

The effects of phase transformation on the heat conduction of hafnium hydrides

B. Tsuchiya^{a,*}, M. Teshigawara^b, K. Konashi^a, S. Nagata^a, T. Shikama^a

^a Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

^b Tokai Research and Development Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan

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Abstract

Thermal diffusivity measurements for hafnium hydrides (HfH_x) with different hydrogen concentrations ($\alpha + \delta'$ - $\text{HfH}_{0.20}$, $\alpha + \delta'$ - $\text{HfH}_{0.92}$, $\alpha + \delta'$ - $\text{HfH}_{1.15}$, δ' - $\text{HfH}_{1.48}$, δ' - $\text{HfH}_{1.57}$, δ - $\text{HfH}_{1.70}$, $\delta + \epsilon$ - $\text{HfH}_{1.76}$, ϵ - $\text{HfH}_{1.88}$ and ϵ - $\text{HfH}_{2.02}$) were carried out within the temperature range of 290–570 K by means of a laser-flash method. The temperature dependence of the thermal diffusivity for $\alpha + \delta'$ - $\text{HfH}_{0.20}$ was the result of a mixture of a hexagonal α -phase and a slightly deformed face-centered cubic (fcc) δ' -phase structure that was similar to that observed in α -Hf. The thermal diffusivities for $\text{HfH}_{0.92-2.02}$ at temperatures below 373 K drastically changed due to the phase transformation, while those at temperatures above 373 K remained almost the same, 0.06–0.08 cm^2/s , which is approximately half that of α -Hf. In particular, the thermal diffusivities for δ' - $\text{HfH}_{1.48}$ and δ' - $\text{HfH}_{1.57}$ changed between 360 and 390 K with the conversion to an ideal fcc structure in the δ -phase. The temperature dependence of the thermal conductivities for $\alpha + \delta'$ - $\text{HfH}_{0.20}$, $\alpha + \delta'$ - $\text{HfH}_{0.92}$, δ' - $\text{HfH}_{1.48}$, δ - $\text{HfH}_{1.70}$ and ϵ - $\text{HfH}_{2.02}$ were evaluated by way of calculations from the experimental thermal diffusivity data and reference data for the specific heat and density.

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1. Introduction

The application of hafnium hydrides (HfH_x) as control rods for the fast neutron flux process in fast reactors was recently proposed [1]. Hafnium (Hf), as a storage metal for pure hydrogen, has both a significantly high neutron absorption capacity and captures cross section with regards to thermal neutrons, and does not generate certain gases such as ^4He during the nuclear reaction. In addition, hydrogen atoms occupying tetrahedral interstitial sites of the hydride play a role as fast neutron moderators in gaining thermal neutrons. Therefore, an HfH_x control rod is expected to be able to efficiently absorb a large number of fast neutrons, and has the additional advantage of a much longer lifetime than the conventional boron carbide (B_4C) rod. In order to design this hydride control rod, it is extremely important to understand changes in the physical, chemical, thermal and

mechanical properties of the hydrides relative to the hydrogen distribution within the rod itself.

At this time, there is a scarcity of reported data concerning the thermal conductivity, which is one of the most important parameters regarding the thermal properties, of HfH_x over a wide range of temperatures and hydrogen concentrations. In the present study, the objectives were to obtain quantitative thermal diffusivity values for HfH_x ($0.20 \leq x \leq 2.02$) and to evaluate the thermal conductivities at these hydrogen concentrations while taking into account the specific heat and the density of the compound. The heat conduction of HfH_x is discussed mainly in terms of its influence on the phase transformation that results from changing the temperature and hydrogen concentration.

2. Experiments

HfH_x compounds with hydrogen compositions in the range of $0.20 \leq x \leq 2.02$ were prepared with a Sieverts apparatus by heating and outgassing hafnium pure metal (99.8% quality) in an evacuated quartz tube at 1073 K, followed by exposure to 99.9% pure hydrogen gas in the tube at pressures ranging from 0.1 to 1.0×10^5 Pa for 4 h. The specimens were then cooled

* Corresponding author. Tel.: +81 22 215 2063; fax: +81 22 215 2061.
E-mail address: tsuchiya@imr.tohoku.ac.jp (B. Tsuchiya).

to room temperature at a rate of 4.5×10^{-3} K/s while still in the tube. The compositions of the specimens were calculated based on mass gain after the hydrogenation.

X-ray diffraction (XRD) measurements confirmed that the hafnium–hydrogen system at room temperature consists of three phases and the presence of mixtures. The crystal structures of the compositions with $1.60 \leq x \leq 1.73$ and $1.84 \leq x \leq 2.02$ were face-centered cubic (fcc) δ -phase and face-centered tetragonal (fct) ε -phase, respectively [2–4]. The HfH_x samples with $1.74 \leq x \leq 1.83$ had $\delta + \varepsilon$ -phase structures that were mixtures of an δ -phase with a ε -phase. The crystal structures of the composition with $1.48 \leq x \leq 1.59$ were distinguishable from the δ -phase structure by the XRD patterns, and exhibited a pseudocubic defect δ -phase (δ' -phase) that has previously been reported in other literature [4–6]. The unit cell of this pseudocubic phase is slightly deformed and displays some tetragonal characteristics, such as the lattice constants for the a and b axes having the same values as those of the δ -phase, while that for the c axis is lower. It was also confirmed from diffraction patterns obtained from TEM observation experiments during annealing up to 673 K that the deformed cubic phase converts into a face-centered cubic phase at temperatures above 353 K. The tetragonal phase in the present study was present for $\text{HfH}_{1.48-1.57}$. The HfH_x samples with $0.20 \leq x \leq 1.47$ had $\alpha + \delta'$ -phase structures consisting of a mixture of a hexagonal α -phase and a δ' -phase [4]. Based on this, the HfH_x samples prepared were determined to be $\alpha + \delta'$ - $\text{HfH}_{0.20}$, $\alpha + \delta'$ - $\text{HfH}_{0.92}$, $\alpha + \delta'$ - $\text{HfH}_{1.15}$, δ' - $\text{HfH}_{1.48}$, δ' - $\text{HfH}_{1.57}$, δ - $\text{HfH}_{1.70}$, $\delta + \varepsilon$ - $\text{HfH}_{1.76}$, ε - $\text{HfH}_{1.88}$ and ε - $\text{HfH}_{2.02}$. It has been reported in the literature [3] that the hydrogen atoms in the ε - and δ -phases are located in vacant tetrahedral interstices. Scanning electron microscope micrographs have shown the existence of microcracks in the surface of the HfH_x samples with $1.83 \leq x$.

The thermal diffusivity measurements were carried out on samples $\phi 10.0 \times 1.0 \text{ mm}^3$ in size using the laser-flash method [7]. This method makes it possible to investigate thermal properties in simple systems. The measurements were carried out during heating of the samples up to 570 K and cooling down to room temperature. The upper limit of 570 K was used so as to avoid the rapid decomposition of the HfH_x samples at temperatures above 600 K. Within the temperature range of 290–570 K, several of the phases in the HfH_x samples were maintained. One exception to this was the Hf-rich tetragonal compound δ' , which approaches δ cubic symmetry at about 358–373 K [5,6].

3. Experimental results and discussion

Fig. 1(a)–(c) show the thermal diffusivities of $\text{HfH}_{0.20-1.15}$, $\text{HfH}_{1.48-1.70}$ and $\text{HfH}_{1.76-2.02}$, respectively, as a function of temperature from 290 to 570 K, where (●, ▲, ◆) and (○, △, ◇) represent the data when heating and cooling the samples, respectively. The dashed curve in Fig. 1(a) represents the thermal diffusivity of α -Hf, which has previously been reported [8]. The agreement between the heating (●, ▲, ◆) and cooling (○, △, ◇) curves indicates no reduction in the hydrogen concentration of the samples due to thermal desorption with heating up to 570 K. For $\alpha + \delta'$ - $\text{HfH}_{0.20-1.15}$, the thermal diffusivities at 300 K were higher than those of α -Hf, as shown in Fig. 1(a). In addition, the thermal diffusivity of $\text{HfH}_{0.20}$ was coincident with that of α -Hf at temperatures above 350 K, while those of $\text{HfH}_{0.92}$ and $\text{HfH}_{1.15}$ exponentially decreased with increasing temperature. Moreover, the diffusivity of $\text{HfH}_{1.15}$ was slightly higher than that of $\text{HfH}_{0.92}$. These results show that the thermal diffusivity of $\alpha + \delta'$ - HfH_x greatly depends on the ratio of α -Hf to δ' - HfH_x , since HfH_x coexist with hafnium metal in these samples. The heat conductions of α -Hf and δ' - HfH_x determine the overall thermal diffusivity of $\alpha + \delta'$ - HfH_x at low and high hydrogen concentrations, respectively. As the total composition of hydrogen increases, the δ' -phase approaches the stoichiometric ratio of an fcc structure like that of CaF_2 , and the incremental changes

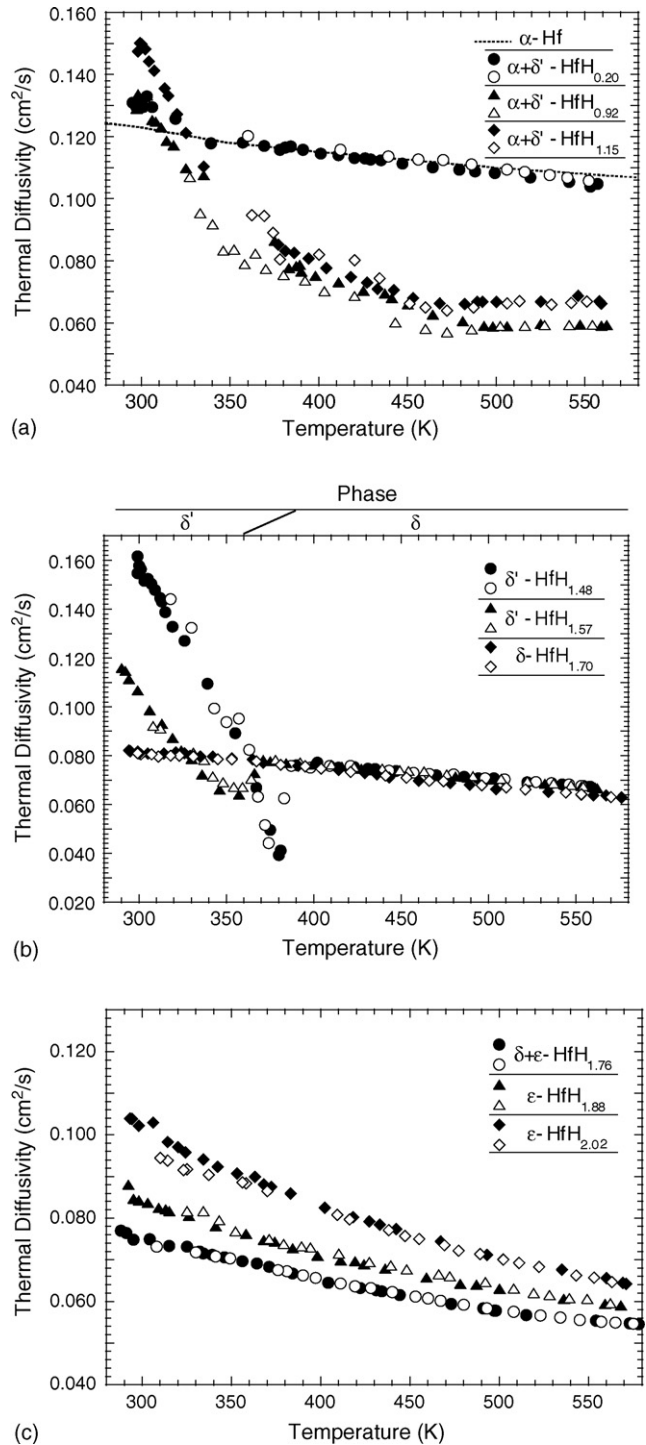


Fig. 1. Temperature dependence of the thermal diffusivities for (a) α -Hf, $\alpha + \delta'$ - $\text{HfH}_{0.20}$, $\alpha + \delta'$ - $\text{HfH}_{0.92}$ and $\alpha + \delta'$ - $\text{HfH}_{1.15}$, (b) δ' - $\text{HfH}_{1.48}$, δ' - $\text{HfH}_{1.57}$ and δ - $\text{HfH}_{1.70}$ and (c) $\delta + \varepsilon$ - $\text{HfH}_{1.76}$, ε - $\text{HfH}_{1.88}$ and ε - $\text{HfH}_{2.02}$

in the diffusivity are caused by the reduction of phonon and electron scattering due to hydrogen vacancies. For δ' - $\text{HfH}_{1.48}$ and $\text{HfH}_{1.57}$, shown in Fig. 1(b), the thermal diffusivity quickly decreased until the temperature reached 360 K, and thereafter quickly increased in the range of 370–390 K, at which point it began to gradually decrease again to 570 K. The thermal diffusivity values at temperatures above the 370–390 K range were

in agreement with those for δ -HfH_{1.70}. This thermal behavior is due to the phase transformation from the δ' - to the δ -structure. Moreover, the migration of hafnium atoms in the lattice cell of the hydride plays an important role in the change in the thermal diffusivity for the δ' -phase. For HfH_{1.76–2.02}, shown in Fig. 1(c), the thermal diffusivity increased with decreasing temperature and increasing hydrogen concentration. It is known that phonon–phonon and electron–phonon scattering contribute to the temperature dependence of the thermal diffusivity according to the relationship between the thermal and electrical conductivities for ϵ -phase zirconium and δ -phase titanium hydrides [9,10]. Additionally, the thermal diffusivity of $\delta + \epsilon$ -HfH_{1.76} is lower yet than that of ϵ -HfH_{*x*}, which decreases with a decrease in the composition (*x*) from 2.02 to 1.88. These results indicate that the decrease in the thermal conduction with decreasing hydrogen concentration can be attributed to the effects of phonon and electron scattering at both the interface between the δ - and ϵ -phases and at hydrogen vacancies at the tetrahedral interstitial sites.

In order to show in more detail the effects of the phase transformation on the thermal diffusivities, the thermal diffusivities at 300, 350, 400, 450, 500 and 550 K for HfH_{0.20–2.02} are plotted as a function of the composition in Fig. 2. However, it should be noted that the data at temperatures above 400 K for the compositions of 1.48 and 1.57 are for the δ -phase. The thermal diffusivities at 300 K for HfH_{0.20–1.48} and HfH_{1.57–2.02} were higher and lower, respectively, than that of α -Hf. Furthermore, the thermal diffusivities at temperatures above 400 K for HfH_{0.92–2.02} were almost constant in the range of 0.06–0.08 cm²/s, and were about a factor of one-half lower than that of α -Hf. Also, the composition dependence of the thermal diffusivity for HfH_{1.76–2.02} indicates that phonon scattering due to electrons and phonons has a greater effect on the mixed phases and non-stoichiometric structures, which is consistent with past results for ZrH_{1.76–2.02} [9].

Fig. 3 shows the thermal conductivities of α -Hf, $\alpha + \delta'$ -HfH_{0.20}, $\alpha + \delta'$ -HfH_{0.92}, δ' -HfH_{1.48}, δ -HfH_{1.70} and ϵ -HfH_{2.02}. The thermal conductivities, λ_i , for $i = \text{HfH}_x$ and Hf were

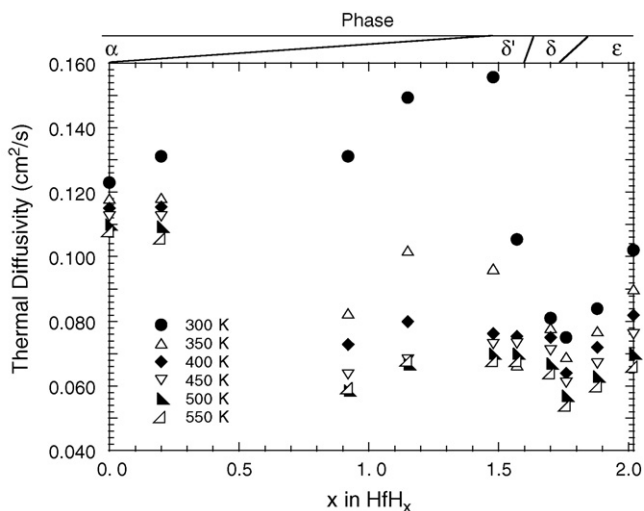


Fig. 2. Composition dependence of the thermal diffusivities at temperatures of 300, 350, 400, 450, 500 and 550 K.

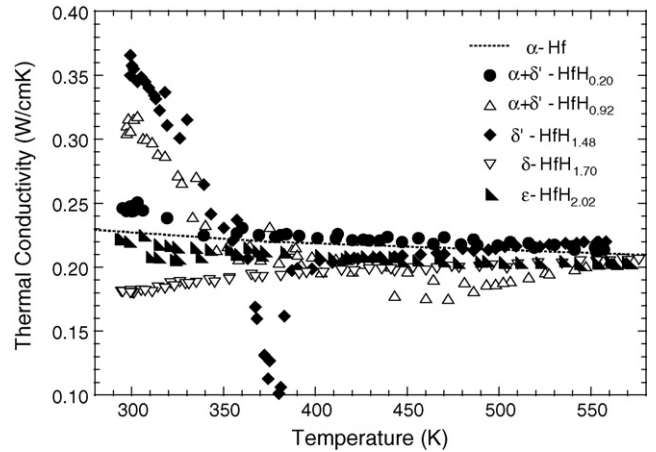


Fig. 3. Temperature dependence of the thermal conductivities for α -Hf, $\alpha + \delta'$ -HfH_{0.20}, $\alpha + \delta'$ -HfH_{0.92}, δ' -HfH_{1.48}, δ -HfH_{1.70} and ϵ -HfH_{2.02}.

calculated for $\lambda_i = \alpha_i C_p^i d_i$, where α_i , C_p^i and d_i are the thermal diffusivity, specific heat and density, respectively, of *i*. The values of C_p^{Hf} can be expressed as a function of temperature *T* with $C_p^{\text{Hf}} = 0.130 + 4.64 \times 10^{-5} T$ [J/g K] [11]. At this time, the values for $C_p^{\text{HfH}_x}$ have not yet been measured. Therefore, the values for $0 \leq x \leq 0.20$ and $0.20 < x \leq 2.02$ were assumed based on the following. $C_p^{\text{HfH}_x} = C_p^{\text{Hf}}$ and $C_p^{\text{HfH}_x} = C_p^{\text{ZrH}_{1.58}} \times C_p^{\text{Hf}} / C_p^{\text{Zr}} = 0.0940 + 3.30 \times 10^{-4} T$ for the above composition ranges, respectively, where $C_p^{\text{ZrH}_{1.58}}$ and C_p^{Zr} are the specific heats of ZrH_{1.58} and Zr, respectively, expressed as $C_p^{\text{ZrH}_{1.58}} = 0.155 + 7.52 \times 10^{-4} T$ [12] and $C_p^{\text{Zr}} = 0.235 + 1.49 \times 10^{-4} T$ ($290 \leq T \leq 570$ K) [11]. The values of d_{HfH_x} and d_{Hf} were expressed as $d_{\text{HfH}_x} = 13.24 - 1.01x$ and $d_{\text{Hf}} = 13.24$ [g/cm³] [13], respectively, where *x* represents the compositions $0 \leq x \leq 2.02$. For 300 K, the thermal conductivities of $\alpha + \delta'$ -HfH_{0.92} and δ' -HfH_{1.48} significantly exceeded that of α -Hf by factors of 1.4 and 1.6, respectively, while that of δ -HfH_{1.70} was less by a factor of 0.8. Those of the other compositions were almost the same as that for α -Hf. For $300 < T < 550$, the conductivity of δ -HfH_{1.70} increased with increasing temperature, while those of the other compositions decreased. However, for the δ' -HfH_{1.48} sample, the conductivity quickly started to increase at 380 K until 387 K, at which point it continued to increase a slower rate. The conductivity of the δ' -HfH_{1.48} sample was similar to that of δ -HfH_{1.70} in that the δ' -phase structure converted to a δ -phase structure. The thermal diffusivity contributes to the thermal conductivity. At 550 K, all of them were at almost the same value, 0.21 W/cm K, as that of α -Hf.

4. Summary

The thermal diffusivities of HfH_{*x*} (HfH_{*x*}; $0.20 \leq x \leq 2.02$), prepared by adjusting the temperature and hydrogen gas pressure with a Sieverts apparatus, were measured within the temperature range from room temperature to 570 K by means of a laser-flash method. The temperature dependence of the thermal diffusivity changed significantly with changes in the hydrogen concentration, which alters the phase transformation. The thermal diffusivities of the $\alpha + \delta'$ - and δ' -phase (HfH_{*x*}; $0.20 \leq x \leq 1.57$)

and δ -, $\delta + \varepsilon$ - and ε -phase HfH_x (HfH_x ; $1.57 < x \leq 2.02$) at room temperature were higher and lower, respectively, than that of metallic Hf. At temperatures above 350 K, the thermal diffusivities for all of the HfH_x were lower than that of metallic hafnium. The change in the heat conduction of $x = 1.48$ and 1.57 caused by the phase transformation from the δ' - to the δ -phase in the temperature range of 360–380 K.

In addition to the above experimental results, the thermal conductivities for several phases of the HfH_x were calculated as a function of temperature from the relationship between the measured thermal diffusivity, the reported density and specific heat. The specific heat for Zr and ZrH_x was used in the calculations. The calculated thermal conductivities at 550 K for $\alpha + \delta'$ - $\text{HfH}_{0.20}$, $\alpha + \delta'$ - $\text{HfH}_{0.92}$, δ' - $\text{HfH}_{1.48}$, δ - $\text{HfH}_{1.70}$ and ε - $\text{HfH}_{2.02}$ were about 0.21 W/cm K, which is similar to that of α -Hf.

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