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Dependence of Thermal and Electrical Conductivities of Actinide-Zirconium-Hydride Composite Materials on Hydrogen Concentration

B. Tsuchiya, K. Konashi, and M. Yamawaki

1. Introduction

High-level radioactive waste generated by the reprocessing of spent nuclear fuel from nuclear reactors includes long-lived radioactive nuclides. The current method for the disposal of such waste involves the vitrifying the waste under rigid control, storing it in monitored areas until the radiation decays to permissible levels, and then disposing it underground. Many types of transmutation methods have been studied to reduce the need for geological disposal. Recently, a transmutation method has been proposed for actinide radioactive waste; this method involves the use of hydride irradiation targets, which are loaded in the form of pellets into the core of fast breeder reactors containing mixed-oxide fuel (Yamamoto et al., 1997), (Yamawaki et al., 1998), and (Konashi et al., 2001). The irradiation hydride targets are composite materials, composed of titanium, zirconium, and hafnium hydrides, which contain hydrogen storage metals, and actinide elements such as $^{237}$Np, $^{241}$Am, and $^{243}$Am. The hydrides in the irradiation targets act as neutron moderators to provide a high flux of the thermal neutron. During irradiation, a temperature gradient occurs between the center and edge of the targets, and the distribution of the hydrogen concentration changes with the hydrogen diffusion (Huang et al., 2000). In the design of irradiation hydride targets, it is extremely important to investigate the changes in the mechanical, thermal, and electrical properties of the hydrides including their various hydrogen concentrations and to understand the basic heat transfer processes. Thermal conductivity is the most important physical property.

In the present study, the effects of the hydrogen content on the electrical and thermal properties of metal-hydride composite materials such as uranium-zirconium hydrides (45 wt% U-ZrH$_x$; $x = 1.60$ and 1.90) and uranium-thorium-zirconium hydrides (UTh$_4$Zr$_{10}$H$_x$; $x =$
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18–27) are investigated, and the heat conduction due to free electrons and that due to free phonons are discussed. From the results we can estimate the absolute values of the thermal conductivities for actinide-hydride composite materials including Np and Am. We also consider the correlation between the thermal transportation and the hydrogen content for the irradiation hydride targets since the hydrogen chemical potential of Th-hydride is close to those of Np- and Am-hydrides.

2. Experiments

Alloys with 45 wt% U-Zr and UTh₄Zr₁₀ were prepared by melting the constituent elements—U and Zr with a purity of 99.9 wt% and Th with a purity of 99.99 wt%—in vacuum in a high-frequency induction furnace, which was manufactured by Mitsubishi Materials Corporation. The composition of the UTh₄Zr₁₀ alloy was selected so as to ensure solid solution formation at high temperatures and more amount of absorbed hydrogen than any other U-Th-Zr alloy (Yamamoto et al., 1997) and (Yamawaki et al., 1998). The microstructure of the UTh₄Zr₁₀ alloy mixing α-Th with β-UZr₂₊ₓ phases, as shown in Fig. 2(a), was observed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The hydrogenation of 45 wt% U-Zr and UTh₄Zr₁₀ alloys was carried out using Sievert’s apparatus, supplied by Mitsubishi Materials Corporation (Tsuchiya et al., 2000). The 45 wt% U-Zr and UTh₄Zr₁₀ alloys, mounted into a quartz tube evacuated under a pressure of 1.3 × 10⁻⁴ Pa, were heated at 1173 K for 3.5 h to remove a small amount of residual hydrogen, absorbed into the alloys during the melting and quenching of the constituent elements. The alloys were then heated at temperatures ranging from 673 to 1173 K and exposed to pure protium gas in the quartz tube at pressures ranging from 1.0 × 10³ to 1.0 × 10⁵ Pa, where the temperature and pressure values were measured using a thermocouple and a baratoron, respectively. When equilibrium for the hydrogenation was achieved, the protium gas was removed from the quartz tube and the annealing temperature was then gradually reduced to room temperature, with the sample still in the tube.

![SEM micrograph of 45 wt% U-ZrH₁.₆₀, composed of α-U (white area) and δ-ZrH₁.₆₀ (dark area) phases](https://www.intechopen.com)
Fig. 2. SEM (BEI: backscattered electron image) micrographs of (a) UTh<sub>4</sub>Zr<sub>10</sub> alloy, which is composed of α-Th (white area) and β-UZr<sub>2+x</sub> (black area) phases, (b) and (c) UTh<sub>4</sub>Zr<sub>10</sub>H<sub>24</sub> which is composed of α-U (white area), ThZr<sub>2</sub>H<sub>5.59</sub> (gray area), and ZrH<sub>1.86</sub> (black area) phases.
The compositions of the 45 wt% U-Zr and UTh$_{10}$Zr$_{10}$ hydrides were measured based on the hydrogen pressure changes at equilibrium and the mass gains before and after hydrogenation. The fabricated products were 45 wt% U-ZrH$_x$ ($x = 1.60$ and $1.90$) and UTh$_4$Zr$_{10}$H$_x$ ($x = 18$–$27$). The surface morphology and crystalline structure of these two hydride composite materials were extensively examined using SEM and XRD. Figure 1 shows an SEM (BEI: backscattered electron image) micrograph of 45 wt% U-ZrH$_{1.60}$. It reveals that the U phase of approximately 1.0 \( \mu \)m in diameter is dispersed in the bulk of the ZrH$_{1.60}$ phase; this is indicative of a composite material mixing an actinide element with a hydride. The morphology of 45 wt% U-ZrH$_{1.90}$ is almost the same as that of 45 wt% U-ZrH$_{1.60}$. The structures of U, ZrH$_{1.60}$, and ZrH$_{1.90}$ are orthorhombic (\( \alpha \)-phase), face-centered cubic (\( \delta \)-phase), and face-centered tetragonal (\( \varepsilon \)-phase), respectively (Tsuchiya et al., 2001).

BEI-SEM micrographs with magnifying powers of 5000 and 10000 for UTh$_4$Zr$_{10}$H$_{24}$ are shown in Figs. 2(b) and (c), respectively. The \( \alpha \)-U (white area) and ZrH$_{1.86}$ (black area) phases of approximately 1.0 \( \mu \)m in diameter are dispersed in the bulk of the ThZr$_2$H$_{5.59}$ (gray area) phase; this is indicative of a composite material mixing an actinide element with two kinds of hydrides. The values of \( x \) in ThZr$_2$H$_x$ and \( \varepsilon \)-ZrH$_x$ were estimated based on the relationship between the measured XR D data and published data (Nakata et al., 1966), (Yamamoto et al., 1997), and (Tsuchiya et al., 2002). The other hydrides of UTh$_4$Zr$_{10}$H$_x$ were determined to be ThZr$_2$H$_{3.30}$ and \( \delta \)-ZrH$_{1.69}$ (UTh$_4$Zr$_{10}$H$_{1.8}$), ThZr$_2$H$_{4.17}$ and \( \varepsilon \)-ZrH$_{1.74}$ (UTh$_4$Zr$_{10}$H$_{2.0}$), ThZr$_2$H$_{5.59}$ and \( \varepsilon \)-ZrH$_{1.83}$ (UTh$_4$Zr$_{10}$H$_{2.3}$), ThZr$_2$H$_{5.79}$ and \( \varepsilon \)-ZrH$_{1.87}$ (UTh$_4$Zr$_{10}$H$_{2.6}$), and ThZr$_2$H$_{9.4}$ and \( \varepsilon \)-ZrH$_{1.90}$ (UTh$_4$Zr$_{10}$H$_{2.7}$), respectively. Therefore, the hydrides of UTh$_4$Zr$_{10}$H$_x$ (\( x = 18$–$27 \)) are mainly three-phase composite materials, composed of \( \alpha \)-U, \( \delta \)-phase ZrH$_x$ (1.5 \( \leq \ x \leq \ 1.7 \)) or \( \varepsilon \)-phase ZrH$_x$ (1.7 \( \leq \ x \leq \ 2.0 \)), and ThZr$_2$H$_x$ (4.0 \( \leq \ x \leq \ 6.3 \)), although there are small quantities of residual Th, Th hydrides, and oxides such as ThO$_2$ and ZrO$_2$.

Figures 3(a) and (b) show the hydrogen release from 45 wt% U-ZrH$_{1.60}$, U-ZrH$_{1.90}$, ZrH$_{1.60}$, ZrH$_{1.90}$, UTh$_4$Zr$_{10}$H$_{2.0}$, UTh$_4$Zr$_{10}$H$_{2.4}$, and UTh$_4$Zr$_{10}$H$_{2.7}$ by isochronal annealing for 10 min at temperatures of 298–973 K. In Fig. 3(a) it is important to note that the decomposition temperature of 823 K for U-ZrH$_{1.60}$ is the same as that for ZrH$_{1.60}$, while the temperature of 773 K for U-ZrH$_{1.90}$ is higher than that for ZrH$_{1.90}$. The decomposition temperatures of UTh$_4$Zr$_{10}$H$_{2.0}$, UTh$_4$Zr$_{10}$H$_{2.4}$, and UTh$_4$Zr$_{10}$H$_{2.7}$ are approximately 823, 723, and 673 K, respectively, as shown in Fig. 3(b). There are two types of stages in the hydrogen molecular re-emission process. The first and second stages of the re-emission are due to hydrogen release from the ThZr$_2$H$_x$ and ZrH$_x$ phases, respectively.

To avoid the reduction of the hydrogen concentration by hydrogen molecular re-emission, special specimen containers, made of sapphire, were used for the thermal diffusivity measurements with a laser flash method (Tsuchiya et al., 2002). The heating temperatures were successful in elevating to 900 K (U-ZrH$_{1.60}$, UTh$_4$Zr$_{10}$H$_{1.8}$, and UTh$_4$Zr$_{10}$H$_{2.0}$), 840 K (U-ZrH$_{1.90}$), 800 K (UTh$_4$Zr$_{10}$H$_{2.3}$ and UTh$_4$Zr$_{10}$H$_{2.4}$), 750 K (UTh$_4$Zr$_{10}$H$_{2.4}$ and UTh$_4$Zr$_{10}$H$_{2.6}$), and 700 K (UTh$_4$Zr$_{10}$H$_{2.7}$) during the thermal diffusivity measurements. In addition, an electrical resistivity measurement was carried out from room temperature to 700–800 K for each hydride using a four-contact method with a direct current (DC) of 350 mA, to clarify the heat conduction due to free electrons.
3. Results and discussion

Figures 4(a) and (b) show the thermal diffusivities of 45 wt% U-ZrH$_{1.60}$, 45 wt% U-ZrH$_{1.90}$, UTh$_{4}$Zr$_{10}$H$_{18}$, UTh$_{4}$Zr$_{10}$H$_{20}$, UTh$_{4}$Zr$_{10}$H$_{23}$, UTh$_{4}$Zr$_{10}$H$_{24}$, and UTh$_{4}$Zr$_{10}$H$_{26}$, measured while increasing (solid marks) and decreasing (open marks) the heating temperature. The agreement between the values on heating and cooling indicates that there is no hydrogen release from the hydrides during the thermal diffusivity measurements. The thermal diffusivities for U-ZrH$_{1.60}$ and U-ZrH$_{1.90}$ increased with increasing hydrogen concentration and with decreasing temperature. The temperature dependence of the thermal diffusivities for U-ZrH$_{1.60}$ and U-ZrH$_{1.90}$ is similar to that for ZrH$_{1.60}$ and ZrH$_{1.90}$ (Tsuchiya et al., 2002), although the absolute values are different, as shown in Fig. 4(a). This is because the thermal diffusivity of U is nearly constant in the temperature range up to 900 K (Takahashi et al., 1988). The present experimental values are approximately 1.5 times those of 10 wt% U-ZrH$_{x}$ (Nakata et al., 1966), depending on the amount of doped-U. On the other hand, the thermal diffusivities of UTh$_{4}$Zr$_{10}$H$_{23}$, UTh$_{4}$Zr$_{10}$H$_{24}$, UTh$_{4}$Zr$_{10}$H$_{26}$, and UTh$_{4}$Zr$_{10}$H$_{27}$ decreased with increasing temperature, while those of UTh$_{4}$Zr$_{10}$H$_{18}$ and
UTh₄Zr₁₀H₂₀ increased gradually up to a temperature of 940 K, as shown in Fig. 4(b). It is interesting to note that the thermal diffusivities at 640 K for UTh₄Zr₁₀H₁₈-27 are equal.

To clarify the electronic heat conduction for U-ZrHₓ and UTh₄Zr₁₀Hₓ, the electrical resistivity was measured when heating to 700–800 K and cooling to room temperature. Figures 5(a) and (b) show the electrical resistivities of 45 wt% U-ZrH₁₆₀, 45 wt% U-ZrH₁₀₀, UTh₄Zr₁₀H₁₈₀, UTh₄Zr₁₀H₂₀, UTh₄Zr₁₀H₂₃, and UTh₄Zr₁₀H₂₆ when heating (solid marks) and cooling (open marks). The electrical resistivities of U-ZrHₓ increased as the temperature increased and the hydrogen concentration decreased, as shown in Fig. 5(a). In the case of U-ZrH₁₉₀, a slight distortion between the values obtained on heating and those obtained on cooling indicates a reduction in the hydrogen concentration, following hydrogen release from ZrH₁₉₀. The hydrogen concentration dependence on the resistivity of U-ZrHₓ strongly dominates that of ZrHₓ (Bickel & Berlincourt, 1970) and (Tsuchiya et al., 2002) and slightly dominates that of U (Bell, 1954). The electron scattering due to hydrogen vacancy in the hydrides significantly affects the resistivity. The scattering of electrons due to optical phonons as well as acoustic phonons affects the resistivity behavior at higher temperature.
The results for UTh$_4$Zr$_{10}$H$_x$ showed gradual decreases in the electrical resistivity with an increase in the hydrogen composition to approximately 690 K, which was higher than the temperature (640 K) for the thermal diffusivity, and an increase above 690 K, as shown in Fig. 5(b). The electron scattering due to hydrogen vacancies in both the ZrH$_x$ and ThZr$_2$H$_x$ phases significantly reflects the temperature dependence of the electronic conduction for UTh$_4$Zr$_{10}$H$_x$. In particular, at higher temperatures the scattering of electrons due to optical phonons in the ThZr$_2$H$_x$ phase may essentially dominate the resistivity, although the resistivity of ThZr$_2$H$_x$ has not been measured yet.

Fig. 5. Temperature dependence of electrical resistivities for (a) U-ZrH$_x$ (x = 1.60 and 1.90), ZrH$_x$ (x = 1.54 and 1.90), U, and (b) UTh$_4$Zr$_{10}$H$_x$ (x = 0, 18, 20, 23, and 26)

Figures 6 (a) and (b) show the thermal conductivities, $\lambda$, of 45 wt% U-ZrH$_{1.60}$ and 45 wt% U-ZrH$_{1.90}$, respectively, at temperatures up to 773 K, which were calculated via $\lambda = \alpha C_p d$, where $\alpha$, $C_p$, and $d$ represent the measured thermal diffusivity, the specific heat, and the density, respectively. The experimental values of $d$ for U-ZrH$_{1.60}$ and U-ZrH$_{1.90}$ were 8.256 and 8.209 g/cm$^3$, respectively. The values of $C_p$ for U-ZrH$_{1.60}$ and U-ZrH$_{1.90}$ were expressed by the following equations as functions of temperature, $T$: $C_p = 0.120 + 4.72 \times 10^{-4} T$ and $C_p = 0.146 + 4.71 \times 10^{-4} T$ [J/(g • K)], respectively, taking into account the weight fractions of U and ZrH$_x$ and reported data on the specific heat of U; $C_p = 0.120$ J/(g • K) and
\[ ZrH_x \quad (x = 1.60–2.00); \quad C_p = \left[ 6.98 \times 10^{-2} T + \left( 34.4 + 14.8 \times (x - 1.65) \right) \right] / M_{ZrH_x} \left[ J/(g \cdot K) \right], \]

where \( x \) and \( M_{ZrH_x} \) are the composition of H in ZrH\(_x\) and the molecular weight of ZrH\(_x\) (Simnad, 1981). The temperature dependence of the thermal conductivity for 45 wt% U-ZrH\(_{1.60}\) was almost constant with increasing temperature, while that for U-ZrH\(_{1.90}\) showed a gradual decrease. The conductivities of approximately 0.27 W/(cm·K) (45 wt% U-ZrH\(_{1.60}\)) and 0.43 W/(cm·K) (45 wt% U-ZrH\(_{1.90}\)) at a temperature of 700 K were higher than the reported value (0.18 W/(cm·K)) for 10 wt% U-ZrH\(_{1.6}\) without temperature dependence; this value has been used for TRIGA reactors. The conductivity strongly depends on the quantities of absorbed hydrogen and doped-U.

Fig. 6. Thermal conductivities, \( \lambda \), of (a) U-ZrH\(_{1.60}\) and (b) U-ZrH\(_{1.90}\). \( \lambda_e \) and \( \lambda_p \) represent the thermal conductivity due to free electrons and that due to phonons, respectively.

Figures 7 (a), (b), (c), and (d) show the thermal conductivities, \( \lambda \), of UTh\(_4\)Zr\(_{10}\)H\(_{18}\), UTh\(_4\)Zr\(_{10}\)H\(_{20}\), UTh\(_4\)Zr\(_{10}\)H\(_{23}\), and UTh\(_4\)Zr\(_{10}\)H\(_{26}\), respectively, calculated using the equation given above. The density and specific heat values of UTh\(_4\)Zr\(_{10}\)H\(_x\) (\( x = 18–27\)) are expressed by considering the experimental results and the reported values of specific heat as follows: \( d = 8.40 - 2.99 \times 10^{-2} x \left[ g/cm^3 \right] \) and \( C_p = -0.110 + 6.87 \times 10^{-4} T + 6.36 \times 10^{-3} x \left[ J/(g \cdot K) \right] \), where \( x \) and \( T \) are the composition of H in UTh\(_4\)Zr\(_{10}\)H\(_x\) and the temperature (Tsuchiya et al., 2000). The high thermal conductivity (approximately 0.13 W/(cm·K)) for UTh\(_4\)Zr\(_{10}\)H\(_x\) (18–27) at a
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温度为700 K，这与报道的值（0.18 W/(cm·K)）吻合，当线性功率高时会增加反应堆的安全等级。对于所有UThZr10Hx，温度对热导率的影响随温度的升高而逐渐增加。另一方面，氢对热导率的影响在690 K的边界温度显著变化，对应于温度和组成对电性能和热扩散的影响。

热导率被评价为电子导电性λe的值，它们从关系λe = LeσT，也就是基于Wydeemann-Franz规则的。在该等式中，σ表示电导率（σ = 1/ρ）并从测量的电阻率获得。更进一步，Le是对应的电子导电性洛伦兹数，用Le = (π²/3)(kB/e)² ≈ 2.45 × 10⁻⁸ WΩ/K²，其中kB和e分别是玻尔兹曼常数和基本电荷。因此，热导率与声子导热λp的关联通过λ = λe + λp被确定，如图6和7所示。

对于U-ZrHx，热是通过每个相在300–800 K的温度范围中进行传递的，因为自由电子和声子的迁移，尽管绝对值取决于氢的含量，且在450 K以下的温度，声子的贡献大于电子的。

对于UThZr10Hx，在300–800 K的温度范围内，电子的迁移对热传导的贡献大于声子的。材料的热性质似乎和金属更相似而不是绝缘体。这可能和重金属的自由电子数量有关。热导率随氢含量的减少而减少，这表明电子和声子的散射对非化学计量的化合物有显著影响。特别是，声子导热随温度的升高而增加。包含ThZr2Hx的复合材料正在进一步研究，以详细地澄清氢对热运输过程的影响。
Fig. 7. Thermal conductivities, $\lambda$, of (a) UTh$_4$Zr$_{10}$H$_{18}$, (b) UTh$_4$Zr$_{10}$H$_{20}$, (c) UTh$_4$Zr$_{10}$H$_{23}$, and (d) UTh$_4$Zr$_{10}$H$_{26}$. $\lambda_e$ and $\lambda_p$ represent the thermal conductivity due to free electrons and that due phonons, respectively.
4. Conclusions

The thermal diffusivities of the actinide-hydride composite materials such as 45 wt% U-ZrH$_x$ ($x = 1.60$ and $1.90$) and UTh$_4$Zr$_{10}$H$_x$ ($x = 18-27$) were measured by the laser flash method, and their thermal conductivities were calculated by taking into account the density and the specific heat. The thermal conductivity was significantly dependent on the quantities of doped actinide metals and formed hydrides in the composite materials and, in particular, on the hydrogen concentration. The heat conduction due to electrons and that due to phonons were determined using the Wiedemann-Franz rule on the basis of the electrical conductivity calculated using the measured electrical resistivity. In the case of thermal conduction by U-ZrH$_x$ at room temperature, phonon-phonon scattering is dominant, and the number of electrons and photons are approximately equal in the case of heat conduction at high temperatures of above 450 K. In addition, the thermal conductivity decreases with a decrease in the hydrogen content; this is indicative of an increase in the hydrogen vacancy, because phonon scattering by electrons and phonons has a significant effect on the nonstoichiometric structures of the hydrides.

The actinide-hydride composite materials of UTh$_4$Zr$_{10}$H$_x$ showed a gradual increase in the thermal conductivities with an increase in the temperature. The dependence of the thermal conductivities on the composition showed an increase with an increase in the hydrogen content at temperatures below approximately 690 K. In contrast, a decrease in the composition dependence was observed at temperatures above 690 K. For heat conduction at temperatures below 690 K, the contribution of the migration of the electrons is considerably larger than that of the migration of the phonons. The increase in the conductivity at higher temperatures may be attributed to the enhancement of phonon conduction in the ThZr$_2$H$_x$ phase.

It is concluded that the actinide-hydride composite materials with high thermal conductivities of approximately 0.27 W/(cm·K) (45 wt% U-ZrH$_{1.60}$), 0.43 W/(cm·K) (45 wt% U-ZrH$_{1.90}$), and 0.13 W/(cm·K) (UTh$_4$Zr$_{10}$H$_{18-27}$) at 700 K, which have thermal properties similar to those of metals, are potential candidates for fabricating the irradiation target used in the transmutation of actinide radioactive wastes.

5. References


Due to their good mechanical characteristics in terms of stiffness and strength coupled with mass-saving advantage and other attractive physico-chemical properties, composite materials are successfully used in medicine and nanotechnology fields. To this end, the chapters composing the book have been divided into the following sections: medicine, dental and pharmaceutical applications; nanocomposites for energy efficiency; characterization and fabrication, all of which provide an invaluable overview of this fascinating subject area. The book presents, in addition, some studies carried out in orthopedic and stomatological applications and others aiming to design and produce new devices using the latest advances in nanotechnology. This wide variety of theoretical, numerical and experimental results can help specialists involved in these disciplines to enhance competitiveness and innovation.

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