Inert Gas Fusion of An Irradiated Oxide Fuel to Determine Its Retained Fission Gas Compositions†

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A clean and simple dissolution procedure involving an inert gas fusion without using mineral acids was developed in order to completely fuse an irradiated oxide fuel as an alloy form and thus quantitatively extract its retained gases. A commercial gaseous element analyzer for metals and alloys equipped with a small but powerful impulse furnace was employed for the fusion experiments. After fusion of an irradiated oxide fuel, the melt was analyzed using a special electron probe micro analyzer (EPMA), high-energy γ-ray shielded, to evaluate the melting state. It was found that a 0.049 g fragment of an irradiated oxide fuel, *ca.* 55 GWd/tU, was clearly melted with 1 g of tin and 1 g of nickel at 850 A for 2 min under a helium atmosphere. The electron micro analysis revealed that the resultant melt under the fusion conditions contained no oxygen and it was assumed to be a kind of an intermetallic alloy form, a mixture of U-Sn-Ni. Recovery test results through the gas flow paths of the fusion instrument, which was equipped with several reagent columns for gas purification, showed that 96-98 % of the krypton and xenon was recovered during a 2 min collection period after injection. No residual gas was retained in the melt after the first fusion of a fragment of an irradiated oxide fuel at the established fusion conditions. Less than 10 min is sufficient to complete the analysis of retained fission gases in a spent fuel sample, including their extraction and measurement.

Key Words: Inert gas fusion, Retained fission gas, Spent fuel.

INTRODUCTION

Among fission products which are produced by neutron activation of an oxide fuel, the combined yield of krypton and xenon is the most abundant. These elements are mostly retained inside the oxide fuel structure and account for more than 90 % of total fission gas generation (FGG). Thus, their presence changes the original physicochemical properties of the fuel and may cause deterioration of fuel performance. Meanwhile, some of the total FGG escape from the oxide fuel structure during its irradiation and are released into the free volume of the fuel rod, the plenum and thus increase internal pressure of the rod. Such fission gas behaviours are regarded as important phenomena in the safety of the fuel/fuel rod and also for the fidelity[1-3]. Therefore, measurements for fission gases, as released gas in a spent fuel rod and as retained gas in an irradiated oxide fuel, being conducted at most post irradiation examination facilities of atomic energy research institutes to evaluate and review the irradiation status of the spent fuel and rod[1-7].

Information about generation of fission gases during irradiation of an oxide fuel can be acquired through an experimental method and/or by a computer code calculation[1-8]. The yields of fission gases are severely affected by various parameters such as initial [235]U concentration and burn-up of the fuel, operation history of the reactor and so on. Therefore, a review of the calculation results of FGG is required by using a computer code with an experimentally determined value. It is possible to get a value for FGG by combining the experimental determination of the amount of fractional fission gas release (FFGR) and the amount of retained fission gas in a spent fuel rod[2,3]. More than 90 % of the generated fission gas during irradiation of an oxide fuel under normal operation of an atomic power plant is retained inside the fuel structure and the FFGR does not increase linearly as burn-up proceeds[1-3]. Consequently, to acquire FFG data that more closely reflects the real value, the development of a more accurate and reproducible measurement of retained fission gases in spent fuel is required.

For a quantitative determination of retained gas concentration, *e.g.*, krypton and xenon, in an irradiated oxide fuel,

the fuel must first be dissolved completely and at the same time, its retained gases must be extracted quantitatively over a fixed period of time. Various methodologies have been reported for the dissolution of an oxide fuel in order to extract its retained gas[1-7]. Among them, an inert gas fusion method commonly applied to a commercial gaseous element analyzer for determinations of hydrogen, nitrogen and/or oxygen in metals/alloys and ceramics has proved to be a rapid, simple and quantitative procedure[7,8]. For irradiated specimens, the development of a simpler and faster analytical method for determination of the chemical composition of the samples is desirable.

The present work describes the development of a simple and rapid analytical procedure to quantitatively extract a small volume of the retained fission gases, krypton and xenon, in a fragment of spent fuel and to quantify their concentrations. A commercial hydrogen analyzer, which was installed inside a hot-cell for measurement of hydrogen content in irradiated specimens such as zircaloy clad or other spent fuel, was employed as a fusion instrument of an irradiated oxide fuel. We conducted a series of recovery tests using standard gas mixtures to determine the retention behaviours of the reagent columns, which were attached in the gas flow paths of the fusion instrument for gas purification and to determine the optimum collection time for the extracted gases. A fragment of a high burn-up oxide fuel was fused with metallic fluxes at a high fusion current for a specified time under an inert gas atmosphere to determine the composition of the retained fission gases as well as their isotopic distributions. After fusion of an oxide fuel, the fusion state of the melt was evaluated using a special electron probe micro analyzer (EPMA), a high-energy γ-ray shielded instrument. Any retention of residual gas in the first melt was investigated by a second fusion of the melt. The experimentally obtained FGG was reviewed with respect to that of a code calculation.

EXPERIMENTAL

Description of a fusion instrument and facility: In our laboratory, a radiation shielded commercial hydrogen analyzer (LECO RH-600) has been employed for measurement of hydrogen content in a radioactive specimen such as an irradiated zircalloy clad or spent fuel. The instrument was modified to allow its easy installation inside an acryl glove box or a hot cell. Fig. 1 shows the radiation shielded facility for handling of an irradiated sample. The main body of the instrument (Fig. 1.A), which works as the control module for the hydrogen

analyzer operation, was installed inside an acryl glove box, which is sealed tightly and maintained under negative pressure but no high-energy γ-ray shielded from a radioactive specimen[9].

The furnace module (LECO EF-500), which functions as a fusion furnace for a highly radioactive specimen, was set up inside a hot cell which was constructed by casting 70 mm thick lead into a steel frame, which can handle a highly radioactive specimen remotely. The impulse furnace is a resistive-type heating unit consisting of two large water-cooled copper electrodes, an upper electrode and a lower electrode, used with a small graphite crucible. It is a powerful furnace, which can heat an object up to 3000 °C and melt it completely within seconds[7,8,10].
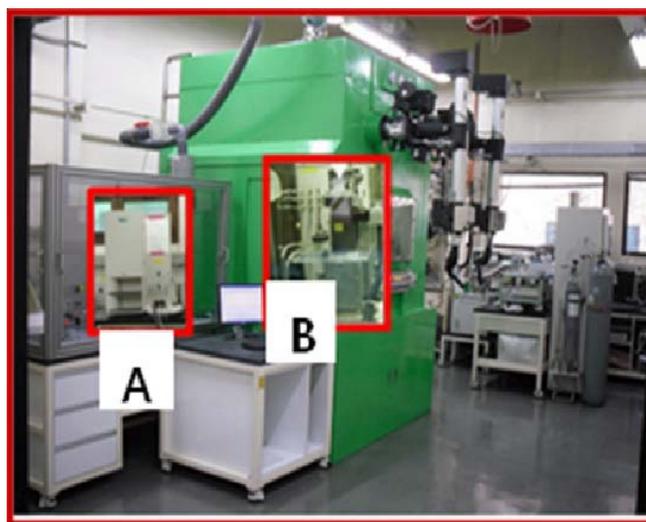

Fig. 1.   Radiation shielded instruments and facility for an irradiated sample. A: main body of hydrogen analyzer; B: impulse furnace

Recovery tests using a standard gas mixture: We conducted recovery tests using a standard gas mixture of 10 % krypton and 10 % xenon in helium balance to investigate any retention of krypton and xenon by the reagent columns for the carrier flow and the measure flow of the hydrogen analyzer. These tests also permitted us to determine the optimum collection time. A quantitative gas injection apparatus was connected to the carrier gas inlet at the gas injection point (Fig. 2). A fraction of the krypton and xenon, which was previously filled in the sampling loop of the injection apparatus, void volume of 1.0 cc, was injected into the gas injection point while the
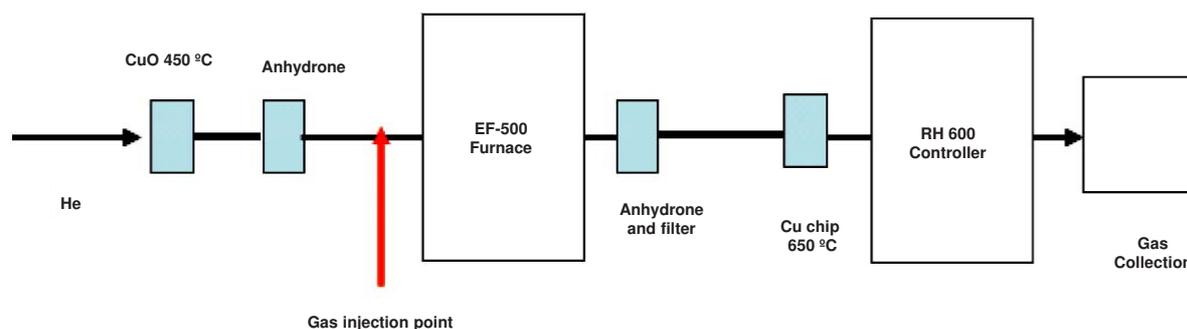

Fig. 2. Mixture standard gas injection point for recovery test

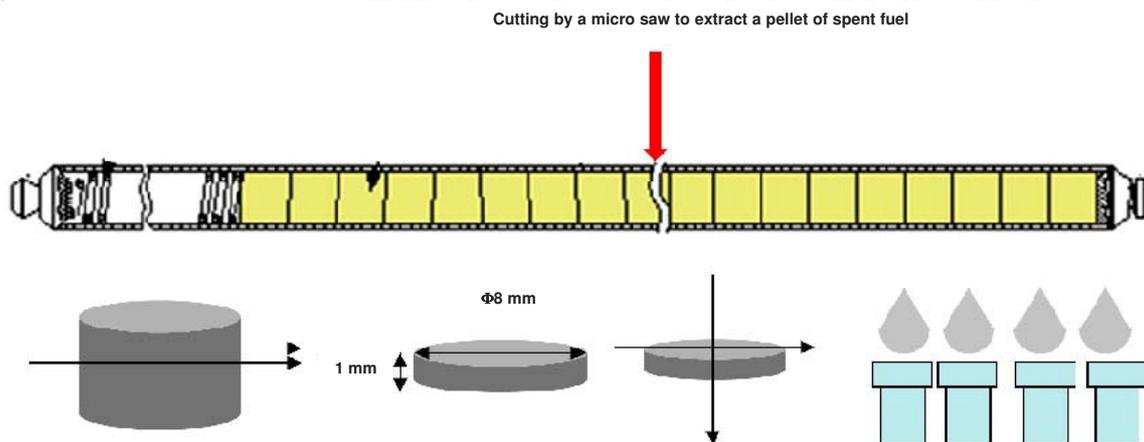**Cutting by a micro saw to extract a pellet of spent fuel**

Fig. 3. Preparation of a bulk specimen from an irradiated fuel rod

fusion instrument was being operated in accordance with the operation manual and the released gas was collected in a sampling bottle (void volume of 1030.59 cc) at a helium carrier gas flow rate of 450 cc/min for a certain time. Krypton and xenon concentrations of the collected gas was measured using a high performance quadrupole mass spectrometer (QMS, HIDEN HRP20, with a 9 mm pole diameter, triple filters, a highly sensitive detector; PIC) equipped with a quantitative gas inlet chamber[9].

Sample preparation of an irradiated oxide fuel: A spent fuel rod from a commercial atomic power plant of a pressurized water reactor (PWR) with a code predicted burn-up of *ca.* 55 GWd/tU was selected for the experiment. The initial 235U enrichment and total uranium weight of the fuel rod is *ca.* 4.5 % and about 1.8 KgU/rod, respectively. The fuel rod was taken from a 17 × 17 fuel assembly that was irradiated at different core locations to about 55 GWd/tU, a code predicted burn-up value, during 3 cycles for 1425 effective full power days (EFPD) and the cooling time was 360 days.

As shown in Fig. 3, the selected spent fuel rod, with a full axial length of 4000 mm, was chopped into 20 mm widths along the cross-section of the rod, including both fuel and cladding at a point around its axial center position, about 2000 mm distance from the bottom or top, using a micro saw. To prepare a bulk specimen for measurement of the average retained fission gas concentration, the removed small fuel rod, 20 mm in width, was chopped again in about 1-2 mm thick pieces along its axial direction and the fuel was separated into small fragments from the cladding using a hydraulic press. An oxide fuel fragment, about 0.05 g, was randomly selected and supplied for the experiment.

Fusion of an irradiated oxide fuel and measurement of the retained fission gas: The oxide fuel fragment was fused with a nickel basket (LECO 502-344), 1 g and two tin pellets (LECO 761-739), 1.0 g, at 850 A for 120 seconds in a high-temperature graphite crucible (LECO 782-720) of helium atmosphere using the hydrogen analyzer. The released gas from the analyzer was collected in a sampling bottle for 120 s. The krypton and xenon concentrations for the collected gas sample were directly measured without any pretreatment using the QMS and their isotopic distributions were determined as well[9].

In order to check any residual fission gas in the melt, it was fused again at the same fusion conditions and the same experimental procedures were followed.

Evaluation of melting state: After inert gas fusion of the irradiated oxide fuel fragment, the resultant melt was carefully separated from the graphite crucible and was mounted in a resin. The surface was polished to a mirror state and then coated with a gold target inside the hot-cell. Since a melt from the fusion of an irradiated oxide fuel fragment is highly radioactive, the melting state was evaluated using a high-energy γ-ray shielded EPMA equipped with 4-channle wavelength dispersive X-ray spectrometers (CAMECA XR 50R); the shield protects the detector and personnel from high radioactivity up to 75GBq. Microscopic data on the surface of the melt such as backscattering electron images (BEI), elemental mapping images and line scan profiles (LSP) were obtained using the shielded EPMA and its quantitative compositions as well.

RESULTS AND DISCUSSION

Evaluation of an irradiated oxide fuel melt: A small 0.049 g fragment of irradiated oxide fuel with a code burn-up of 55 GWd/MtU (Fig. 4(a)) was fused with two tin pellets, 1 g and a nickel basket, 1 g, at a fusion current of 850 A for 120 s. After fusion of the fragment, a melt of small button shape, shown in Fig. 4(b), was obtained and it was present freely inside the graphite crucible.

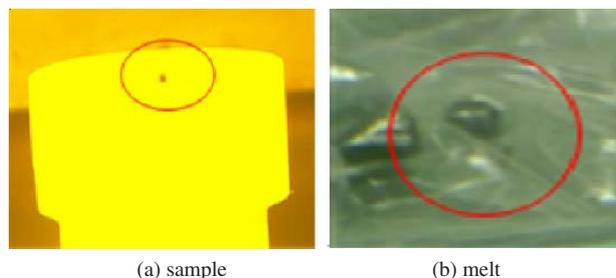(a) sample   (b) melt

Fig. 4. A fragment of an irradiated oxide and its melt

Because of the poor resolution of the secondary electron image (SEI) for the highly radioactive and non-etched specimen, its microscopic observations were accomplished using
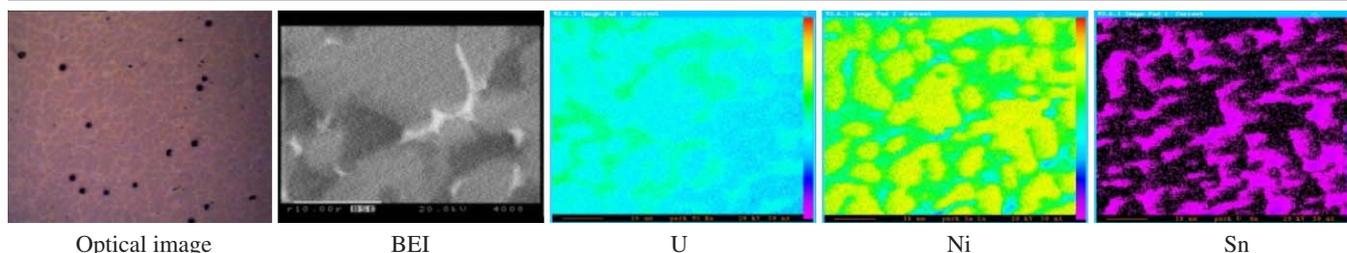
| Optical image | BEI | U | Ni | Sn |

Fig.5. Morphology and elemental mapping images of the melt obtained after fusion of a 0.049 g fragment of an irradiated oxide fuel with a nickel basket, 1 g and two tin pellets, 1 g, at 850 A for 120 seconds

an optical microscope attached to the shielded EPMA and operated at a backscattering electron image (BEI) mode. Fig. 5 shows the microscopic and elemental images for the melt. As shown in Fig. 5, no oxide phases were found over any surface of the melt even when a high magnification of 4000 was employed.

The elemental LSPs of the melt over the surface of the melt at electron beam or stage scan mode showed that the oxygen peak intensities were approximately at background level (Fig. 6), indicating that its concentration was below detection limits. In contrast, nickel and tin were distributed relatively homogeneously, but the distribution of uranium was severely segregated depending on the melt surface positions. Also elemental distribution trends of tin and nickel of the melt showed an opposing trend between them. Namely, nickel intensity become higher at low tin intensity position and *vice versa*. In spite of that, according to the quantitative analysis results of the melt over 50 fields, the melt contained almost the same initial compositions for the fusion experiment within relative uncertainty of 4 %, but the standard deviation of uranium measurement was very high. Therefore, the obtained melt is a mixture of metals and alloys, an intermetallic alloy form[7,8,10].

Recovery tests using a standard gas mixture: The fusion instrument used for this work has several reagent columns containing compounds such as high temperature CuO, alkali adsorbed rare earth asbestos and anhydrone in order to purify the helium carrier gas flow and the gases in the measure flow, including helium and gases extracted by the fusion of an
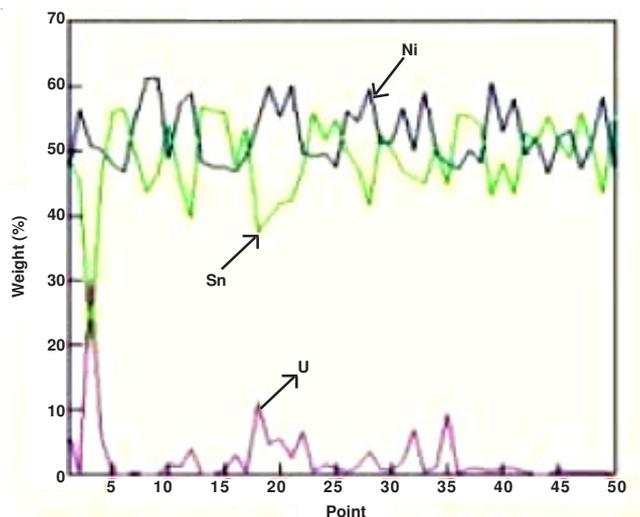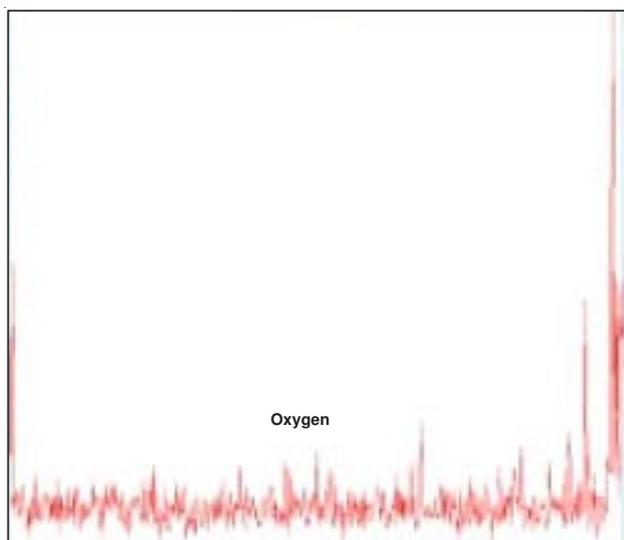

Fig. 6. Line scan profiles of the melt for oxygen, uranium, nickel and tin

oxide fuel. These columns may delay the release time of the extracted gas such as krypton or xenon according to their chemical properties.

Thus, an optimum gas collection time for the fusion instrument must be determined in order to quantitatively collect the released gas during fusion of a fuel fragment and to avoid unnecessary high volume sampling, which would dilute krypton and xenon concentration in the sampling bottle. During the normal operation of the fusion instrument, we conducted recovery tests of krypton and xenon by injecting known aliquots of krypton and xenon into the inlet of the carrier gas flow, as shown in the injection position in Fig. 2, using a gas injection apparatus[10,11]. Recovered krypton was *ca.* 98 %, while less than 10 % of xenon was recovered during a 1 min collection period at a flow rate of 450 cc/min. This result indicated that the retention time of xenon through the gas purification columns was longer than that of krypton due to the higher mass of xenon. However, if the collection time was extended to 2 min, *ca.* 96 % of the injected xenon was recovered.

In recovery test results for krypton and xenon (Fig. 7), the linearity between the amount of gas injected and the amount found was very good ($R^2 = 0.999$) over the injected volume range of 0.46-100 μL at 0 ºC, 1 atm, STP, with a quantitative gas injection apparatus equipped with a sampling loop of a 6-port sampling valve[9,11]. These values correspond to 4.6-100 ppm of krypton and xenon of collected gas in the sampling bottle. The test results indicated that average recovery of krypton and xenon was 98 ± 1 % and 96 ± 3 %, respectively.
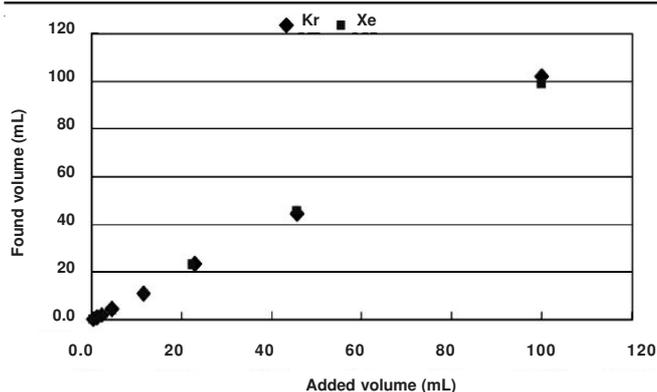
Fig. 7. Recovery test results of krypton and xenon depending on their injection volume

Measurement of retained fission gases in an irradiated oxide fuel: Tables 1 and 2 show the distributions of krypton and xenon isotopes for a code calculation and the percentages of gas released or retained from and in the tested fuel. According to the puncturing/collection test of the fuel rod, the amount of krypton and xenon, which was released during irradiation, totaled 45 cc, corresponding to 1.57 % FFGR based on a code FGG[12]. As shown in Tables 1 and 2, the isotopic distributions of retained krypton and xenon obtained by our fusion and collection method displayed typical fission gas characteristics.

TABLE-1
ISOTOPIC DISTRIBUTIONS OF KRYPTON
DEPENDING ON MEASUREMENT SOURCES

Isotopes	Measurement results of Kr by a code (%)[12]	Measurement results of released Kr (%)	Measurement results of retained Kr (%)
83	10.7	10.2	11.0
84	33.6	33.3	32.7
85	6.1	5.9	5.7
86	49.6	50.7	50.5
Total	100	100	100

TABLE-2
ISOTOPIC DISTRIBUTIONS OF XENON
DEPENDING ON MEASUREMENT SOURCES

Isotopes	Measurement results of Xe by a code (%)[12]	Measurement results of released Xe (%)	Measurement results of retained Xe (%)
131	6.8	5.6	7.1
132	22.3	23.5	22.7
134	28.4	28.6	28.4
136	42.5	42.3	41.8
Total	100	100	100

The isotopic distributions of a released fission gas represent an average value for a fuel rod, but those of the retained gas may be affected by local irradiation history of a fuel sample. The code calculation also contains various uncertainties and cannot fully describe the real irradiation situation and thus, some discrepancies among these values are to be expected. Based on the comparisons of relative uncertainty calculation results among the three fission gas sources, krypton and xenon, a code calculation, released and retained gas, it was found that the relative measurement uncertainty of ^{131}Xe was the highest, about 13 % and the uncertainties of the rest of the values were less than 4 %.

Under conditions of carrier gas flow rate of 450 cc/min, at 0 ℃, 1 atm, STP, the collected volume of gas in the sampling bottle during 120 seconds fusion of the irradiated oxide fuel fragment was 848 cc. According to the analysis result of the collected gas in the sampling bottle during the first fusion of the fragment, the krypton and xenon concentrations were 7.3 ppm and 70 ppm, respectively, corresponding to a Xe/Kr ratio of 9.7. Their quantitative concentrations, as shown in Table-3, were calculated as 0.143 cc Kr/gU, 1.384 cc Xe/gU and 1.527 cc fission gas/gU. If the measurement results of retained fission gas in this work can be regarded as an average value for the tested rod, then the total retained amount of fission gas for the rod would be 2697 cc/rod, *ca.* 94 % of total FGG of 2874 cc, a value calculated by the code calculation[12]. Namely, around 94 % of the FGG is retained in the oxide fuel structure for the tested rod and the rest is released into the plenum of the fuel rod.

TABLE-3
MEASUREMENT RESULTS OF RETAINED FISSION GAS
IN A FRAGMENT OF AN IRRADIATED OXIDE FUEL

Nuclide	(cc/gU)
Kr	0.143
Xe	1.384
Total	1.527

However, the combined amount of retained and released fission gas which was experimentally obtained is about 2742 cc, which amounts to *ca.* 95 % of FGG by a code calculation. Considering the various input parameters and uncertainties for a code calculation and the intrinsic variations of experimental procedures and the local sample itself, the less than 5 % difference between them would be negligible and the developed procedure for retained gas measurement in an irradiated oxide fuel would be acceptable for the purpose.

The gas collected during the second fusion of the melt with the same experimental conditions showed no krypton and xenon isotopic distributions for fission gas, illustrating that no residual gas was present in the melt. Noble gases such as krypton and xenon in metals or ceramics are rarely soluble and thus most of them tend to precipitate and form bubbles in the structure[1-3,6,7]. Consequently, they may be easily liberated from the solid matrix through fusion with metallic fluxes at a higher temperature.

Less than 10 min, including the time for fusion of a sample, gas collection and its quantitative measurement, are required for analysis of a sample by this new method. For refinement, however, greater data accumulation on the retained fission gases will be necessary in the future. A previous report indicated that fuel temperature is the most important parameter for deciding on a FGR among many fuel design parameters and irradiation factors[1,3].

Conclusion

It was found that a 0.049 g fragment of irradiated oxide fuel with a code burn-up of *ca.* 55 GWd/tU was clearly melted with *ca.* 1.0 g of tin and 1.0 g of nickel at 850 A for 2 min under a helium atmosphere, producing an intermetallic alloy

form. According to the recovery test results through the gas flow system of the fusion instrument, which was equipped with several reagent columns for gas purification, 96-98 % of the krypton and xenon was recovered during a 2 min collection after injection. No residual gas was found in the first melt and the experimentally obtained FGG, combined amount of released and retained fission gas in the tested spent fuel rod, was about 2742 cc/rod, a value that approached 95 % of a code calculation. Less than 10 min is sufficient to complete the measurement of retained fission gas in an irradiated oxide fuel sample, including its extraction and quantification.

ACKNOWLEDGEMENTS

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