



The effect of RE-rich phase on the thermal conductivity of U–Zr–RE alloys

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ABSTRACT

Thermal conductivity of RE-bearing U–Zr fuels was investigated. Under an assumption of a RE-rich phase forming a macroscopic mixture with the matrix, the thermal conductivity was estimated for U–Zr–RE alloy. It was evaluated that the thermal conductivity of the U–Zr fuels would be lowered by less than 5% due to the addition of RE. The measurement of the thermal properties of U–Zr–Ce supported the present estimation.

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1. Introduction

In Korea, a sodium-cooled fast reactor (SFR) has been adopted in conjunction with developing the pyroprocessing technology for a spent nuclear fuel. In the long run a closed fuel cycle will be accomplished to efficiently manage actinides and to reduce a high radioactivity level. U–Zr and U–Pu–Zr metallic fuel are used in the SFR. KAERI has designed metallic fuels and evaluated their performance in a SFR [1]. Recently, the fuel fabrication technology has also started to be developed.

The spent fuel is transformed into new fuel materials through a pyroprocess. An electrorefining process produces U, Pu, and minor actinides (MA) along with a carryover of rare earth (RE) elements. The foreign constituents such as MA and RE could vary the fuel properties, thus affecting the fuel performance. There exists a few works on fuels containing MA and RE materials [2,3]. The addition of RE is known to result in the precipitation of a second phase. In U–Zr binary alloy, a cerium-rich phase was formed by adding Ce. In U–Pu–Zr alloys, MA such as Am and Np can be dissolved without RE, but an Am–Pu–RE second phase was precipitated in the matrix of U–Pu–Zr–Np due to the presence of RE.

Thermophysical properties of metallic fuels for a SFR could be varied by an influence of the RE-rich second phase. Among these, the thermal conductivity is one of the most important parameters dominating the in-reactor performance of these fuels. It is degraded by adding alloying elements, and is affected by the distribution of the second phases.

In this work, we have investigated the variation of the thermal conductivity for U–Zr fuel containing RE. By examining the microstructural characteristics of U–Zr–RE, the thermal conductivity of the alloy was estimated by using macroscopic mixture models. A measurement of the thermal properties of U–Zr–Ce was also

performed to compare the evaluated results with the experimental data.

2. Thermal conductivity bounds of U–Zr–RE alloys

2.1. Microstructural characteristics of RE in metallic fuels

RE with U as well as Zr is nearly completely immiscible in a liquid state, and the solubility of RE is extremely low; the solubility of cerium in U at 909 K is less than 0.1 at.% [4]. These characteristics are also applied to U–Zr alloy. For example, the solubility of Ce in U–10Zr alloy is less than 0.5 at.% at a higher temperature of 873 K, and Ce-rich precipitates are dispersed in the U–10Zr matrix [5].

A similar phenomenon was observed in the specimens we prepared. Fig. 1 shows the microstructure of the U–10Zr–6Ce alloy taken in a backscatter image with an SEM. The ingot was prepared with an induction furnace under a vacuum environment of 10^{-3} torr. Raw materials were melted in a crucible of zirconia, and cooled to room temperature in the furnace. Large stringer-like precipitates with a length of 50–100 μm were distributed all over the specimen. They are found to be the Zr-rich phase which is thought to be stabilized by ingress of oxygen, and could affect the thermal conductivity of the specimen. Meanwhile the Ce-rich precipitates are seen with a higher magnification. They are formed as very small round-shape particles. The average Ce content in the specimen is less than 3 wt%. Considering that Ce_2O_3 is more stable than UO_2 , and ZrO_2 [5], it seems that a fraction of Ce was not dissolved due to the oxidation of Ce. The cerium concentration in the matrix is likely to be less than 0.5 at.%. The small particles were confirmed as Ce-rich phases by EDX analyses.

2.2. Thermal conductivity bounds of macroscopic mixtures

Thermal conductivity of a material is reduced by increasing the solute concentration. The compositional dependency of the

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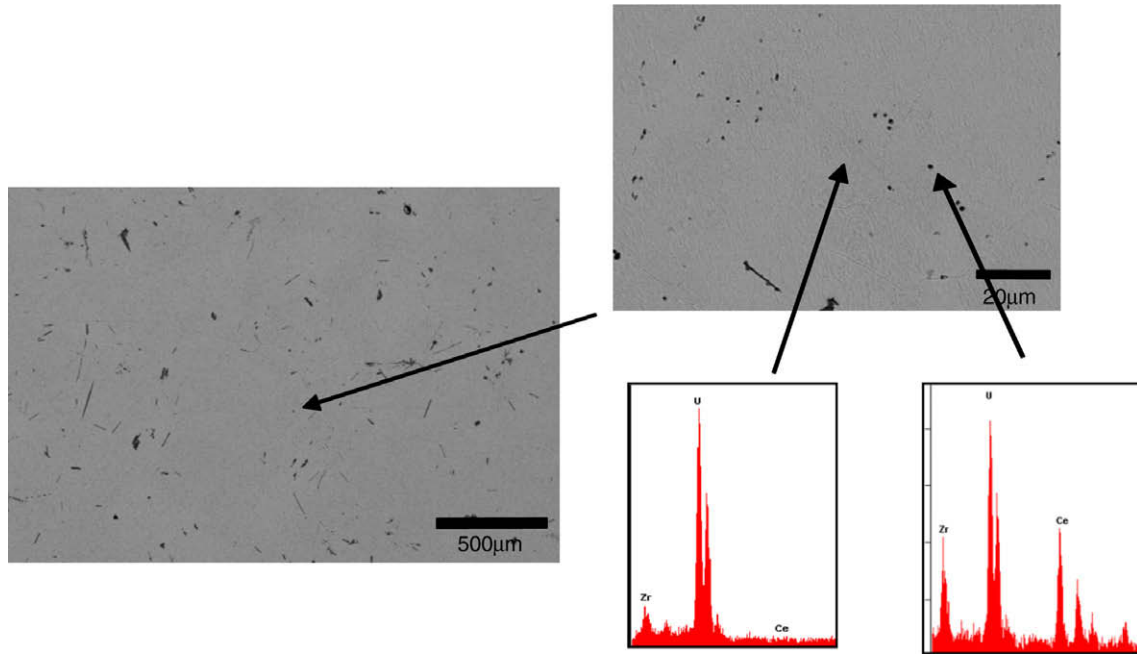


Fig. 1. Microstructure of U–Zr–Ce alloy in a backscatter electron SEM, and the Ce-rich precipitates in the U–Zr matrix under a higher magnification.

thermal conductivity for binary alloy systems can be described by Nordheim's relation [6]. Nordheim's relation has been applied fairly well for isoelectronic binary alloy systems. However the relationship is somewhat skewed for non-isoelectronic alloy systems, deviating from the parabolic relationship.

U–Zr alloy exhibits a very small solubility of RE. The solubility is an order of a total impurity level normally encountered during a fabrication of metal fuel [7]. Furthermore, an Ag–Ni binary system, which is also almost insoluble with each other, showed no compositional dependency of the electrical conductivity [8]. Thus the effect of RE elements on the thermal conductivity of the U–Zr matrix itself is assumed to be negligible, thus the present analysis is confined to U–Zr alloys with a distribution of a heterogeneous RE-rich phase. It is also assumed that RE-rich precipitates are distributed rather randomly in the matrix with preserving their volume fraction. Lastly the thermal resistance at the interface between the matrix and RE-rich phase is neglected. Therefore the thermal conductivity of U–Zr–RE can be estimated by the effective thermal conductivity for the heterogeneous composites of the U–Zr matrix and the RE second phase.

The effect of the RE precipitates on the effective thermal conductivity is evaluated based on models for the thermal conductivity bounds for heterogeneous mixtures [9,10]. The material is composed of phase 1 of the U–Zr matrix, and phase 2 of the RE precipitate. k_e , the effective thermal conductivity is represented by k_1 , the thermal conductivity of the matrix, k_2 , the thermal conductivity of the second phase, and v_2 , the volume fraction of the dispersed phase.

The upper and lower bounds are calculated by means of series and parallel models, respectively:

$$k_e = \frac{1}{(1 - v_2)/k_1 + v_2/k_2}, \quad (1)$$

$$k_e = (1 - v_2)k_1 + v_2k_2. \quad (2)$$

Narrower bounds are provided with two forms of the Maxwell models of which type to use is determined by way of choosing the continuous phase. Phase 1 is continuous for Eq. (3), and phase 2 is for Eq. (4). Spheres are considered to be distributed regularly in the matrix:

$$k_e = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)v_2}{2k_1 + k_2 + (k_1 - k_2)v_2}, \quad (3)$$

$$k_e = k_2 \frac{2k_2 + k_1 - 2(k_2 - k_1)(1 - v_2)}{2k_2 + k_1 + (k_2 - k_1)(1 - v_2)}. \quad (4)$$

Bruggeman's asymmetric theory extends the range of the Maxwell's equation to the volume fraction of spheres close to one:

$$1 - v_2 = \frac{k_e - k_2}{k_1 - k_2} \sqrt[3]{\frac{k_1}{k_e}}. \quad (5)$$

The shape factor and the orientation factor were derived to account for a deviation from the spherical dispersions [11]. In the case of a second phase randomly distributed with neither phase being necessarily continuous or dispersed, Bruggeman's symmetric theory, so called the Effective Medium Theory (EMT), is applied:

$$(1 - v_2) \frac{k_1 - k_e}{k_1 + 2k_e} + v_2 \frac{k_2 - k_e}{k_2 + 2k_e} = 0. \quad (6)$$

3. Thermal conductivity of U–Zr–RE alloys

3.1. Estimation for U–Zr–RE alloys

The dependency of the thermal conductivity on the temperature and the Zr content for U–Zr alloys is available in the literature [12]:

$$k_{U-Zr} = 17.5 \frac{1 - 2.23W_z}{1 + 1.61W_z} + 1.54 \times 10^{-2} \frac{1 + 0.061W_z}{1 + 1.61W_z} T + 9.38 \times 10^{-6} T^2, \quad (7)$$

where, T is the temperature in Kelvin and W_z is the weight fraction of zirconium.

Temperature relationships of the thermal conductivity have been reported for RE such as Ce and Nd [13,14]. These show that thermal conductivity for Ce and Nd fall in a similar range. In this work, we assume that Ce represents all RE. In the temperature range less than a phase transition, the thermal conductivity of Ce is around 20% smaller than that of the U–Zr fuel as shown in Fig. 2.

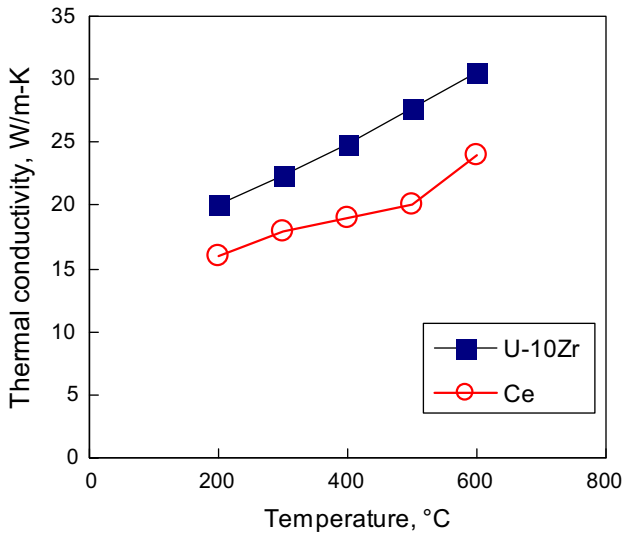


Fig. 2. Thermal conductivities for U-10Zr and Ce [12,13].

Material density of the U-Zr-RE alloys can be evaluated from the density of the U-Zr alloy and the RE. The estimated density for U-Zr alloy is in good agreement with the measured one [15]. From the density of the heterogeneous mixture, the volume fraction of the RE-rich phase is calculated. With the ratio of the thermal conductivity of RE to that of U-Zr, and the volume fraction, the thermal conductivity bounds for U-Zr-RE alloys are evaluated. These are performed for six different models for the macroscopic mixtures.

Fig. 3(a) shows the estimated thermal conductivity of U-10Zr-6Ce relative to that of U-Zr as a function of the ratio of the thermal conductivity of Ce normalized to that of U-Zr. It is shown that the series and parallel models serve as lower and upper bounds, respectively. The other models lie in a very narrow range, although there is a slight deviation from such a trend for the Maxwell's model under the assumption of a continuous distribution of the Ce phase. Fig. 3(b) shows the estimated thermal conductivity of U-10Zr-6Ce relative to that of U-Zr as a function of the volume fraction of the Ce-rich precipitate. Except for the extreme bounds, i.e., series and parallel models, it is difficult to discriminate any

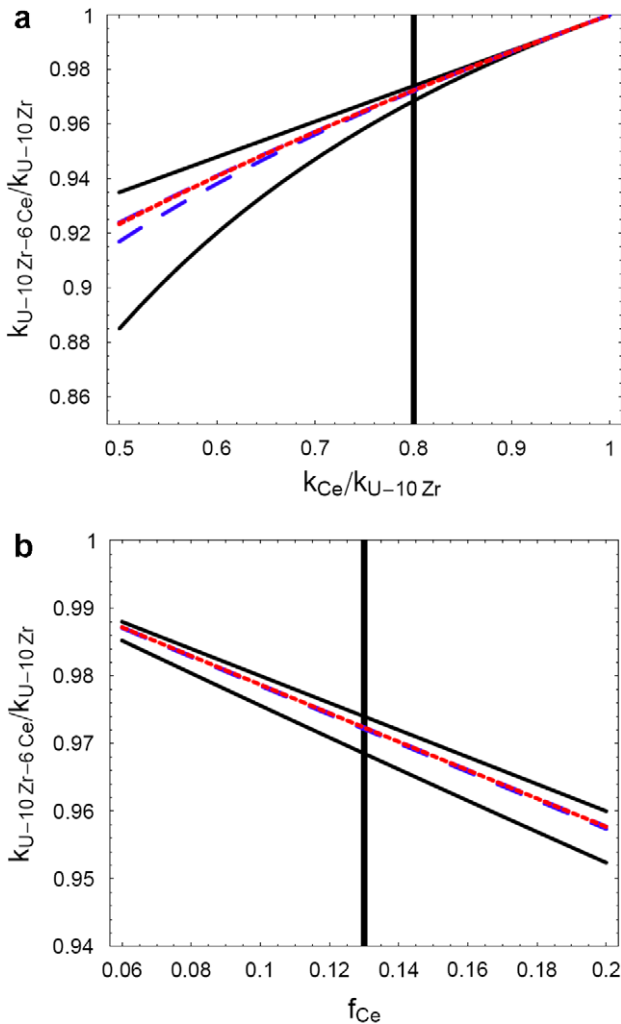


Fig. 3. Relative thermal conductivity of U-10Zr-6Ce; (a) as a function of the relative thermal conductivity of Ce, (b) as a function of the volume fraction of Ce (upper solid line: parallel, upper long dashed line: Maxwell, upper dotted line: Bruggeman, lower dotted line: EMT, lower long dashed line: Maxwell with continuous Ce phase, and lower solid line: series).

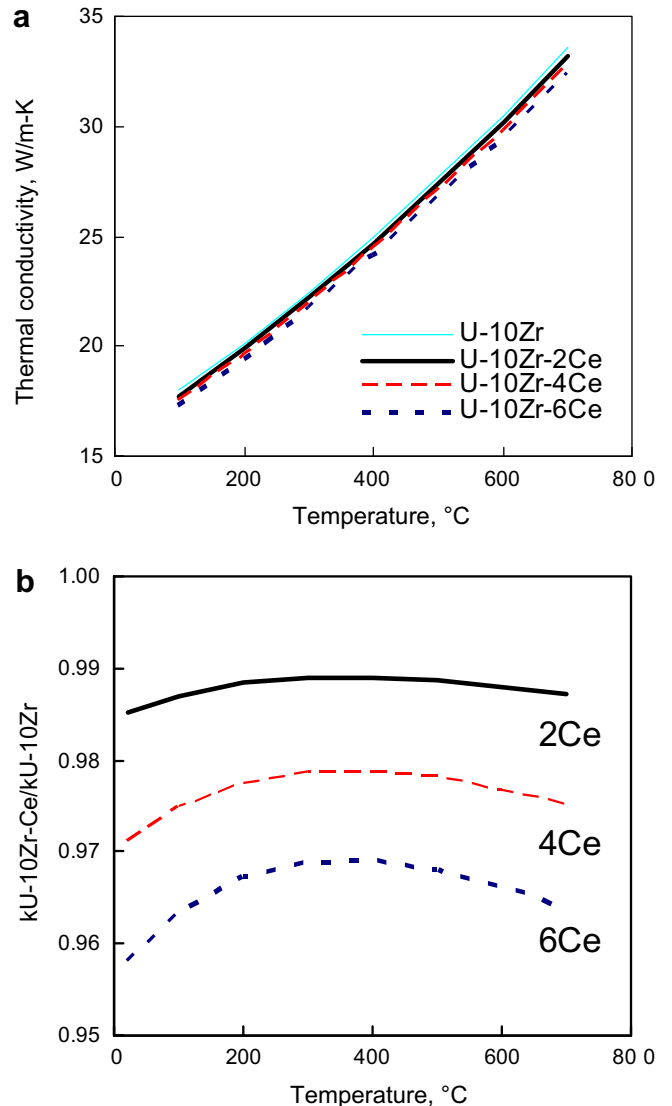


Fig. 4. Effect of the Ce content on the thermal conductivity of U-10Zr; (a) thermal conductivity, (b) relative value.

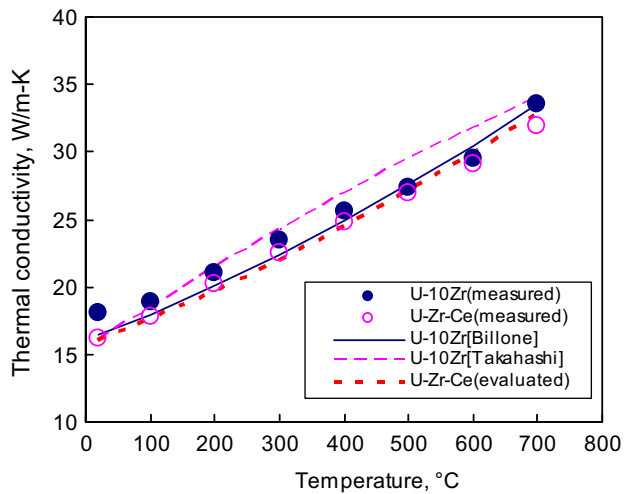


Fig. 5. Comparison of the thermal conductivities for U–Zr–Ce alloys.

difference among the thermal conductivities obtained from the other models.

Fig. 4 shows the estimated thermal conductivities as a function of temperature for U–Zr alloys containing Ce from 2, 4, to 6 wt%. As shown in Fig. 4, the addition of Ce up to 6 wt% is estimated to lower the thermal conductivity of the U–Zr alloy by less than 5%. This small change is attributable to the low volume fraction of the Ce phase, and the relatively high thermal conductivity of Ce. Thermal conductivity of the U–Zr alloy is reduced almost linearly with an increasing Ce content at all temperatures. It is expected that a similar conclusion can be drawn for a Nd addition because of its thermal conductivity, and very low solubility in U–Zr alloy.

3.2. Measurement of the thermal properties for the U–Zr–Ce alloy

Thermal properties of the U–Zr–Ce alloy were measured. Specimens were prepared by melting Ce together with U and Zr. Thermal diffusivity was measured using a laser flash (Netzsch, LFA-427). Disc specimens were used with dimensions of 8–12 mm ϕ \times 1 mm. Density was determined by an immersion technique. Kopp-Neumann's law was used to estimate the specific heat of the specimen.

The density of the specimen for the diffusivity measurement was close to that of U–10Zr alloy. It was also found that the diffusivity of the U–Zr–Ce specimen was reduced. This means that the Zr content is less than 10 wt% to account for the density increase,

and the diffusivity decrease due to the Ce addition, which was confirmed by EDX analyses.

The measured thermal conductivity of the U–Zr–Ce alloy is plotted in Fig. 5. Thermal conductivity was calculated by the product of the thermal diffusivity, density, and specific heat. The contribution of the density change to the thermal conductivity is more significant than those of the other. Thermal conductivity of U–Zr lies in between the reported ones [12,16]. It is slightly decreased by adding Ce of which the content is also below the target value as stated previously. Also the predicted thermal conductivity is decreased less than the measured value, which might be caused by the stabilized zirconium phases. Therefore, the effect of Ce on the thermal conductivity of U–Zr alloy is well described by the present heterogeneous mixture models.

4. Conclusion

Thermal conductivity of RE-bearing U–Zr fuels was investigated. Under an assumption of a RE-rich phase forming a macroscopic mixture with the matrix, the thermal conductivity was estimated for U–Zr–RE alloy. It was evaluated that the thermal conductivity of the U–Zr fuels would be lowered by less than 5% due to the addition of RE. The measurement of the thermal properties of U–Zr–Ce supported the present estimation.

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