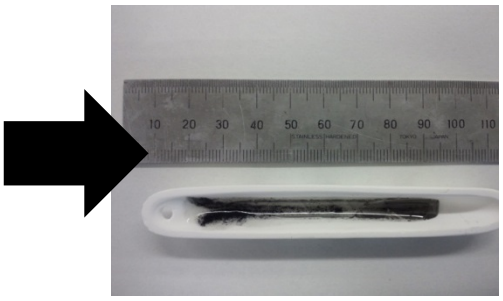

Fig. 6(d) Sample No.2 after the exam (RuO_2, RuO_2 0.67wt%)

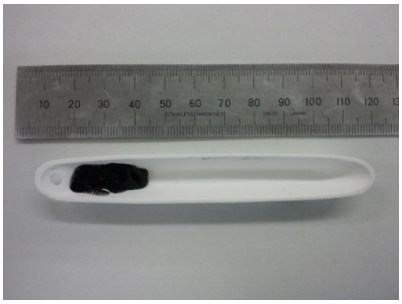

Fig. 6(e) Sample No.3 before the exam (Nitric acid nitrosyl Ru, RuO_2 10wt%)

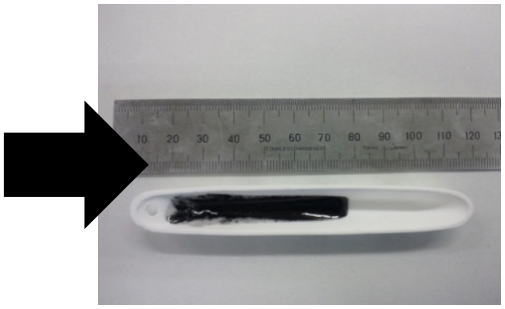

Fig. 6(f) Sample No.3 after the exam (Nitric acid nitrosyl Ru, RuO_2 10wt%)

Fig. 6(g) Sample No.4 before the exam (RuO_2, RuO_2 10wt%)

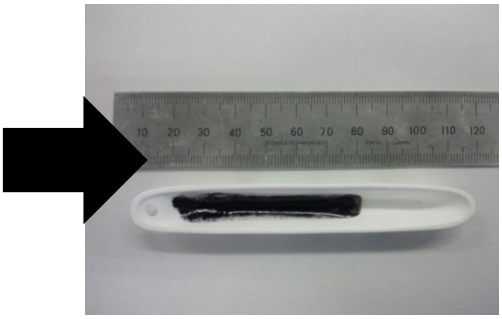

Fig. 6(h) Sample No.4 after the exam (RuO_2, RuO_2 10wt%)

TABLE VI. shows the conditions of glass samples making. The glass beads were the borosilicate glass containing 4wt% Na_2O and diameter 2mm. We used the reagents which were $NaNO_3$, RuO_2 powder, the nitric acid nitrosyl ruthenium (III) solution. We added the glass beads and reagents into the alumina crucible and melted them in the electric furnace. After cooling and crushing the glass samples, we put 1.5g of them on the alumina combustion board and solidified them on 800°C and retention time 1h. We used these samples for the fluidity examinations.

TABLE VI. The conditions of glass samples making

Sample No.	5	6	7
Glass beads	Base	Base	Base
Ru type [d)]	n-Ru	n-Ru	RuO_2
RuO_2(wt%)	0.67	10	10
Na_2O(wt%)	10	10	10
Temperature(°C)	1150	1150	1150
Retention time(h)	40	40	40

[d] n-Ru: nitric acid nitrosyl ruthenium (III) solution, RuO_2:RuO_2 powder

TABLE VII. and Fig. 7(a) – (f) show the examination conditions and results.
With the glass which we made for 1,150 °C 40h, the difference of the flow distances by the origin of the ruthenium was remarkable (the glass of the nitric acid nitrosyl ruthenium (III) adding which generated the needle shape ruthenium particles was inferior in the fluidity). In addition, the flow distance of the glass of making with 1150°C 40h shortened in comparison with the result of the 1150°C 4h in the same

ruthenium addition type and ruthenium concentration. For this reason, it may be estimated that the size of the ruthenium particles and the quantity of the needle shape ruthenium particles increased. Fig. 8 shows the result of the optical microscope observation for the sample No.6. The needle shape ruthenium particles existed in the sample No.6.

TABLE VII. The examination conditions and results

Sample No.	5	6	7
Ru type [e)]	n-Ru	n-Ru	RuO_2
RuO_2(wt%)	0.67	10	10
Temperature(^oC)	1000	1000	1000
Inclination angle(^{o})	15	15	15
Retention time(min)	15	30	30
Flow distance(mm)	15	15	22

[e] n-Ru: nitric acid nitrosyl ruthenium (III) solution, RuO_2:RuO_2 powder

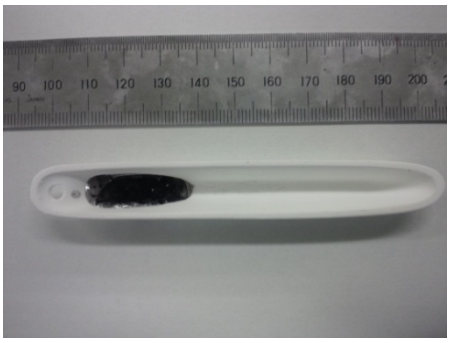

Fig. 7(a) Sample No.5 before the exam (Nitric acid nitrosyl Ru, RuO_2 0.67wt%, 40h)

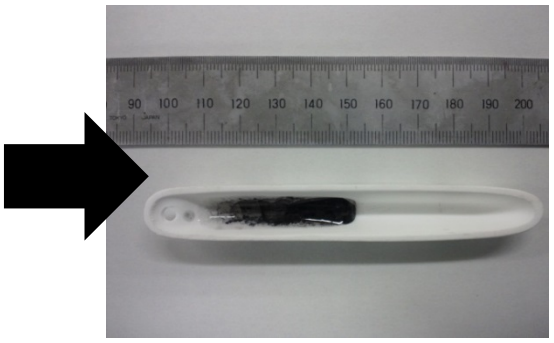

Fig. 7(b) Sample No.5 after the exam (Nitric acid nitrosyl Ru, RuO_2 0.67wt%, 40h)

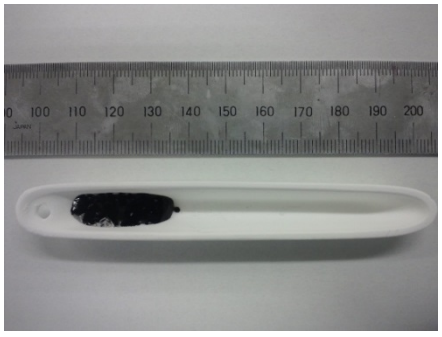

Fig. 7(c) Sample No.6 before the exam

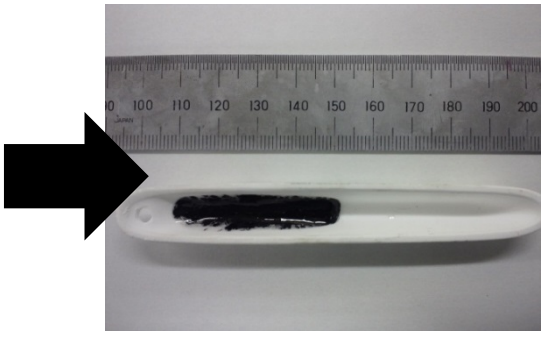

Fig. 7(d) Sample No.6 after the exam

(Nitric acid nitrosyl Ru, RuO_2 10wt%, 40h)

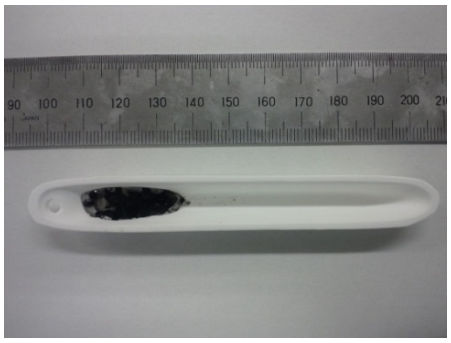

Fig. 7(e) Sample No.7 before the exam (RuO_2, RuO_2 10wt%, 40h)

(Nitric acid nitrosyl Ru, RuO_2 10wt%, 40h)

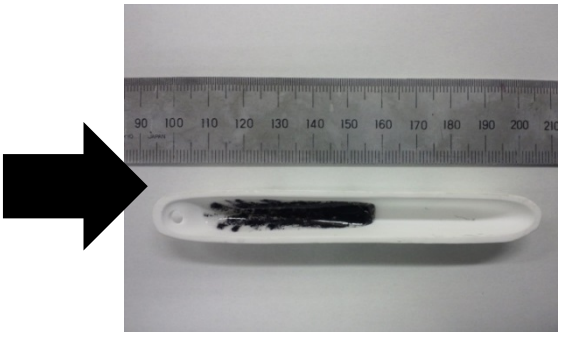

Fig. 7(f) Sample No.7 after the exam (RuO_2, RuO_2 10wt%, 40h)

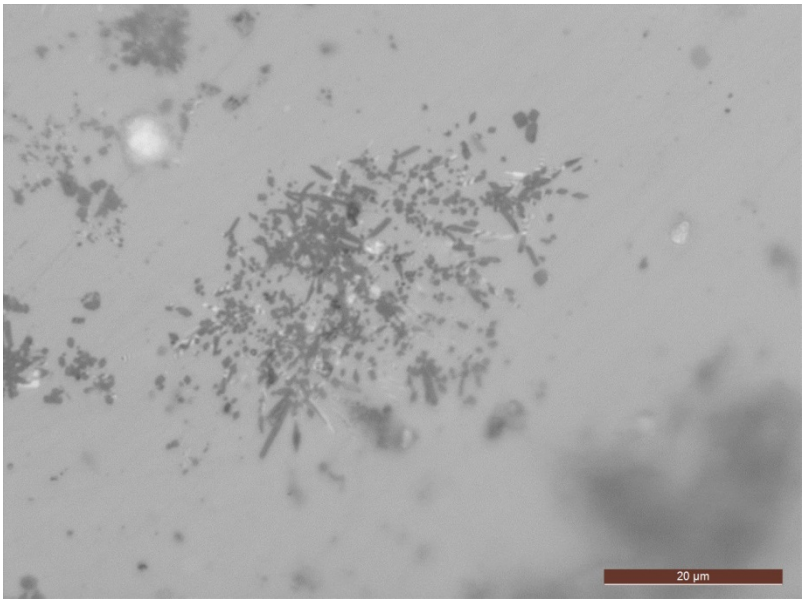

Fig. 8 The photo of the needle shape ruthenium particles (Sample No.6 by the optical microscope observation))

DISCUSSION

The needle shape ruthenium particles were formed from the ruthenium derived from the nitric acid nitrosyl ruthenium, but not formed from the ruthenium derived from the RuO_2. The ruthenium derived from the nitric acid nitrosyl ruthenium dissolves in the molten glass, but the ruthenium derived from the RuO_2 is suspended in the molten glass because its solubility for the molten glass is extremely low. Therefore it is necessary for the generation of the needle shape ruthenium particles that the

ruthenium once dissolves in the molten glass. The chemical form of the ruthenium dissolution in the molten glass might be Na_3RuO_4 [5]. If the temperature of the molten glass increases, the number and size of the needle shape ruthenium particles may swell because the Na_3RuO_4 solubility rises. But it did not happen in this study and we could not find the cause about this reason in this study. We estimate that the generation and growth of the needle shape ruthenium particles are influenced by the retention time as well as the temperature of the molten glass and the Na_3RuO_4 solubility. But we do not understand which most affect the generation and growth of the needle shape ruthenium particles in the retention time, temperature of the molten glass and the Na_3RuO_4 solubility

About the glass fluidity, the glass containing the ruthenium derived from the nitric acid nitrosyl ruthenium is inferior to the glass containing the ruthenium derived from the RuO_2 by the result of the glass fluidity examinations. We estimate that the reason of these results may be the needle shape ruthenium particles are spiky and harder to roll over than the grainy shape ruthenium particles in the molten glass.

CONCLUSION

The results that this study provided and the conclusions are as follows.

(1) The needle shape ruthenium particles are formed from the nitric acid nitrosyl ruthenium (III) solution, but they are not formed from the RuO_2.

(2) The needle shape ruthenium particles are formed, only the condition of the glass beads, the sodium nitrate and the nitric acid nitrosyl ruthenium (III) solution.

(3) Rh and Pd which are the noble metal elements and Mo such as the coexistence elements do not have the influence for the needle shape ruthenium particles growth.

(4)The generation temperature of the needle shape ruthenium particles is approximately 800 ^{0}C.

(5)The retention time in melting affects for the generation of the needle shape ruthenium particles, but the cooling rate does not influence them.

(6) The glass which adds the ruthenium with the nitric acid nitrosyl ruthenium (III) solution is inferior to the fluidity.

REFERENCES

1. T. Hartmann, H. Pentinghaus, The ternary system palladium–rhodium–tellurium: A Study to understand phase formation in the vitrification process of high-level waste concentrates (HLWC), Journal of Nuclear Materials, 422, (2012), 124-130
2. R. Pflieger, L. Lefebvre, Behaviour of ruthenium dioxide particles in borosilicate glasses and melts, J. Nuclear Materials,355, (2009), 221-227
3. Y. Enokida, K. Sawada, K. Uruga, Crystallization of Ruthenium Dioxide during Vitrification of HLW, and its Effect on Leachability of the Glass, WM2009 Conference, 9032, (2009)
4. C.Krause, B. Luckscheiter, Properties and behavior of the platinum group metals in the glass resulying from the vitrification of simulated nuclear fuel reprocessing waste, J. Mater. Res., Vol6, No12, (1991), 2535-2546
5. Y. Enokida, K. Sawada, T. Shimada, D. Hirabayashi, Formation Mechanisms of the Needle-shaped Crystals of Ruthenium Dioxide during Vitrification of Nitric Acid Solution Containing Nitrosyl Ruthenium Nitrate, WM 2011 Conference, 11265, (2011)