High Temperature Physicochemical Properties of Irradiated Fuels

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Abstract

Research and development (R&D) on high temperature behavior of irradiated fuels have been conducted for many years in the Alpha-Gamma Facility (AGF) of the Japan Atomic Energy Agency (JAEA). An apparatus for measuring melting temperatures for irradiated fuels and an apparatus for the evaluation of radionuclide (fission products, FPs, and actinides) release behavior from the irradiated fuels were installed in hot cells in the AGF. In this paper, R&D activities on the high temperature behavior of irradiated fuels are reviewed, and detailed descriptions of the apparatuses are provided.

1. Introduction

Nuclear fuels are generally used under high temperature conditions in nuclear power plants (NPPs). The high temperature behavior of the fuels, therefore, must be taken into consideration in fuel design for normal operational conditions. As the maximum temperature of the fuels during irradiation is limited to within the design criterion to prevent fuel melting, melting temperature is an important physical property in the evaluation of the thermal behavior of the fuels. The melting temperature for non-irradiated fuels is indispensable to understanding the irradiation behavior of the fuels at the beginning of life. On the other hand, the melting temperature of highly burnt fuel is also of crucial importance in evaluating the integrity and soundness of the fuels at the end of life.

In addition to knowledge on high temperature behavior under normal operational conditions, an understanding of fuel behavior in severe accidents involving NPPs is also important. In particular, radionuclide release behavior from fuels at high temperatures under transient and accident conditions has been a main safety concern.

Post irradiation examination (PIE) data including fuel melting temperatures and radionuclide release behavior from the fuels are needed for a better understanding of high temperature behavior of irradiated fuels. Available information for evaluating the high temperature behavior of the fuels based on PIE results, however, is limited due to experimental difficulties encountered in the handling of irradiated fuels at high temperatures.

Research and development (R&D) on the high temperature behavior of irradiated fuels has been conducted for many years at the Alpha-Gamma Facility (AGF) of the Japan Atomic Energy Agency (JAEA). An apparatus for measuring the melting temperatures of irradiated fuels and an apparatus for the evaluation of radionuclide (fission products, FPs, and actinides) release behavior from the irradiated fuels were installed in hot cells at the AGF.

In this paper, the activities of R&D on the high temperature behavior of irradiated fuels are reviewed and detailed descriptions of the apparatuses are provided. Representative experimental data such as melting temperature and radionuclide release behavior during heating tests of irradiated uranium-plutonium mixed oxide (MOX) fuels are also presented.

2. Melting temperature of irradiated fuels

2.1. Apparatus, including capsule and heating system

Some studies have reported the melting temperature of irradiated or irradiation simulated fuels [1]. In early studies, the melting temperatures of uranium dioxide (UO_2) [2] and MOX [3-4] fuels were measured by the V-shaped filament method. Temperature measurements by this method may be influenced by vaporization of the specimen at high temperatures, and the oxygen to metal (O/M) ratio may also change during heating [5]. Later studies [1, 6-14], therefore, have employed the thermal arrest method, in which the specimen is enclosed in a sealed tungsten (W) capsule to avoid composition changes during measurement.

A schematic illustration of the apparatus for measuring the melting temperature of irradiated fuels in AGF is shown in Fig. 1 [15]. A specimen is put into a rhenium (Re) inner capsule, which is contained in a W capsule, because plutonium (Pu) in MOX fuels reacts with W. The W capsule has an outer diameter of 14 mm and a height of 40 mm. The capsule wall thicknesses are 1.5 mm in the periphery and 1.0 mm in the top and bottom lids. The black body sight tube, made of W, for temperature measurement has a diameter of 2 mm and a height of 10 mm. Its wall thickness is reduced to 0.5 mm to improve thermal response during temperature measurement.

The Re inner capsule has an outer diameter of 10.5 mm and a height of 11 mm. Its wall thickness is 0.5–0.8 mm except for the Re top lid, which is 2.0 mm thick, to allow for easy closing of the inner capsule. The top lid is held in place with a W stop tube to prevent movement of the Re inner capsule during transport and measurement. Finally, the W capsule is sealed shut by electron beam welding. The W capsule, including the Re inner capsule, is heated in a high frequency induction furnace (maximum output, 40 kW) through a W susceptor.

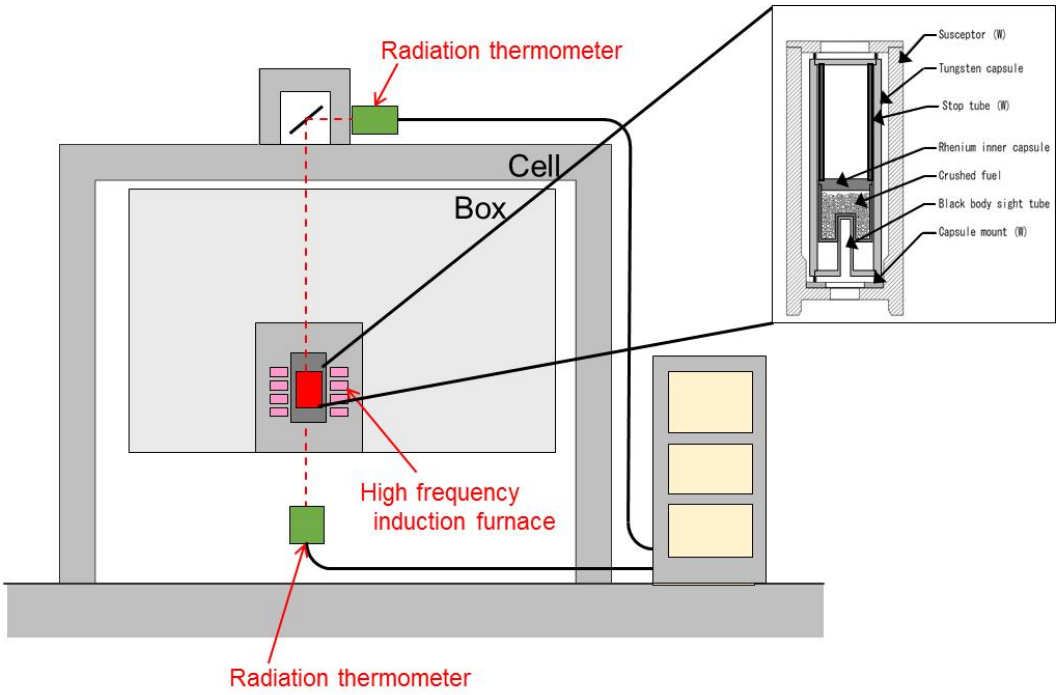

Fig. 1 Schematic illustration of the apparatus for measuring the melting temperature of irradiated fuels

2.2. Temperature measurement and determination of melting temperatures

The configuration of the temperature measurement system is also shown in Fig. 1 [15]. Temperature during heating is measured by a radiation thermometer through the black body sight tube. The melting temperature is determined by the thermal arrest technique. The power increase rate of the high frequency induction furnace remains constant throughout heating. This power corresponds to a temperature increase rate of 40 K/min up to the melting temperature. A change in the temperature slope versus time takes place at the inception of melting of the encapsulated specimen.

The solidus temperatures measured by the thermal arrest technique are calibrated by measuring the melting temperatures of four standard materials; namely, almina (Al_2O_3), niobium (Nb), molybdenum (Mo) and tantalum (Ta). The melting temperatures of Al_2O_3, Nb, Mo and Ta in the international temperature scale of 1990 (ITS-90) [16] are 2326 ± 2 K, 2745 ± 7 K, 2895 ± 4 K and 3280 K, respectively. Standard materials are encapsulated and melted under the same conditions as employed for test specimens. The uncertainty of the melting temperatures is estimated to be ±35 K from the uncertainty in the measurement of the melting temperatures of the standard materials and in the determination of melting temperature during heating.

2.3. Burnup dependence of the melting temperature of MOX fuels for fast reactors (FR-MOX)

Fig. 2 shows representative data on burnup dependence of the melting temperature of MOX fuels irradiated in the experimental fast reactor Joyo. The characteristics and irradiation conditions for specimens are shown in Table 1. Specimens were obtained from (U, Pu)O_{2-x} fuels burnt in the Joyo MK-II core. Two types of as-fabricated fuels were used. The first type was a core fuel for Joyo MK- II with a theoretical density (TD) of 92 - 94%. The second type was developed for the prototype fast reactor, Monju, with a TD of nearly 85%. The former fuel radius was smaller than the latter. The Pu contents for both types were 29.0 ± 0.7 wt% and their oxygen to metal (O/M) ratios ranged from 1.96 to 1.98. The maximum local burnup reached 112.5 GWd/t. As shown in Fig. 2, the melting temperatures of the irradiated MOX fuels measured by the thermal arrest method with encapsulated specimens decreased with increasing burnup due to the accumulation of FPs in the fuel matrix. These results are useful in evaluating the performance of irradiated MOX fuels for fast reactors.

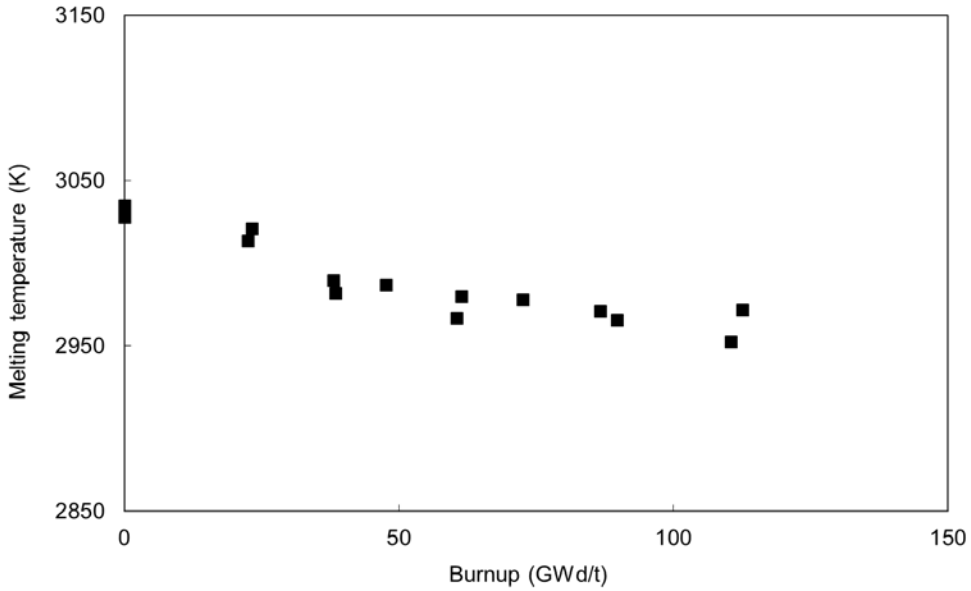

Fig. 2 Burnup dependence of the melting temperature of the irradiated MOX fuels [15]

Table 1 Characteristics of and Joyo irradiation conditions for specimens [15]

No.	Characteristics of as-fabricated fuels				Irradiation data		Melting temperature (K)
	Pellet diameter (mm)	Pu Content (wt%)	Density (%TD)	O/M ratio*1	Burnup (GWd/t)	Irradiation days EFPD (day)	
035-1	4.6mm	28.4	93.4	1.97	22.5	247	3014
035-2	4.6mm	28.4	93.4	1.97	23.3	247	3021
035-3	4.6mm	28.4	93.4	1.97	38.1	247	2990
035-4	4.6mm	28.4	93.4	1.97	38.5	247	2982
207-3	4.6mm	29.0	92.8	1.98	47.7	503	2978
207-1	4.6mm	29.0	92.8	1.98	60.6	503	2967
207-2	4.6mm	29.0	92.8	1.98	61.5	503	2980
549-1	4.6mm	28.4	94.3	1.99	72.6	455.2	2987
030-1	5.4mm	29.7	85.7	1.96	86.7	837	2971
030-2	5.4mm	29.7	85.7	1.96	89.7	837	2966
030-3	5.4mm	29.7	85.7	1.96	110.5	837	2953
030-4	5.4mm	29.7	85.7	1.96	112.5	837	2972
MOX-1	4.6mm	28.0	93.6	1.99	Unirradiated	—	3130
MOX-2	4.6mm	28.0	93.6	1.99	Unirradiated	—	3028
UO_2	5.4mm	—	95.0	2.00	Unirradiated	—	3035

＊1：Measured with the oxidation reduction gravimetric method during the fabrication process.

3. Radionuclide release behavior from the irradiated fuels

3.1. Apparatus for heating test of irradiated fuels

In order to obtain knowledge on radionuclide release behavior from fuels, heating tests and the subsequent analyses of the FPs and actinides released were carried out using specimens of MOX fuel pellets irradiated in the experimental fast reactor Joyo.

The heating tests were performed using a FP release behavior test apparatus at the AGF [17]. Fig. 3 shows the schematic illustration of the apparatus. This apparatus was originally developed for evaluation of the FP release behavior of irradiated MOX fuels for fast reactors. This apparatus is equipped with a high frequency induction furnace, solid FP sampling systems, a fission gas sampling system, gas analysis equipment and a gamma-ray spectrometer [17]. Irradiated fuel pellets (without cladding) were placed into a W crucible, and then loaded into the induction furnace. The induction furnace is capable of heating fuel specimens to a maximum temperature of 3273 K at a heating rate of between 1 and 25 K/s in a flowing argon (Ar) gas atmosphere. The solid FP sampling system consists of a temperature gradient tube (TGT) and five layers of sintered metal filters. The inner surface temperature of the TGT is maintained between 1023 K (on the inlet side) and 423 K (on the outlet side), changing linearly along the tube. Separable sampling tubes made of nickel (Ni) are positioned along the inside of the TGT, and filters are included in a stainless steel case at the top end of the TGT. The mesh sizes of the five filters were 43, 30, 10, 5 and 1 μm. FPs deposited on the inner surface of the sampling tubes depending on their volatility. The other released materials that passed through the sampling tubes were captured by sintered metal filters. Gamma-ray spectra were measured continuously by a gamma-ray spectrometry of the filter set during the heating test. The released gas was collected in ten sampling bottles. During the heating test, magnetic valves upstream from each bottle were opened in turn to collect the carrier gas, including helium and fission gases. After the test, the composition of the captured gas was analyzed by gas chromatograph to evaluate the amounts of helium and fission gases.

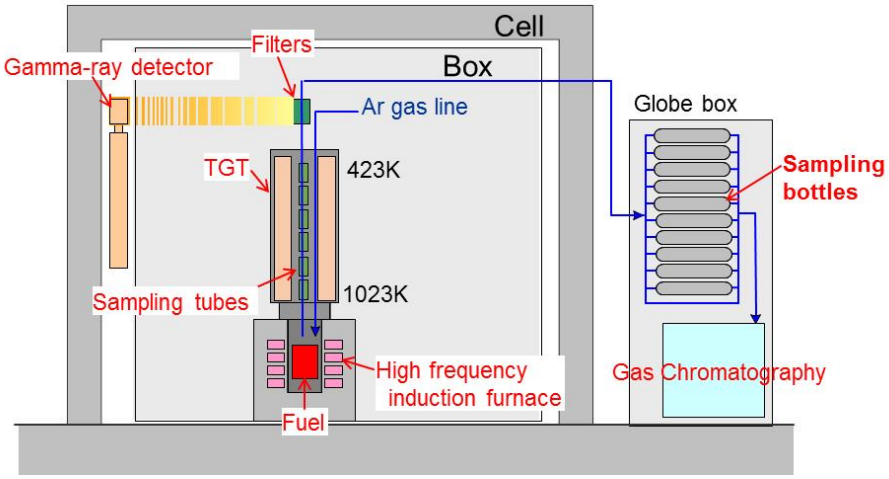

Fig. 3 Schematic illustration of the FP release behavior test apparatus

3.2. Summary and results of heating tests of irradiated fuels

Our research group conducted several heating tests under various conditions [17-21]. In this section, a brief overview of past heating tests is provided, and the findings are summarized.

The first experiment, which consists of two heating tests, was conducted around 2000 in order to obtain experimental data on the behavior of FPs released from irradiated FR-MOX fuels [17]. Two heating tests were carried out using MOX fuel pellets irradiated in the Joyo Mk-II core up to a burnup of approximately 65 GWd/t. In the first heating test, the specimen was heated to 2273 K at a heating rate of 15 K/s, and then maintained at that temperature for 30 min. After that, it was immediately heated to 3273 K at the same heating rate and maintained there for a further 30 min. In the second test, the terminal temperatures were 1773 and 2773 K. The heating rate and the holding time were equal to those in the former test. Findings obtained from the heating tests were as follows [17, 18]:

- The release fractions of FPs of Cs, Sb, Ru, Ce, Eu were evaluated by gamma spectrometry of specimens before and after testing. It was found nearly all of Cs and Sb, and approximately 10% of Ru were released in both heating tests. The majority of the Ce and Eu was retained [17].
- The fission gases (Xe, Kr) were rapidly released from the specimens in a very short time as a result of heating. In the case of volatile FPs, Cs release was gradual compared to that of fission gases [17].
- The mechanism of Cs release was found to be controlled largely by diffusion, and the gross diffusion coefficients of Cs in the MOX fuels were obtained by the Booth model [22]. The diffusion coefficient obtained in the heating test agreed well with the data reported in other experiments using light water reactor (LWR) fuels [17].
- After the heating tests, the residual fuel specimen from the first heating test as well as a reference specimen were subjected to EPMA and the compositions of the specimens were determined. In addition, gamma- and alpha-ray spectrometry were conducted on materials deposited on the sampling tubes. The results obtained from these chemical analyses revealed that Pu and Am were released from the fuel specimen as a result of heating. This implies that Pu and Am are more easily released than U under a low oxygen partial pressure atmosphere. This tendency agreed well with the calculation results of oxygen partial pressure dependence for partial pressure of gaseous actinide chemical species using a chemical equilibrium calculation code [18].

For estimating He, Kr and Xe release behavior, three heating tests were carried out using MOX fuel pellets irradiated in the Joyo Mk-III core. Three specimens were obtained from the top, middle and bottom positions of the same fuel pin, with a burnup of 36 Gwd/t, 63 Gwd/t and 54 Gwd/t, respectively. The roughly crushed pieces of fuel pellet specimens were loaded into the W crucible and then loaded into the induction furnace. The temperature was raised continuously at a heating rate of 10 K/s to the targeted values of 2773 K (specimens from middle and bottom) and 2973 K (from top) [19]. The findings were as follows:

- From the analysis of sampling gas, He release was more rapid than fission gases (Kr, Xe) due to its high diffusion coefficient. The difference between He and fission gas release rates was understood largely in terms of the difference of mobility in fuel.
- As for fission gas behavior, the diffusion coefficient obtained from the release history was in good agreement with literature values.

Heating tests for U–Pu mixed nitride fuels irradiated in Joyo up to approximately 40 GWd/t were also performed for evaluation of fission gas release and nitride decomposition behavior. Gas analyses during tests, metallography and EPMA for heated specimens after tests produced the following results [20]. The findings obtained in this study were as follows [20]:

- The fission gas release onset temperature of irradiated nitride fuel was higher than that of oxide fuel at same heating rate. This difference may have resulted from the different mechanical properties of these fuel types.
- Uranium may leave the fuel more easily than Pu, having reacted with traces of oxygen in the carrier gas and become a gaseous chemical species such as UO_3.

In addition to the experimental activities, chemical forms included in irradiated fast reactor fuels were evaluated by thermochemical equilibrium calculations based on simulated experiments with irradiated fuels during overheating [17, 21]. The calculation results, however, did not completely agree with the experimental results. This is due to the model used, limited thermodynamic data in the high temperature range and other reasons [17].

3.3. Heating tests for release rate coefficients of radionuclides from MOX fuels

Recently, experimental data concerning the release rate coefficients of radionuclides from MOX fuel irradiated in Joyo Mk-III core have been accumulated and compared with literature data for LWR fuels. In this section, heating tests conducted to obtain the release rate coefficient of Cs from FR-MOX fuels are described as examples.

The specimens for the heating tests were sections of irradiated $(U_{0.8}Pu_{0.2})O_{2-x}$ fuel pellets. The roughly crushed pieces of fuel pellet specimens were loaded into the W crucible and then loaded into the induction furnace. The temperature was raised continuously at a heating rate of 10 K/s to the targeted values of 2773 K, 2973 K and 3173 K, and maintained for 500 s. Following this, the temperature was lowered at a cooling rate of 15 K/s to 1273 K followed by furnace cooling. Fig. 4 shows temperature history during heating tests. Argon, as a carrier gas, flowed through the system at a constant flow rate of approximately 1 l/min during the heating test.

The gamma-ray spectra of cesium (^{137}Cs) were measured continuously during the heating test with gamma-ray spectrometry of the filter set to evaluate the FP release rate. The total fractional releases of FPs were obtained by off-line gamma-ray measurements before and after heating tests.

The values of fractional release of FPs were estimated by comparing the count rate of the gamma spectra of the specimen before and after heating tests. Table 2 shows the release rate of ^{137}Cs and ^{134}Cs for each heating test. The majority of Cs was released during the heating tests.

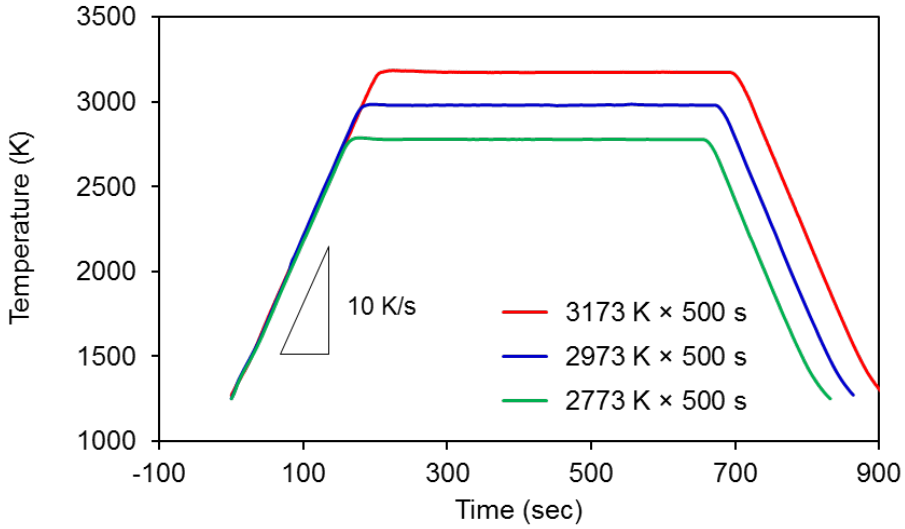

Fig. 4 Temperature history during the heating tests.

Table 2 Fractional release of ^{137}Cs and ^{134}Cs

Nucleus	Gamma ray energy (keV)	Temperature (K)	Release rate (%)
^{137}Cs	662	2773	99.5
		2973	99.9
		3173	99.9
^{134}Cs	796	2773	98.8
		2973	99.0
		3173	99.9

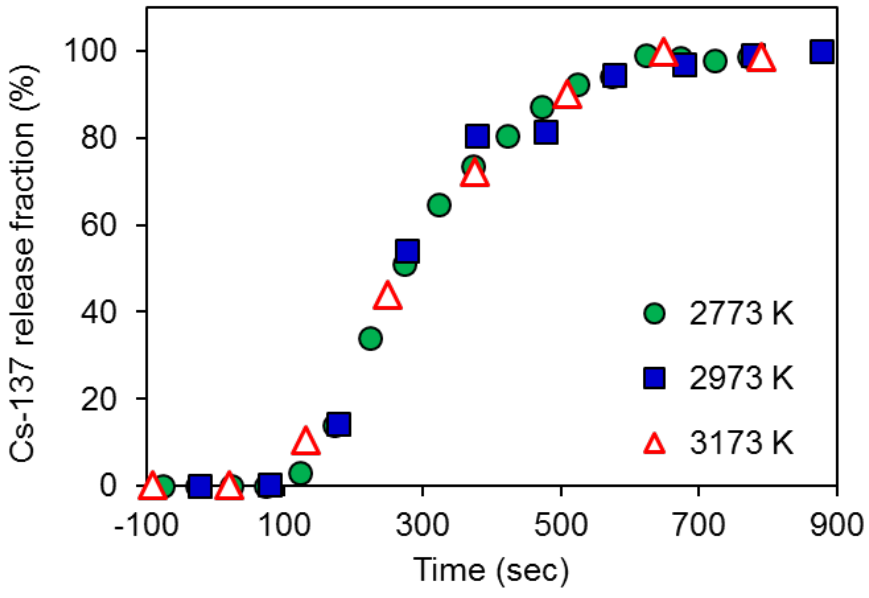

Fig. 5 Fractional release histories of ^{137}Cs

Fig. 5 shows the estimated fractional release histories of ^{137}Cs during heating test. The fractional release of Cs increased with temperature, and then remained constant after the temperature decreased. Although the holding temperature of the three heating tests differed, the curve shapes of fractional release of ^{137}Cs among the three heating tests resembled one another. This implies that the release rate of Cs during heating test up to 2773 K was sufficiently high, similar to the case of the fuel melting condition (heating test up to 3173 K) at a heating rate of 10 K/s. This is due to the existence of interconnected pores which developed in the FR-MOX fuel pellets during irradiation. At a heating rate of 10 K/s, Cs migrated rapidly through the pores even at a temperature of 2773 K, resulting in almost the same release rate of Cs as the case of the fuel melting condition.

The release rate coefficient of ^{137}Cs was evaluated by the following equation taking the fractional release histories of ^{137}Cs during the heating tests shown in Fig. 5 into consideration.

$$k(T) = -\frac{ln[1-(F_2-F_1)/(1-F_1)]}{t_2-t_1}$$

where, F_1 is the fractional release at the time t_1(-) and F_2 is the fractional release at the time t_2(-).

Fig. 6 shows the release rate coefficient as a function of temperature obtained in this study together with the evaluated temperature dependence of the release rate coefficient reported in NUREG-0772 [23]. In each element, the release rate coefficients obtained in this study were lower than the literature values. This implies that the temperature dependence of the release rate coefficients reported in NUREG-0772 [23] is conservative for the evaluation of radionuclide release behavior in the case of FR-MOX fuels as well. This implies that knowledge accumulated through numerous experiments using LWR fuels would be applicable for FR-MOX fuels. For a better understanding of the release behavior of radionuclides from FR-MOX fuels, additional experiments which include the effect of heating rate and plateau temperature, fuel specifications and irradiation condition (i.e., burnup) are needed.

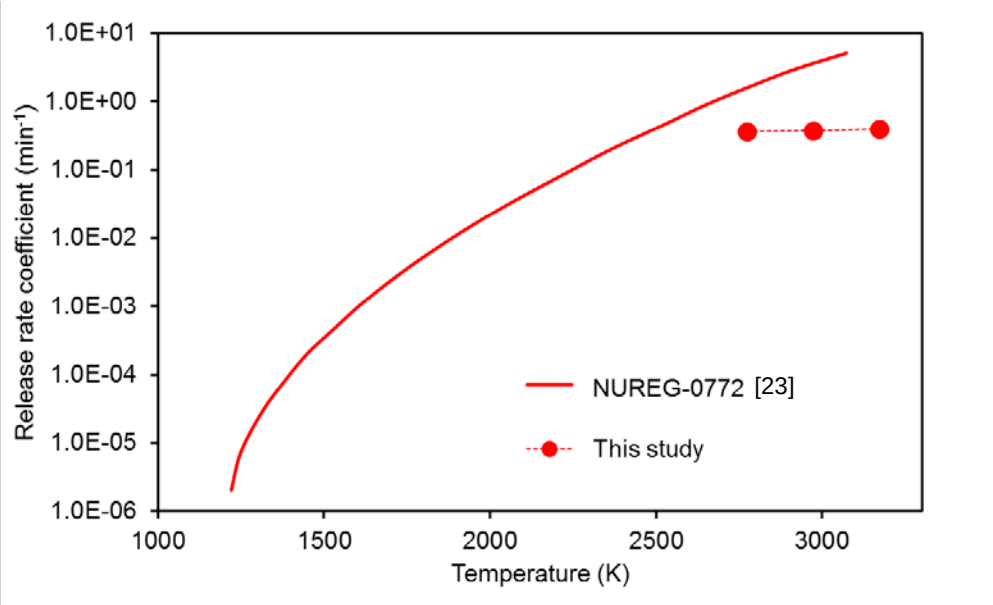

Fig. 6 Release rate coefficient of ^{137}Cs as a function of temperature

4. Summary

R&D on high temperature behavior of irradiated fuels has been conducted for many years at the AGF of JAEA. PIE data, including the melting temperatures of the fuels and the radionuclide release behavior from the fuels, have been accumulated.
It is indispensable for the safe operation of NPPs to prevent fuel melt from the beginning to the end of life. Evaluating burnup dependence of the melting temperature of FR-MOX fuels, therefore, contribute to accurate fuel design and the definition of operating conditions of NPPs.
Concerning radionuclide release behavior, types of nuclides released, the release fraction and the release rate are essential parameters for safety assessment of NPPs under accident conditions. Although numerous experiments using LWR fuels have been conducted, experimental results using FR-MOX fuels are scarce. The experimental results obtained in this study are useful for a better understanding the behavior of radionuclides released from FR-MOX fuels. The evaluation results of radionuclide release behavior from FR-MOX fuels reasonably agree with those from LWR fuels. Therefore, it would be possible to predict radionuclide release behavior from FR-MOX fuels using knowledge obtained from the experimental data for LWR fuel.

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References

[1] K. Konno, T. Hirosawa, J. Nucl. Sci. Technol. 36 (1999) 596.
[2] J. L. Bates, J. Nucl. Mater. 36 (1970) 234.
[3] J. K. Krankota, C. N. Craig, General Electric Report GEAP-13513 (1969).
[4] M. Koizumi, Power Reactor and Nuclear Fuel Development Corporation Report PNC SN 843-71-38 (1971).
[5] M. G. Adamson, E. A. Aitken, R. W. Caputi, J. Nucl. Mater. 130 (1985) 349.
[6] S. Yamanouchi, T. Tachibana, K. Tsukui, M. Oguma, J. Nucl Sci. Technol. 25 (1988) 528.
[7] T. Tachibana, T. Ohmori, S. Yamanouchi, T. Itaki, J. Nucl. Sci. Technol. 22 (1985) 155.
[8] T. Namekawa, T. Mitsugi, T. Tachibana, S. Yamanouch, Proc. 35th Conf. on Remote Systems Technology (1987) p.105.
[9] J. Komatsu, T. Tachibana, K. Konashi, J. Nucl. Mater. 154 (198) 38.
[10] K. Yamamoto, T. Hirosawa, K. Yoshikawa, K. Morozumi, S. Nomura, Trans. Am. Nucl. Soc. 66 (1992) 179.
[11] K. Yamamoto, T. Hirosawa, K. Yoshikawa, K. Morozumi, S. Nomura, J. Nucl. Mater. 204 (1993) 85.
[12] K. Konno, T. Hirosawa, J. Nucl. Sci. Technol. 35 (1998) 494.
[13] K. Konno, T. Hirosawa, J. Nucl. Sci. Technol. 39 (2002) 771.
[14] K. Konno, T. Hirosawa, J. Nucl. Sci. Technol. 39 (2002) 1299.
[15] T. Hirosawa, I. Sato, J. Nucl. Mater. 418 (2011) 207.
[16] R.E. Bedford, G. Bonnier, H. Maas, F. Pavese, Metrologia, 33(1996)133.
[17] I. Sato et al., J. Nucl. Sci. Technol. 40 (2003) 104.
[18] I. Sato et al., J. Nucl. Mater. 437 (2013) 275.
[19] I. Sato et al., J. Nucl. Mater. 416 (2011) 151.
[20] I. Sato et al., Prog. Nucl. Energy 82 (2015) 86.
[21] I. Sato et al., J Alloy Com 444–445 (2007) 580–583.

[22] A. H. Booth, CRDC-721, (1960).
[23] United States Nuclear Regulatory Commission, NUREG-0772, 1981.