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Measurement of the specific heat of Zr–40 wt%U metallic fuel

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Abstract

The specific heat capacities of un-irradiated and irradiated metallic Zr–40 wt%U fuel have been measured between 50 °C and 1000 °C with a differential scanning calorimetry. The irradiated fuels have three different burnup levels of 0.38, 0.70 and 0.92 g-fission product (FP)/cm^3. The measured specific heat for the un-irradiated fuel is representative and consistent with the values estimated from the Neumann–Kopp rule. The irradiated fuels exhibited a complicated behavior of the heat capacities. The unique characteristics of the specific heat capacities can be explained by the recovery of radiation damage, the formation of fission gas bubbles and fission gas release, and a phase transition in the irradiated fuels. An examination of the microstructure revealed that multiple large bubbles were formed in the irradiated fuel during specific heat measurement. The measured specific heat is expected to enable us to estimate the stored energy in the metallic fuel during certain accident scenarios and to determine the thermal conductivity of zirconium–uranium metallic fuel.

1. Introduction

The heat capacity is important since it is one of the essential thermal properties and it determines the thermal behavior in heat generating substances. In addition, it is a prerequisite in deriving the thermal conductivity along with the density and thermal diffusivity.

The metallic uranium–zirconium fuel has been developed as a fuel in advanced integral reactors [1]. In order to estimate the thermal behavior and calculate the thermal conductivity for the metallic fuel, the heat capacity has generally been estimated by the Neumann–Kopp rule [2] since there is no measured data for the heat capacity for the irradiated zirconium–uranium alloy.

In the case of uranium oxide, the specific heat shows a simple behavior [3] which increases with the temperature until melting. However, metallic fuel consisting of uranium and zirconium exhibits a more complicated behavior in that the fuel experiences a phase transition in a temperature range far below the melting point. Furthermore, the irradiated uranium–zirconium fuel reveals more complicated changes in the heat capacity. This happens because heat capacity can be camouflaged by radiation damage and fission gas release which would be induced by the heating for measuring the specific heat.

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In this regard, specific heat measurements have been made on metallic uranium–zirconium fuel (Zr–40 wt%U) from 50 °C to 1000 °C by a differential scanning calorimeter (DSC). The effect of irradiation and annealing on the heat capacity is discussed in detail.

2. Experimental

2.1. Specimen preparation

The Zr–40 wt%U specimens were prepared from fresh (un-irradiated) and irradiated metallic fuel. The un-irradiated metallic fuel consists of the δ-phase (UZr_2) matrix and regularly distributed α-zirconium in the δ-phase matrix [4]. The irradiation was performed in the MR reactor in the Kurchatov Institute in Russia. The irradiated specimens with three different burnup levels were cut from a fuel rod. The preliminary burnup of the accumulated fission product was estimated by a gamma spectrometry in the fuel rod as shown in Fig. 1. The activity analysis of Cs-137 in the specimens showed that the burnups of the three samples were 0.38, 0.70, and 0.92 g-FP/cm^3, respectively. The burnup of 1.0 g-FP/cm^3 approximates 29 at.% [5]. The pellet specimens were 3.0 ± 0.1 mm in diameter and 1.0–0.1 mm thick. The weight of each sample was approximately 50 mg.

2.2. Specific heat measurement

Specific heat of the uranium–zirconium fuel was measured by DSC Netzsch 404C Pegasus in an inert atmosphere. The DSC system was additionally shielded from the radiation activity during the measurement. The measurements were carried out at an interval of 0.1 °C in the temperature range of 50 °C to 1000 °C. Heating rate was 15 °C/min. The inert atmosphere was obtained by the argon gas with a purity of 99.998% and its flow rate was 50 ml/min.

The imprecision of the measurements was confirmed by using sapphire and molybdenum standard samples to be within ±3.0% in the entire measuring temperature range. Sapphire standard reference sample was used to calculate specific heat capacity.

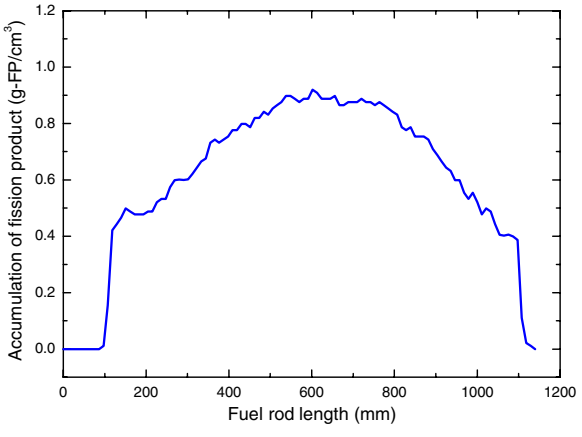

Fig. 1. The distribution of the burnup along the metallic fuel rod determined by a gamma spectrometry.

3. Results and discussion

3.1. Un-irradiated fuel

The specific heat capacity of un-irradiated metallic fuel was measured. The measured specific heat is displayed in Fig. 2 along with the values estimated by the Neumann–Kopp rule. The calculation by the Neumann–Kopp rule was made from the summation of the products of an atomic fraction of the constituent elements and their atomic heat capacity. For an application of the Neumann–Kopp rule, the heat capacity of uranium [6] was fitted as follows:

$$C_p(\alpha\text{-U}) = 24.959 + 2.132 \times 10^{-3}\mathrm{TK} + \frac{2.370 \times 10^{-5}}{\mathrm{TK}^2} \quad (298 \leqslant \mathrm{TK} \leqslant 942\ \mathrm{K}), \tag{1}$$

$$C_p(\beta\text{-U}) = 42.928 \quad (942 \leqslant \mathrm{TK} \leqslant 1049\ \mathrm{K}), \tag{2}$$

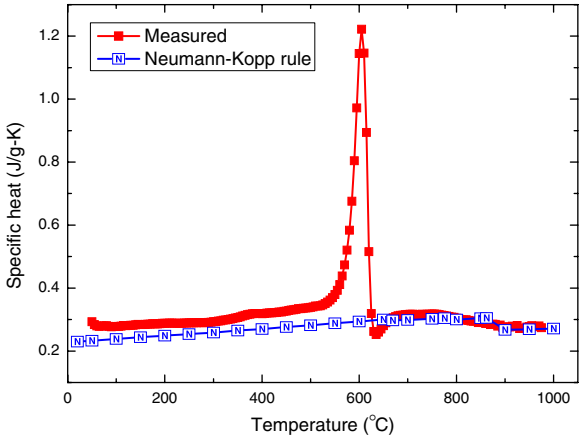

Fig. 2. The measured specific heat of the un-irradiated metallic fuel along with the specific heat estimated by the Neumann–Kopp rule.

$$C_p(\gamma\text{-U}) = 38.284 \quad (1049 \leqslant \text{TK} \leqslant 1408\ \text{K}), \tag{3}$$

where C_p is in J/K-mol and TK in Kelvin.

On the other hand, the zirconium heat capacity [6] was recommended as

$$C_p(\alpha\text{-Zr}) = 22.839 + 9.091 \times 10^{-3}\text{TK} - \frac{2.132 \times 10^4}{\text{TK}^2} \quad (298.15 \leqslant \text{TK} \leqslant 1135\ \text{K}), \tag{4}$$

$$C_p(\beta\text{-Zr}) = 12.885 + 9.976 \times 10^{-3}\text{TK} + \frac{5.158 \times 10^6}{\text{TK}^2} \quad (1135 \leqslant \text{TK} \leqslant 2125\ \text{K}). \tag{5}$$

It can be seen in Fig. 2 that the measured specific heat for the un-irradiated metallic fuel tends to increase gradually with the temperature and subsequently a sharp peak is observed. This peak results from the energy absorbed in the phase transition. The maximum specific heat capacity of the peak was observed at 605 °C which was slightly lower than the phase transition temperature of 613 °C [4]. The sharp peak of the specific heat is followed by a small dip and then a slight decrease up to the end of the measurement. Except for the sharp peak, the specific heat of metallic fuel was about 0.3 J/g K between 50 °C and 1000 °C.

3.2. Irradiated fuel

Fig. 3 displays the measured specific heat capacities of the irradiated fuels with three different burnup levels. In contrast to the un-irradiated fuel, the specific heat for the irradiated fuels exhibited a complicated behavior. As shown in Fig. 3, the specific heat capacities decrease from 50 °C to 425 °C, peak between 450 °C and 600 °C, followed by a plateau (or blunt peak). The first peaks result from the phase transition similar to the un-irradiated fuel. The plateaus seem to be very unique and peculiar only for the irradiated fuel, which indicates that sophisticated phenomena occurred during the specific heat measurement up to the high temperature of 1000 °C. Since the specific heat for the irradiated fuel can be classified into three zones as shown in Fig. 3, the details at each zone are discussed as follows.

The specific heat for the irradiated fuel in the first zone is illustrated in Fig. 4 together with the linear fitting curves for each burnup level. The specific heat decreases with the temperature and the degree of reduction in the specific heat is inversely proportional to the burnup. The linearly fitted slope is larger for the higher burnup fuel than for the lower burnup fuel. The reduction of the specific heat with the temperature could be attributed to the recovery from the as-irradiated condition such as a release of the residual energy stored in the irradiated fuel, an annealing out of the radiation damage and/or a recovery of the distorted lattice structure. These can be explained by the fact that the fuel with higher burnup which, in general, underwent an irradiation at a higher temperature would be less recovered at the lower temperature region than the lower burnup fuel. It should be noted that the intercepts of specific heat capacities near the room temperature converged to approximately 0.23 J/g K for three

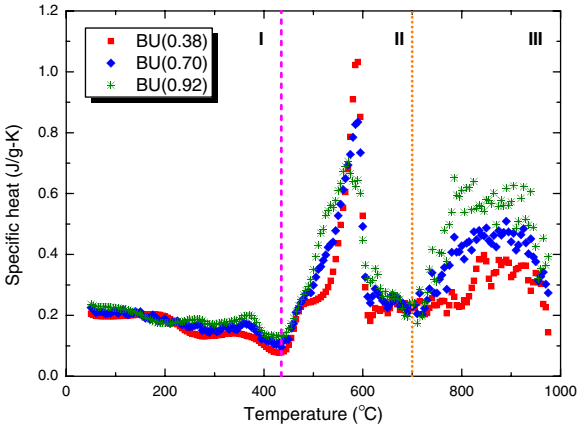

Fig. 3. The measured specific heat capacity of the three irradiated fuels.

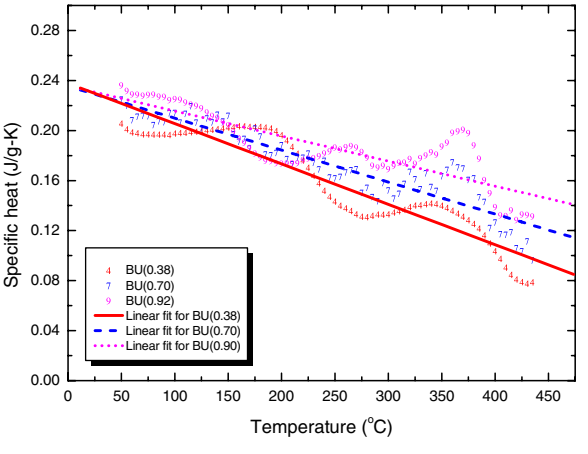

Fig. 4. The specific heat capacity of the irradiated metallic fuel in the first zone.

different burnup fuels. This coincidence reveals that the three specimens with different burnup levels have more or less the same specific heat at the room temperature before measuring the specific heat.

The observed specific heat in the second zone is displayed in Fig. 5. The specific heat capacities show peaks with a different degree of sharpness. It is interesting that the temperatures for covering the peaks are the same for all three specimens. The specific heat capacities begin to increase at almost the same temperature of ~450 °C with a different increasing rate which is proportional to the burnup. However, the maximum specific heat and the sharpness of the peak are inversely proportional to the burnup. The maximum specific heat is observed at the temperature of ~580 °C for the fuel with the burnup of 0.38 and 0.70 g-FP/cm^3. For the fuel with the highest burnup of 0.92 g-FP/cm^3, the maximum specific heat is attained at the temperature of 570 °C which is slightly lower than these of the other two fuels. Phase transition temperatures were obtained from the specific heat measurements. The temperatures of the onset and the completion of phase transition are presented in Table 1. The phase transition temperature decreases with the burnup.

As in the un-irradiated fuel, these peaks are caused by the phase transition in Zr–40 wt%U. The sharpness of the peaks was blunted with the burnup so that the maximum specific heat was reduced and the width of peaks was extended.

The reduced and extended peaks could be associated with the shift of phase transition of the irradiated specimens where the significant strain was accumulated during irradiation. The apparent peaks appeared by the superimposition of the multiple shifted peaks. This superimposition can be also confirmed by the fact that the integrated area of a peak is estimated to be almost the same for all the irradiated fuels by using the baseline of null specific heat.

Table 1
Phase transitions of metallic uranium–zirconium fuel (Zr–40 wt%U)

Burnup (g-FP/cm^3)	Onset temperature (°C)	Peak temperature (°C)
Un-irradiated	576.6	605.2
0.38	545.9	587.9
0.70	510.7	577.6
0.92	477.3	569.3

Fig. 6 presents the behavior of the specific heat for the irradiated metallic fuel in the third zone. In Fig. 6, the polynomial fitted lines are also displayed. After the peak caused by phase transition, the specific heat increases again and shows plateaus or blunt peaks for all the irradiated metallic fuels. The maximum specific heat, in this region, is proportional to the burnup. The peaks or plateaus in the specific heat is expected to be due to the behavior of fission gases which exist initially as single isolated atoms or in tiny bubbles. The fission gases commence to move and precipitate, thereby forming large gas bubbles. Furthermore, part of the fission gases may even be released. In this regard, it can be inferred that the specific heat in the third zone is influenced by the movement of the fission gases and the formation of fission gas bubbles during the measurement. This is supported by the fact [7]

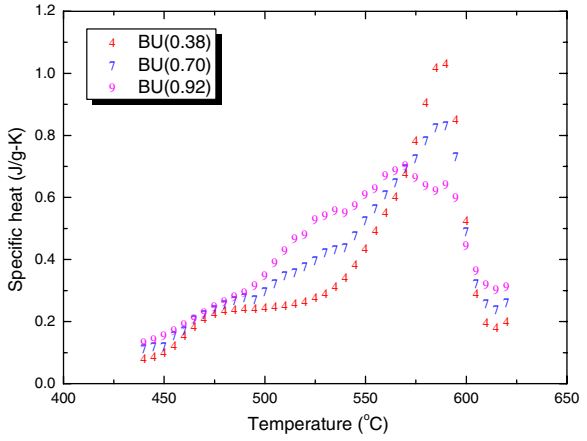

Fig. 5. The specific heat capacity of the irradiated metallic fuel in the second zone.

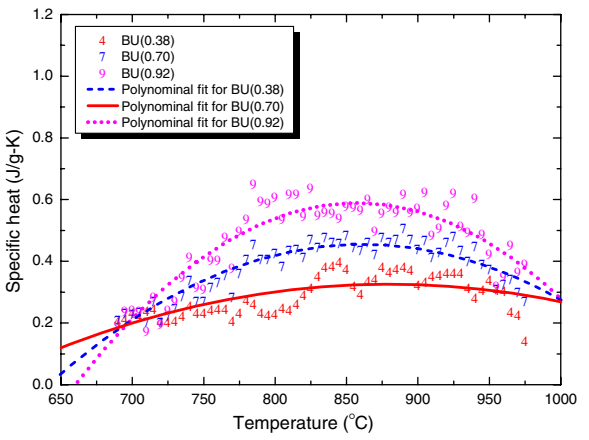

Fig. 6. The specific heat capacity of the irradiated metallic fuel in the third zone.

that the majority of volume change in the metallic fuel is observed after phase transition.

To a lesser extent, the fitted lines indicate another possibility to explain the plateaus. The zirconium contained in the un-irradiated metallic fuel undergoes a phase transition at the temperature of approximately 600 °C. On the other hand, the phase transition of the zirconium atoms liberated from the fission of uranium atoms in the δ-phase of UZr_2 and generated by the fission yield could be retarded at the phase transition temperature of the un-irradiated fuel. Instead, the zirconium contained in the irradiated specimens experiences a phase transition similar to the pure zirconium. This can be explained by the fact that the height of the plateau (peak) increases with the burnup since the liberated and fission-yielded zirconium elements would be proportional to the burnup. The phase transition of zirconium is additionally confirmed by the maximum values at the polynomial fitted lines located around the temperature of the pure zirconium phase transformation (862 °C).

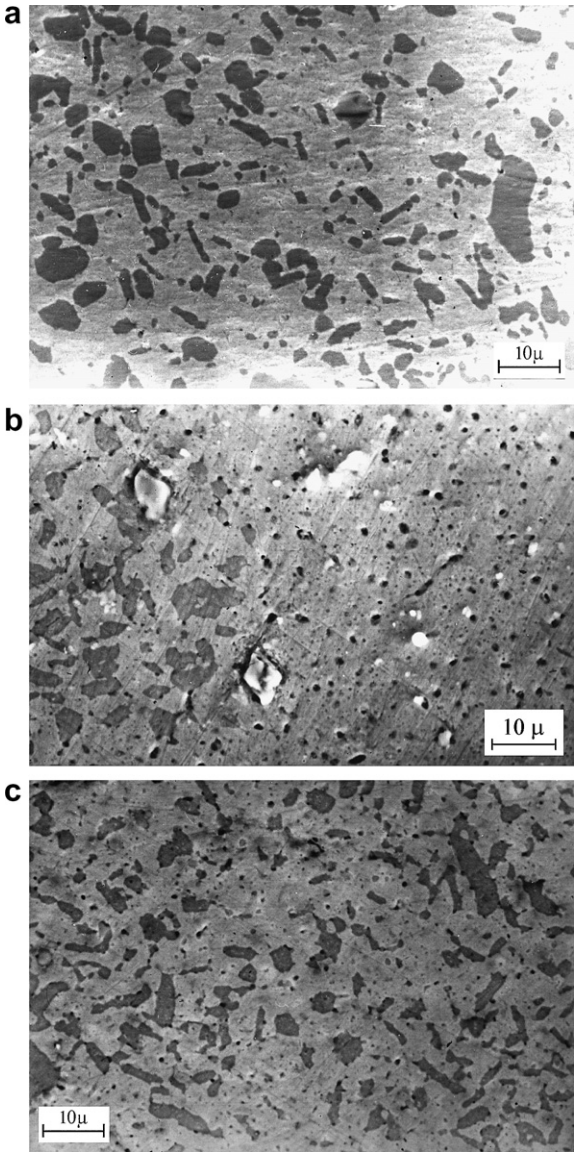

Fig. 7. Microstructure of the metallic fuel with the burnup of (a) 0.38, (b) 0.70, and (c) 0.92 g-FP/cm^3 before the specific heat capacity measurement.

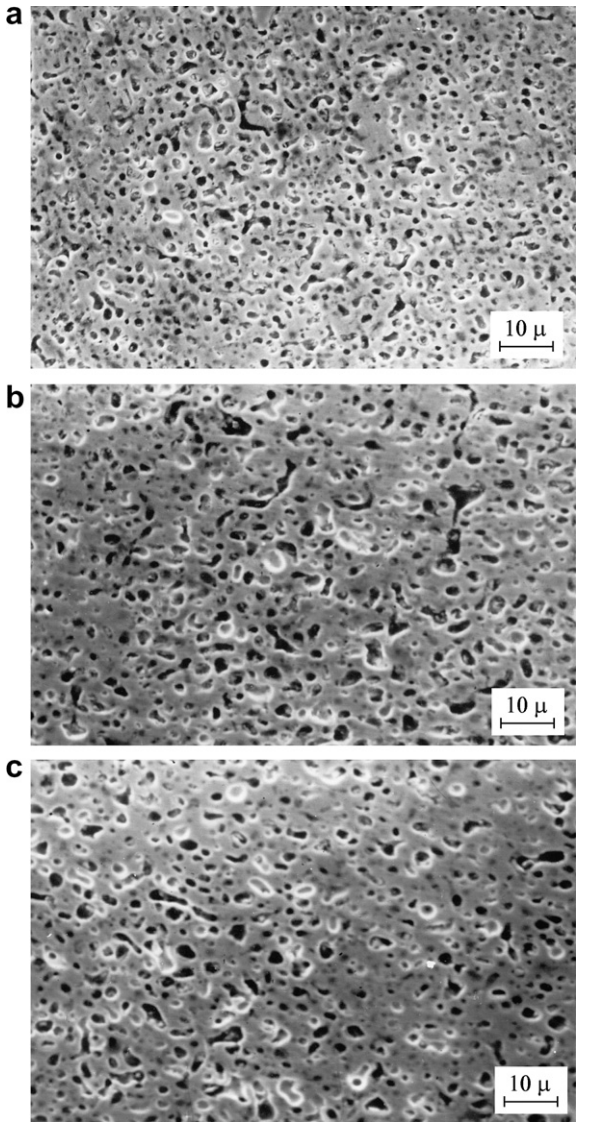

Fig. 8. Microstructure of the metallic fuel with the burnup of (a) 0.38, (b) 0.70, and (c) 0.92 g-FP/cm^3 after the specific heat capacity measurement.

Table 2
The change in weight before and after heat capacity measurement

Burnup (g-FP/cm^3)	Before test (mg)	After test (mg)	Change (%)
0.38	50.49	50.18	0.61
0.70	54.11	53.77	0.63
0.92	59.54	57.86	2.82

3.3. Change in the microstructure

Microstructures of the irradiated metallic fuel before and after performing the specific heat measurement were examined to analyze their changes. Figs. 7 and 8 illustrate the microstructures before and after the specific heat tests. Fig. 7 shows that the general characteristics of the microstructure in the irradiated fuel was maintained throughout the irradiation in that the irradiated fuels are composed of the δ-phase (UZr_2) matrix and a regularly distributed α-Zr in the δ-phase matrix similar to the un-irradiated fuel. The small dots correspond to the bubbles in the fuel. It can be seen that the average bubble size and density increase with the burnup. The image analysis revealed that the average bubble sizes are 0.64 μm for 0.38 g-FP/cm^3, 1.74 μm for 0.70 g-FP/cm^3, and 1.90 μm for 0.92 g-FP/cm^3.

As shown in Fig. 8, multiple and grown bubbles are observed after measuring the specific heat for the irradiated fuel. The average bubble size increased with the burnup.

The specimens used for the specific heat measurements were weighed and the results are summarized in Table 2. The weights decreased after the specific heat measurement and their changes were proportional to the burnup levels. The reduction in the weight is attributed to the fission gas released during the heating for the specific heat measurement.

4. Conclusions

The specific heat was measured from 50 °C to 1000 °C for both un-irradiated and irradiated metallic uranium–zirconium (Zr–40 wt%U) fuel.

The measured specific heat for the un-irradiated fuel showed a peak during a phase transformation, and was consistent with the values estimated from the Neumann–Kopp rule.

For the irradiated fuels of three different burnup levels, complicated specific heat capacities were observed. The specific heat capacities decreased, in general, with the temperature but had peaks and plateaus. These behaviors of the specific heat seem to be attributed to the recovery of radiation damage, a fission gas bubble formation and release, and, possibly, an additional phase transformation of the zirconium liberated from the δ-phase (UZr_2) and generated by fission yield. This second phase transition temperature decreased with the burnup.

Examination of the microstructure revealed that many bubbles were formed in the irradiated fuel after performing the specific heat measurement. This is due to the fission gases which are precipitated into the bubbles and then released significantly during the specific heat measurement.

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