A Simple and Fast Procedure for Dissolution of An Oxide Fuel Fragment to Extract Its Retained Fission Gases†

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A fast and simple dissolution procedure using a commercially available electrode furnace has been developed to extract the retained fission gases in an oxide fuel fragment. A commercial hydrogen analyzer equipped with an electrode furnace was applied in the fusion experiments of a fresh, non-irradiated oxide fuel fragment. Approximately 0.1-0.2 g fragments of an oxide fuel were fused with a single flux and/or multiple fluxes such as tin, nickel, or copper, while varying the fusion current and time. After fusion of the oxide fuel fragment, the melting state of the resultant melt was investigated using an electron microscope, an X-ray diffraction spectrometer (XRD) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES). A fresh UO_2 fragment (*ca.* 0.1 g) for a pressurized water reactor (PWR) was melted completely with *ca.* 1 g of a metallic flux, such as tin or nickel at a fusion current of 800 A and a fusion time of 50 s as an uranium-metal (flux) alloy. However, complete fusion of a simulated spent fuel (SIMFUEL) fragment with a burnup of 60 GWd/tU requires a higher fusion current, 850 A and a longer fusion time, 120 s and simultaneous double metal fluxing, using tin and nickel. Since the physicochemical properties of SIMFUEL and spent oxide fuel are very similar, the fusion conditions may be applicable for fusion of the latter as well.

Key Words: Electrode furnace, UO_2, Simulated spent fuel, Fusion.

INTRODUCTION

During the neutron activation of an oxide nuclear fuel, the fission gases such as krypton and xenon account for more than 25 % of the total fission products. Most of the generated fission gases are retained in the fuel matrix. The maximum quantity of the retained fission gas in UO_2 is 0.012 gas atoms/U atom, corresponding to 1.0 cc/g UO_2, STP, at temperatures below 1250 K, but the quantity decreases at higher temperatures, *e.g.* 0.002 gas atoms/U atom at 2000 K, corresponding to 0.2 cm³/g UO_2, STP[1].

The retained fission gas has a strong influence upon the thermal and mechanical properties of the reactor fuel. Therefore, analytical data on the amount and isotopic distribution of a retained fission gas in an irradiated nuclear fuel are needed to characterize the irradiation behaviour of a nuclear fuel and are very useful for the theoretical analysis and computer code modeling of the behaviour of a fuel pin[2-4].

First of all an oxide fuel fragment should be dissolved using a method that can extracts completely the retained fission gases, krypton and xenon. Methods for dissolution of an oxide nuclear fuel include a chemical reaction using mineral acids, formation of a molten salt by $NaNO_3$ or $KHSO_4$, laser extraction, high temperature annealing or a fusion, *etc.*[2-9]. Chemical dissolution procedures are time consuming, laborious and produce corrosive by-product gases, NOx, SOx, which must be removed from the extracted gas[2,3]. Furthermore, the apparatus for this method is made of glass, which is weak and difficult to control remotely. The laser system is also composed of very delicate precision instrumentation and requires skillful operation. The molten salt method requires exposure to high temperature for a long time (10 h at 550 ºC), to dissolve a fragment of oxide fuel and uses a large mass of sodium salt, at least a 5-fold excess over the mass of the sample and thus produces much waste after the experiment[4]. The melting point of UO_2 is about 2600-2800 ºC and thus high annealing temperature makes complete dissolution and extraction of retained gases difficult[4]. Fusion under an inert gas atmosphere has many advantages including the short time of the process, completeness of dissolution and no off-gas generation, *etc.*[7-9]. When selecting an oxide fuel dissolution method for measurement of its retained gas, the important factors to

be considered are completeness of sample dissolution and of its gas extraction.

An electrode furnace is a very powerful furnace which can heat an object up to 3000 °C within a few seconds. The inert gas fusion technique with a metallic flux using an electrode furnace has the capability to decompose an oxide nuclear fuel[7,8]. One outstanding advantage of the inert gas fusion method is that the fusion is carried out in an inert gas atmosphere and produces no by-product gases[9]. In this work, dissolution experiments of an oxide fuel fragment with various metal fluxes were conducted using an inert gas fusion method. A commercially available electrode furnace was used. The fusion current, fusion time and the quantity and/or constituents of the flux were examined to establish an optimum melting condition for a fresh, non-irradiated fragment of an oxide fuel. Two kinds of fresh oxide nuclear fuel, a fuel for a pressurized water reactor (PWR) and a simulated spent fuel (SIMFUEL)[10] which was prepared for the simulation of a high burn-up spent fuel were employed for an inert gas fusion experiment[10]. Additionally, the fusion state of the melt was evaluated using several analytical methods.

EXPERIMENTAL

Materials and an electrode furnace: A commercially available electrode furnace, a LECO EF-400 attached to a LECO RH-404 hydrogen determinator and a graphite crucible (LECO 782-720) were used for this work. The original purpose of the instrument is to measure the hydrogen content of a metal, alloy or ceramic sample. The electrode furnace is a resistive-type heating unit consisting of two large water-cooled copper electrodes, an upper electrode and a lower electrode, using a small high temperature graphite crucible. It is a powerful furnace, which can heat an object up to 3000 °C and melt a sample completely within seconds.

Two kinds of UO_2 pellets were used in the inert gas fusion experiment: a fresh sample of non-irradiated fuel of PWR type and a simulated spent fuel (SIMFUEL) which was prepared for the simulation of spent fuel with a burnup of 60 GWd/tU after 15 years cooling[10]. Table-1 shows the composition of SIMFUEL. The chemical additives simulate fission products which would be produced while irradiating an oxide fuel to 60 GWd/tU.

TABLE-1
CHEMICAL COMPOSITION OF THE SIMFUEL [Ref. 10]

Compounds	(wt %)	Compounds	(wt %)
UO_2	94.5	$BaCO_3$	0.28
Y_2O_3	0.09	MoO_3	0.61
La_2O_3	0.23	RuO_2	0.60
CeO_2	1.41	Rh_2O_3	0.06
Nd_2O_3	1.05	PdO	0.27
SrO	0.16	TeO_2	0.09
ZrO_2	0.66	–	–

Fusion of an oxide fuel fragment: A fragment (*ca.* 0.1 g) of oxide fuel was randomly selected after crushing a PWR or SIMFUEL UO_2 pellet using a small pulverizer. It was fused with an excess of a single flux or a double flux such as a tin pellet (LECO 761-739), nickel basket (LECO 502-344) or a copper chip (LECO 501-263) in a graphite crucible heated to

a high temperature by the aforementioned electrode furnace under a helium atmosphere. The fusion current and fusion time of the furnace were adjusted to establish the optimum melting condition of the oxide fuel. Also the quantity or composition of the flux were varied to convert the oxide fuel fragment to a pure metal alloy by the inert gas fusion process, leading to complete fusion of a refractory oxide.

Evaluation of melting state: To evaluate the melting state of an oxide nuclear fuel, the obtained melts were analyzed using several analytical instruments. After an inert gas fusion of an UO_2 fragment with metallic fluxes while varying the fusion conditions, the fusion current, the fusion time and the constituents of the flux, the resultant melt was carefully separated from the graphite crucible and prepared for evaluation of fusion state. The morphology and elemental composition of the melts were analyzed using an electron probe micro analyzer (EPMA, JEOL JXA 8600) and an energy dispersive X-ray spectrometer (EDS, Oxford Inka Energy). The crystallographic characteristics were obtained using an X-ray diffraction spectrometer (XRD, SIMENS D5000) as well. After finishing the non-destructive tests, the melts were dissolved using acids and the bulk chemical compositions of them were determined with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, HORIBA JOBIN YVON ACTIVA).

RESULTS AND DISCUSSION

Evaluation of non-irradiated PWR UO_2 melts: When a fragment (0.14 g) of non-irradiated PWR UO_2 underwent fusion with 1.4 g of a copper chip at a fusion current of 800 A for 50 s, a black, button-like melt was produced and readily separated from the graphite crucible. However, the electrode furnace was contaminated with a large quantity of red-coloured dust. As shown in Fig. 1, several uranium oxide phases were found on the melt, but the copper concentration of the melt was lowered due to its evaporative loss at a high fusion temperature. This outcome indicates that a PWR UO_2 fragment cannot be melted as an alloy form with a copper flux under these fusion conditions.
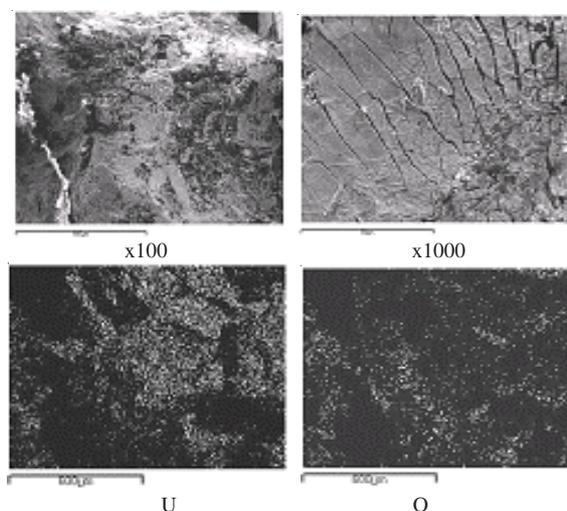

x100	x1000
U	O

Fig. 1. Secondary electron images (SEI) and elemental mapping images of a melt from fusion of a non-irradiated PWR UO_2 fragment, 0.14 g, with a copper flux, 1.40 g, at a fusion current of 800 A for 50 s

An irregular black melt was obtained by a fusion of a non-irradiated PWR UO_2 fragment, 0.103 g, with a nickel flux, 1.0 g, at a fusion current of 800 A and a fusion time of 50 s and it was attached to the inside of the graphite crucible. According to the elemental mapping of the melt by EPMA at a x1000 magnification, no residual oxide was found and uranium and nickel were distributed as displayed in Fig. 2. The average composition of the melt was determined to be UNi_{43}.
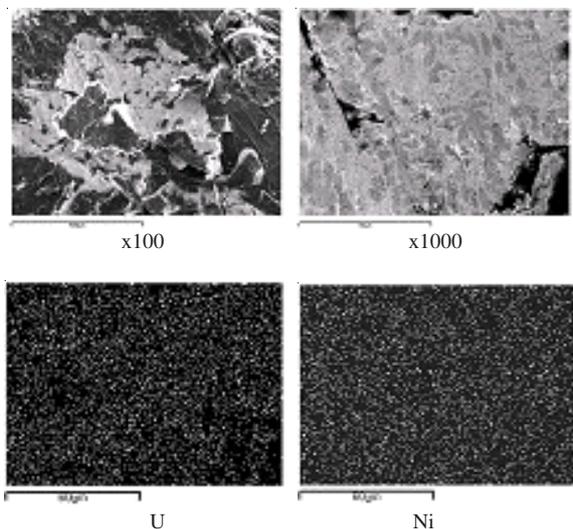

Fig. 2.   Secondary electron images(SEI) and elemental mapping images of a melt from a fusion of a non-irradiated PWR UO_2 fragment, 0.103 g with a nickel flux, 1.0 g, at a fusion current 800 A for 50 s

As shown in Fig. 3, a melt from the fusion of a non-irradiated PWR UO_2 fragment with a nickel flux at a fusion current of 800 A and a fusion time of 50 s is crystalline. However, it is difficult to identify an exact alloy phase because no peaks could be clearly assigned from the XRD library file. It is likely that the fusion conditions are good for a complete dissolution of a non-irradiated UO_2 fragment as an alloy form because no oxides were found by EPMA.
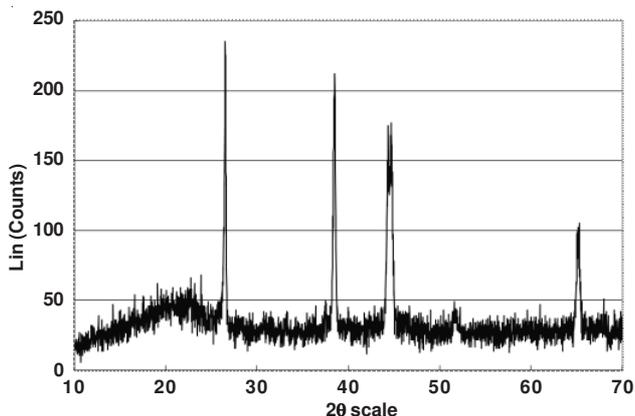

Fig. 3.   X-ray diffraction pattern of a melt of a non-irradiated PWR UO_2 fragment fused with a nickel flux at a fusion current of 800 A for 50 s

Fusion of a PWR UO_2 fragment (*ca.* 0.087 g) with 1.0 g of tin flux at 800 A for 50 s produced a melt that was a shiny, silver-coloured bead and it was clearly separated from the graphite crucible. The secondary electron image (SEI) at x100

magnification and at x1000 magnification and the elemental mapping images of tin and uranium appear in Fig. 4. No oxide phase was found on the melt surface.
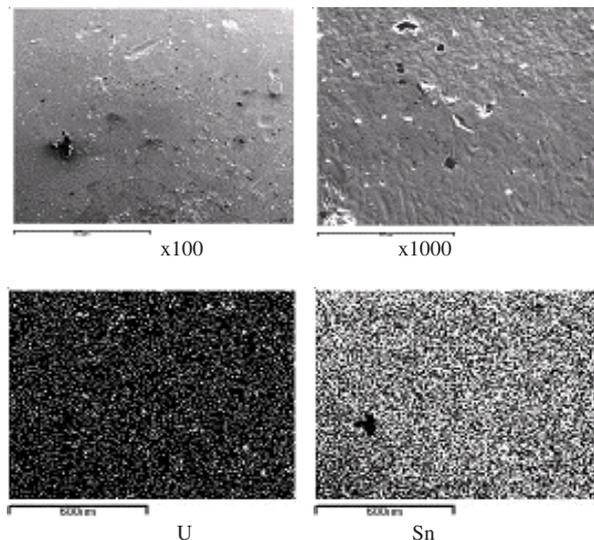

Fig. 4.   Secondary electron images (SEI) and elemental mapping images of a melt from fusion of a fresh, non-irradiated, PWR UO_2 fragment, 0.087 g, with a tin flux, 1.0 g, prepared at a fusion current of 800 A for 50 s

When the melt was examined at x4000 magnification, a very small uranium oxide phase in a tin phase, *ca.* 10 µm in size, was found (Fig. 5). This small uranium oxide phase had no typical morphology and grain size of a UO_2 pellet. Therefore, it is likely that the non-irradiated UO_2 fragment was almost completely converted to a metallic alloy form under these fusion conditions.
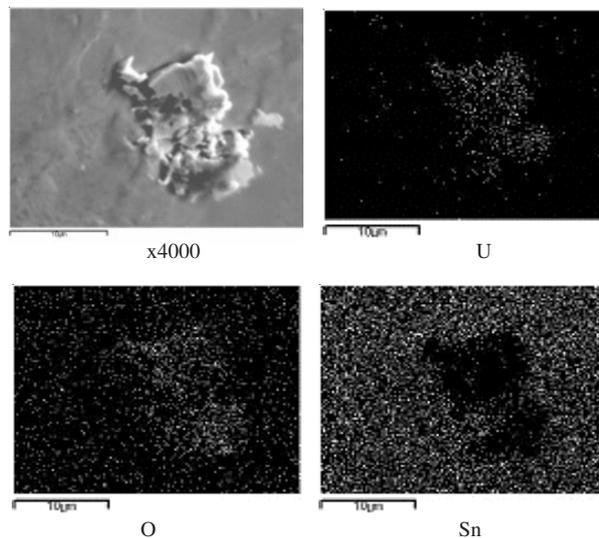

Fig. 5.   Secondary electron images (SEI) and elemental mapping images of a very small oxide phase dissolved in an alloy phase from a fusion of a non-irradiated PWR UO_2 fragment, 0.087 g, with a tin flux, 1.0 g, at a fusion current 800 A for 50 s

The melting temperature of UO_2 is about 2600-2800 ºC while that of the corresponding carbide[7] is only about 2350 ºC. According to the manufacturer's provided data, the estimated crucible temperature is about 2400 ± 200 ºC at a fusion

current of 800 A. As shown in Fig. 6, the melt from the fusion of non-irradiated PWR UO_2 fragment with the tin flux at a fusion current of 800 A is crystalline. Even at very high magnification, x4000, uranium oxide phase was rarely found on the melt by EPMA. Thus, the oxide fuel was melted completely and converted to a metal alloy form under these fusion conditions. However, no exact U alloy phase of the melt could be assigned by the XRD analysis results because the acquired XRD peaks did not exactly match the library data.
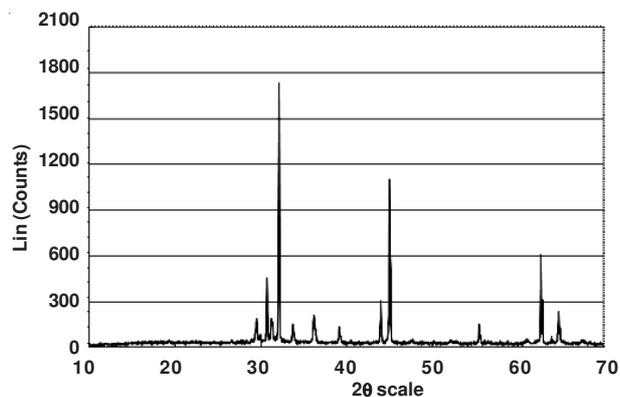

Fig. 6. X-ray diffraction pattern of a melt of a non-irradiated PWR UO_2 fragment fused with a tin flux at a fusion current 800 A for 50 s

After complete characterization of the melts prepared from the non-irradiated PWR UO_2 fragments by EPMA and XRD, we confirmed their bulk compositions by dissolving them in an acid medium and then performing a quantitative analysis by ICP-AES. The ICP-AES analysis results for the melts fused with various metallic fluxes are presented in Table-2. As shown in Table-2, the melt obtained by the fusion of UO_2 with nickel contained nearly the same compositions of the input materials for the fusion experiment, but the copper or tin contents of their respective melts were slightly lower than their input compositions, 3-4 %. Due to the low melting points of both metals, copper and tin, some of them must be evaporated during the fusion experiment.

TABLE-2
ICP-AES ANALYSIS RESULTS OF THE MELTS OF THE
NON-IRRADIATED PWR UO_2 FRAGMENTS FUSED
WITH CERTAIN METALLIC FLUXES

Starting compositions of the fusion experiments (g)		Compositions of the melt after fusion of PWR UO_2 with metallic flux (wt %)	
UO_2	Ni	U	Ni
0.103	1.0	9.5	90
UO_2	Cu	U	Cu
0.144	1.4	9.2	87
UO_2	Sn	U	Sn
0.087	1.0	8.2	89

Evaluation of the SIMFUEL UO_2 melts: After a fusion of *ca.* 0.11 g of a SIMFUEL UO_2 fragment with 1 g of a tin flux at a fusion current of 800 A and a fusion time of 50 s, a melt of a silver-coloured bead was obtained and it was clearly separated from the graphite crucible. However, the appearance of the melt was less shiny compared to that of the non-irradiated PWR UO_2 pellet fused with a tin flux at the same fusion conditions. This result may reflect the difference in

composition between the two samples. The SIMFUEL is composed of many chemical compounds that simulate the composition of spent fuel[10].

No oxide was found at the upper side of the melt (Fig. 7). Also molybdenum, which was added to simulate the fission product of a spent fuel, was found on the melt surface. Considering only the EPMA analysis results of the upper side of the melt, the fusion conditions seemed to be appropriate for a complete melting of the SIMFUEL UO_2.

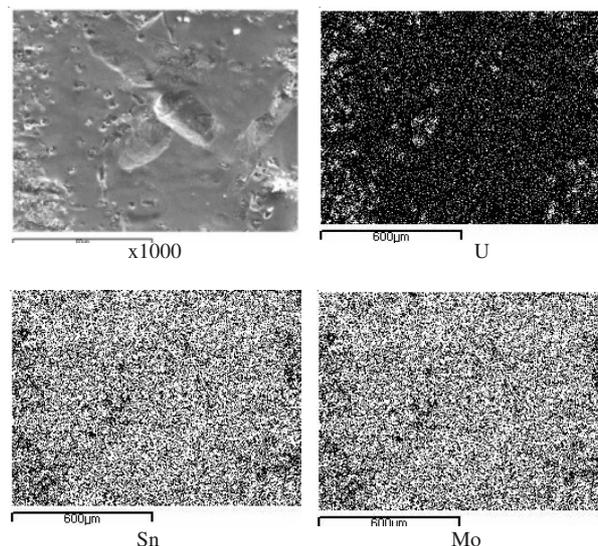
Fig. 7. Secondary electron images (SEI) and elemental mapping images of a melt of a SIMFUEL UO_2 fragment, 0.11 g, fused with a tin flux, 1.0 g, at a fusion current of 800 A for 50 s

However, an examination of the other side of the melt, in contact with the bottom of the graphite crucible, showed many uranium oxide phases embedded in the tin alloy phase (Fig. 8). The grain size of the oxide phase also became smaller after fusion of the SIMFUEL[10], indicating that although the SIMFUEL UO_2 cannot dissolve as a pure alloy form under these fusion conditions, it still underwent a melting process as
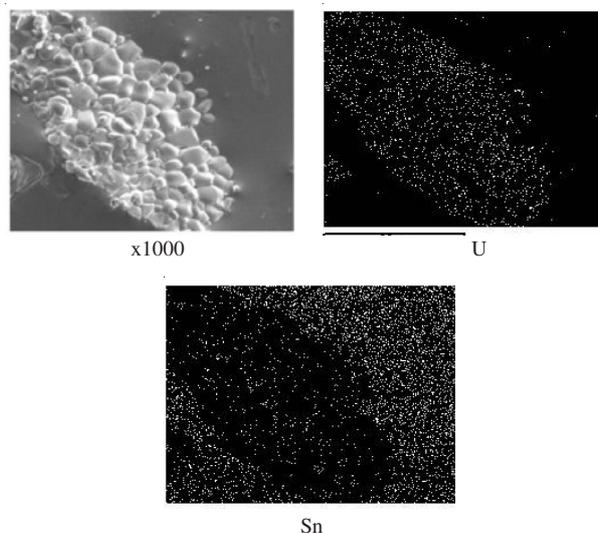

Fig. 8. Secondary electron image (SEI) and elemental mapping images of a melt of a SIMFUEL UO_2 fragment, 0.11 g, fused with a tin flux, 1.0 g, at a fusion current of 800 A for 50 s

an oxide phase. Based on the experimental results, it is likely that a SIMFUEL UO_2 structure became more resistant to an inert gas fusion because the UO_2 had undergone the sintering process twice during its preparation[10].

A melt obtained by fusion of a SIMFUEL UO_2 fragment, 0.096 g, with a copper flux, 1.0 g, at a fusion current of 800 A and a fusion time of 50 s showed a separation phase of an oxide and a metal at a x1000 magnification of the SEI (Fig. 9). The melt also showed that the grain size of the oxide phase had contracted as compared to the original SIMFUEL prior to the fusion experiment[10], indicating that the SIMFUEL UO_2 could not be completely dissolved as a pure alloy form under the given fusion conditions, but it could still undergo a melting process as an oxide phase.
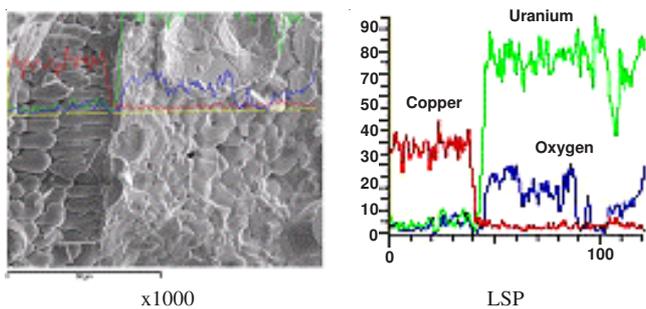

x1000   LSP

Fig. 9.   Secondary electron images (SEI) and line scan profiles (LSP) of a melt of a SIMFUEL UO_2 fragment, 0.096 g, fused with a copper flux, 1 g, at a fusion current of 800 A for 50 s

After fusion of a SIMFUEL UO_2 fragment (0.13 g) with double fluxing agents, a tin flux (1.0 g) and a nickel flux (1.0 g), at a fusion current of 750 A and a fusion time of 50 s, a black, button-shaped melt was produced and it was separated from the graphite crucible. Many large particles of uranium oxide, *ca.* 1 mm, were embedded in a nickel and tin alloy layer (Fig. 10). In spite of using double metal fluxes, the oxide fuel did not melt as an alloy form at the specified fusion current and time. Evidently the fusion current, 750 A, was too low to fuse a fragment of SIMFUEL as an alloy form containing no oxide phase and furthermore, no double fluxing effect could be obtained at such a low fusion current.

x100   U
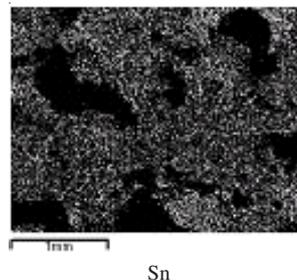
O   Ni

Sn

Fig. 10. Secondary electron images (SEI) and elemental mapping images of a melt of a SIMFUEL UO_2 fragment, 0.13 g, fused with a tin flux, 1.0 g and a nickel flux, 1.0 g, at a fusion current of 750 A for 50 s

The microstructure of the SIMFUEL was similar to that of a sintered UO_2 pellet with polygonal equiaxed grains[10]. However, as discussed, the shapes and sizes of the grains of the uranium oxide-rich phases of the melts were different from their original structure. Although the uranium oxide of the SIMFUEL was not completely converted with the metals and/or alloys, the oxygen of the UO_2 phases partly escaped as CO through a reaction with the carbon from the graphite crucible under the inert gas atmosphere at high temperature, thus resulting in an oxygen-deficient state of UO_{2-x}[8,9].

As presented in Fig. 11, a melt of a 0.14 g SIMFUEL UO_2 fragment fused with a nickel flux, 1 g, at a fusion current of 900 A and a fusion time of 100 s showed a good alloy appearance and many U-Ni island-like bubbles were found on the nickel layer. No oxide phase was found on any areas of the melt, suggesting that the SIMFUEL UO_2 was completely converted to a U-Ni alloy form.

However, the melt of a SIMFUEL UO_2 fragment fused with a nickel flux at a fusion current of 900 A was solidified at the upper position of the graphite crucible due to the extremely high fusion current. This event may cause damage to the electrodes if the melt comes into contact with the electrode surfaces during the fusing of an oxide fuel fragment at such high fusion current. Therefore, the application of such a high fusion current with an excessive amount of metal flux to fuse an oxide fuel should be avoided.
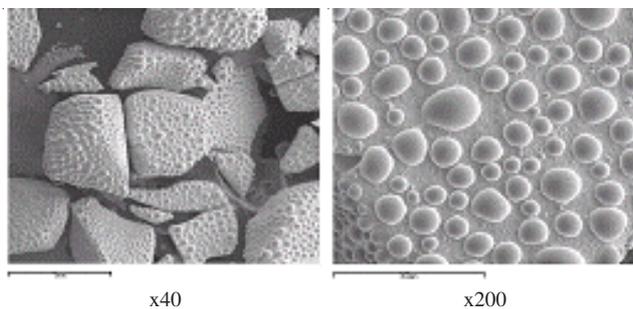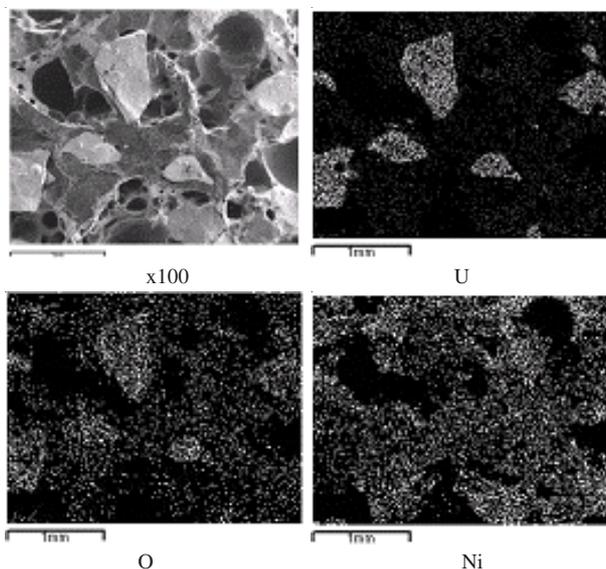

x40   x200

Fig. 11. Secondary electron images (SEI) of a melt of a SIMFUEL UO_2 fragment, 0.14 g, fused with a nickel flux, 1.0 g, at a fusion current of 900 A for 100 s

After a fusion of a SIMFUEL UO_2 fragment, *ca.* 0.100 g, with a nickel flux, 1 g and a tin flux, 1 g, at a fusion current of 850 A and a fusion time of 120 s, a black, button-shaped melt was produced and it was readily separated from the graphite crucible. As displayed in Fig. 12, no oxide phase was found

over all areas of the melt at x1000 magnification by EPMA. Due to a higher fusion current and a longer fusion time using double metal fluxes, any uranium oxide phase would have been completely converted to a uranium alloy, U-Ni-Sn. We confirmed that there was no danger of damaging the electrodes under the given fusion conditions. A fused melt was present at the bottom of the graphite crucible and was not attached to the crucible.
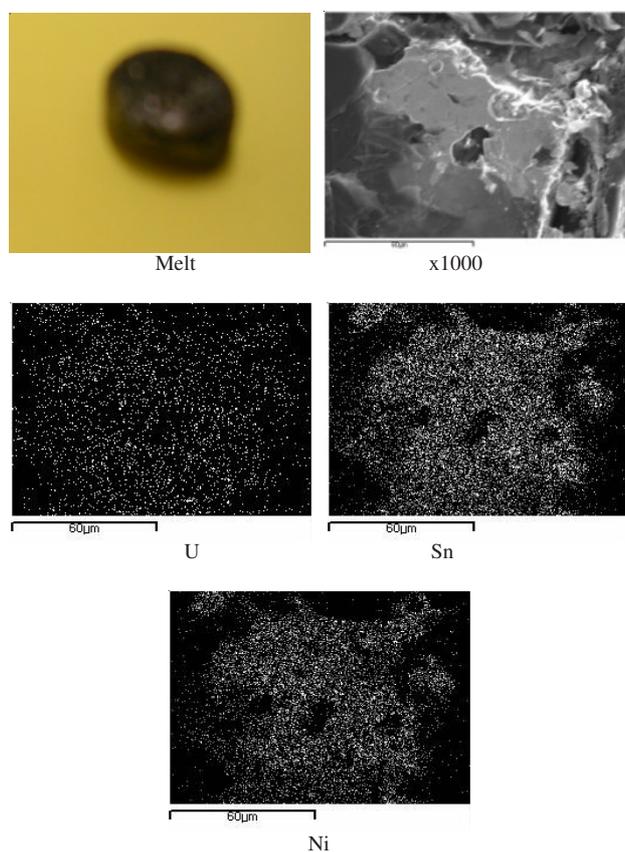

Melt   x1000

U   Sn

Ni

Fig. 12. A photograph, secondary electron images (SEI) and elemental mapping images of a melt of a SIMFUEL UO_2 fragment, 0.1 g, fused with a nickel flux, 1.0 g and a tin flux, 1.0 g, at a fusion current of 850 A for 120 s

According to the quantitative analysis results over the melt surface using EDS, the average compositions of the melt were similar to the initial value, $USn_{20}Ni_{44}$, but the standard deviation of the uranium measurement was very high. This outcome showed that the melt was not composed of a pure metal or alloy form, but mixtures of metals and/or alloys, an intermetallic form. The slightly lower tin concentration of the melt compared to the initial material may be due to its high vapour pressure.

As shown in Fig. 13, the XRD pattern did not show any uranium phase, but rather free nickel, free tin and nickel-tin alloy phases. The XRD pattern did not exactly matched any XRD library files. This result may reflect an inappropriate sample type, a polished small melt instead of a fine powder, the low concentration of uranium for the XRD measurement, or the fact that the melt was produced in the presence of excess metallic fluxes without any mechanical agitation during the short reaction time of 120 s.
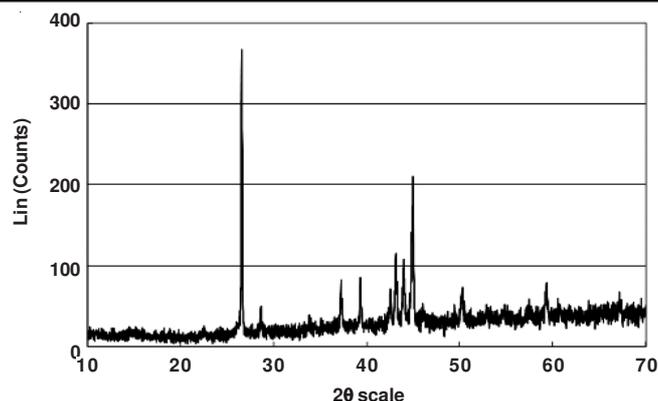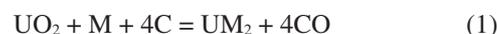

Fig. 13. X-ray diffraction pattern of a melt of a 0.100 g SIMFUEL UO_2 fragment fused with two tin pellets, 1.0 g and a nickel basket, 1.0 g, at 850 A for 120 s

The mechanisms by which the uranium oxide decomposes in a graphite crucible are not fully understood[7]. One likely chemical reaction is as follows, eqn. 1:

$$UO_2 + M + 4C = UM_2 + 4CO \qquad (1)$$

where M represents a metallic flux such as Sn, Ni, Cu.

Here the metal acts as a fluxing agent and a catalyst with reaction of carbon from the graphite crucible and oxygen from the sample and lowers the melting point of an oxide fuel. The reaction between the oxide fuel and the graphite crucible under an inert gas atmosphere at a high temperature, in the molten metal bath, converts the oxide to an alloy form. Tin is commonly used as a fluxing agent during inert gas fusion to extract hydrogen in various metals and alloys. Due to its low carbon solubility and high vapour pressure at fusion temperature, the tin acts not only to increase the fluidity of the melt but also to stir the melt and form a metal layer on the graphite crucible wall.

Tin is a better fluxing agent when alloyed with another metal such as nickel than when used alone[9]. In this work, double metallic fluxes were used to melt an oxide fuel. The use of nickel increases the oxygen activity and hinders the formation of a graphite layer on the melt, which reduces the fluidity of the melt and prevents the reduction of an oxide into CO. With respect to the thermodynamics of the fusion reaction, inert gas fusion is favoured at higher temperatures[9].

According to the EDS analysis results of the melts, the product was not a pure and/or a homogeneous alloy as chemical reaction eqn. 1. Rather, it was a mixture of alloys and/or metals, an intermetallic alloy. Previous reports demonstrated that oxides fused as a mixture of alloys and metals in intermetallic forms rather than as a homogeneous alloy form under inert gas fusion at short reaction times and in the absence of mechanical agitation during fusing[9]. In this work, a fragment of uranium oxide was fused with excess metal fluxes, nickel and tin, in a graphite crucible under a helium atmosphere at 850 A, which corresponds to about 2600 ± 200 ℃ based on the manufacturer's provided data. Since krypton and xenon are chemically inert gases and they are rarely soluble in a uranium oxide matrix, they are retained mostly as precipitates and/or bubbles in an irradiated oxide fuel. Therefore, the retained krypton and xenon in an oxide fuel would be easily extracted by inert gas fusion with excess metallic fluxes.

Conclusion

A fresh non-irradiated PWR UO_2 fragment (*ca.* 0.1 g) was melted completely with about 1.0 g of a metallic flux, a single flux, such as tin or nickel at a fusion current of 800 A and a fusion time of 50 s as a uranium-metal(flux)-alloy. These same fusion conditions did not convert a SIMFUEL UO_2 fragment to a pure uranium metal alloy. According to the present experimental results, a higher fusion current, 850 A and a longer fusion time, 120 s and a simultaneous double metal fluxing with tin and nickel are required for a complete fusion of a SIMFUEL UO_2 fragment by an inert gas fusion method. However, too high a fusion current, *e.g.* 900 A, may damage the electrode furnace by the contact of a melt with the upper and lower electrodes.

REFERENCES

1. T. Jonsson, STUDSVIK/K4-80/83 (1980).
2. W. Jennsion and M.L. Clark, TRG Report 1382(D) (1966).
3. A. Takeo and O. Mamoru, JAERI-M-91-010 (1991).
4. M. Mogensen, *Int. J. Mass Spect. Ion Phys.*, **48**, 389 (1983).
5. D.G. Graczyk, ANL-79-86 (1979).
6. Y. Hatakeyama, K. Sudou and H. Kanazawa, JAERI-Tech2004-033 (2004).
7. D.L. Baldwin, HEDL-7004 (1981).
8. T. Hiyama, T. Wada and T. Takahashi, *Donen-Giho*, **91**, 105 (1994).
9. M. Laben, L. Melnick, L. Lewis and D. Ben, Determination of Gaseous Elements in Metals, A Wiley-Interscience, New York (1974).
10. G.I. Park, J.W. Lee, J.W. Lee, Y.W. Lee and K.C. Song, *Nucl. Eng. Technol.*, **40**, 191 (2008).