Thermal expansion and thermal conductivity of $RT_2$ ($R$: Gd, Dy, Er; $T$: Al, Ni) intermetallic compounds for magnetic refrigerator

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Abstract. Highly efficient hydrogen liquefaction is required for upcoming hydrogen energy society. Magnetic refrigeration is expected as a method to realize efficient hydrogen liquefaction, and the performance depends on properties of magnetic materials. $RT_2$ ($R$: rare-earth; $T$: Al, Ni) Laves phase intermetallic compounds with a second-order magnetic phase transition are one of the promising magnetocaloric materials. Thermal expansion, magnetostriction, and thermal conductivity of ErAl$_2$, DyNi$_2$, DyAl$_2$ and GdNi$_2$ were measured in magnetic fields using polycrystalline samples because of the important properties for practical use in a magnetic refrigerator. Thermal expansions showed anomalies at the magnetic transition temperature. However, those in 0 T were nearly the same as copper. Magnetostriction were not as large as magnetocaloric materials with a first-order magnetic phase transition such as TbMn$_2$. Thermal conductivities in 0 T were almost in agreement with the literature data, and magnetic field dependence was small. These results indicate that $RT_2$ compounds are suitable as magnetic refrigerants for hydrogen liquefaction in practical use.

1. Introduction

Hydrogen is currently considered one of possible candidates for clean energy resources, because of no greenhouse gas production. Liquid hydrogen is economically superior to other forms of hydrogen in its transportation and storage due to high energy density. However, practical application of liquid hydrogen is crucial to highly efficient liquefaction method and adiabatic storage, because the boiling point is much lower than that of natural gas. To realize highly efficient liquefaction, a hydrogen liquefaction magnetic refrigeration system has been developed by NIMS and Kanazawa University group [1, 2]. Magnetic refrigeration is a refrigeration method based on the magnetocaloric effect of magnetic materials. It has a great potential for highly efficient hydrogen liquefaction because its cooling cycle can closely follow the Carnot cycle.

$RT_2$ ($R$: rare-earth; $T$: Al, Ni, Co) Laves phase intermetallic compounds with cubic MgCu$_2$ structure have large magnetocaloric effect, and magnetic phase transition temperature $T_C$ are adjustable in accordance with de Gennes factor [3, 4, 5, 6, 7]. RAl$_2$ and RNi$_2$ compounds undergo a second-order magnetic phase transition from a paramagnetic to ferromagnetic state, and show large magnetocaloric
effect over a wide temperature range. It has been reported that these materials are one of the promising magnetic refrigerants used for a hydrogen liquefaction magnetic refrigerator in previous studies [6, 7].

It is necessary that the thermal expansion and magnetostriction are small to use magnetic refrigerants for a long time, because large thermal expansion and magnetostriction may cause deterioration and pulverization of materials. High thermal conductivity is required to realize high cooling power and highly efficient refrigeration cycle. Therefore, it is important to evaluate thermal expansion, magnetostriction, and thermal conductivity.

In this study, polycrystalline samples of ErAl$_2$, DyNi$_2$, DyAl$_2$ and GdNi$_2$ were prepared because actual magnetic refrigerators use polycrystalline materials in terms of cost. Thermal expansion, magnetostriction and thermal conductivity were measured in magnetic fields.

2. Experimental procedures

Polycrystalline samples of ErAl$_2$, DyNi$_2$, DyAl$_2$ and GdNi$_2$ were prepared by arc melting. These samples were cut by electrical discharge machining into about 3×3×3 mm cubes for thermal expansion and magnetostriction measurements as shown in figure 1. We also prepared these sample rods for thermal conductivity measurement as shown in figure 2, the sample sizes were about 3×3×20 mm.

In the measurement of thermal expansion and magnetostriction, we used a homemade capacitive dilatometer that was installed in Quantum Design PPMS [8]. Capacitance method is one of the most sensitive methods for measuring thermal expansion and magnetostriction. The dilation $\Delta L$ of a sample with length $L$ along to magnetic field direction was detected as a change in the gap $D$ between capacitor plates.

Thermal conductivity was measured by the steady heat flow method using a homemade equipment installed in the Quantum Design PPMS. Thermal contact was improved by applying a small amount of Apiezon N grease to the sample and thermometer holder. Heat from the heater flows from one end of the sample rod to the other one connected to the heat sink. From the temperature difference $\Delta T$ between two points of the sample, the thermal conductivity $\kappa$ is determined using Fourier’s law $\kappa = -Q \cdot \Delta x / (A \cdot \Delta T)$, where $Q$ is applied heat flux, $A$ is the cross-section area of samples and $\Delta x$ is the distance between the thermometers.

![Figure 1. Photograph of the GdNi$_2$ cube for thermal expansion and magnetostriction measurement.](image1)

![Figure 2. Photograph of the GdNi$_2$ rod for thermal conductivity measurement.](image2)

3. Results and discussion

3.1. Thermal expansion and Magnetostriction

Thermal expansion of $RT_2$ intermetallic compounds were measured in 0 and 5 T. Figure 3(a) shows temperature dependence of thermal expansion for $RT_2$ compounds in 0 T. $\Delta L/L$ is plotted as relative change from 273 K and shifted vertically for clarity. Thermal hysteresis was not observed in every sample. As the temperature decreases from 273 to 4 K, ErAl$_2$ shrinks by 0.34 % and DyNi$_2$, DyAl$_2$ and GdNi$_2$ shrink by 0.3 %. These results are nearly the same as ordinal metal such as copper [9]. Figure 3(b) shows temperature dependence of thermal expansion of $RT_2$ compounds in 0 and 5 T below 80 K in order to represent behavior in paramagnetic state around $T_C$ and ferromagnetic one. It is observed that $RT_2$ compounds showed small anomalies at $T_C$ in thermal expansion in zero magnetic field. Thermal expansion of ErAl$_2$, DyNi$_2$ and DyAl$_2$ had large magnetic field dependence compared to that of GdNi$_2$.
These results agree with magnetostriction measurements shown in figure 4. Magnetostriction of GdNi$_2$ was one order of magnitude smaller than those of ErAl$_2$, DyNi$_2$ and DyAl$_2$. Magnetic anisotropy possibly causes these differences. Magnetostriction of DyAl$_2$ single crystal associated with magnetic anisotropy has been reported in Ref. [10]. Isotropic nature of Gd$^{3+}$ ion resulted in small magnetostriction of GdNi$_2$.

Magnetostriction of $RT_2$ compounds are much smaller than that of magnetic materials with a first-order phase transition such as TbMn$_2$ which is a kind of Laves phase intermetallic compounds [11]. In addition, the change of thermal expansion $\Delta L/L$ around $T_C$ in 0 T for $RT_2$ compounds was much smaller than that of La(Fe$_{0.88}$Si$_{0.12}$)$_3$ hydrides with a first-order magnetic phase transition [12]. La(Fe$_{x}$Si$_{1-x}$)$_3$ compounds are magnetocaloric materials with large magnetic entropy changes and transition temperature can be raised to room temperature by hydrogen absorption [12, 13]. From the above, $RT_2$ compounds are suitable as magnetic materials used for magnetic refrigeration.

Two DyNi$_2$ samples were cut from the same ingot and magnetostriction was measured for each sample. Their magnetostriction showed different magnetic field dependence. However, magnetostriction of them had the same order of magnitude as that of DyAl$_2$ single crystal. Crystal grain structure and orientation distribution of the polycrystalline samples possibly cause magnetostriction difference because Dy$T_2$ single crystal has large magnetic anisotropy.

**Figure 3.** Temperature dependence of thermal expansion of $RT_2$ intermetallic compounds (a) between 4 and 300 K in 0 T, (b) between 4 to 300 K in 0 and 5 T. $\Delta L/L$ is plotted as relative change and shifted for clarity.
3.2. Thermal conductivity

Figure 5 shows temperature dependence of thermal conductivity for \( RNi_2 \) compounds in zero magnetic field. The thermal conductivity of \( DyNi_2 \) is in agreement with the literature [14]. The temperature dependence of \( DyNi_2 \) and \( GdNi_2 \) are almost the same, and this monotonic change was also observed in other \( RA_2 \) compounds. Thermal conductivity of \( RA_2 \) compounds coincided with the results of the literature [15]. All samples showed no significant anomalies around \( T_C \). Thermal conductivity of them are nearly the same as that of stainless steel [16].

Thermal conductivity \( \kappa \) of \( RT_2 \) intermetallic compounds were measured in 0, 2 and 5 T. Figure 6 shows magnetic field dependence \( \Delta \kappa / \kappa_{0T} \) of thermal conductivity of \( GdNi_2 \) as functions of magnetic field at various temperatures, where \( \Delta \kappa \) is variation of \( \kappa \) caused by magnetic fields. \( GdNi_2 \) has magnetic field dependence as several percent by 5 T. \( \Delta \kappa / \kappa_{0T} \) of the other samples had similar values. From the view point of thermal conductivity, these results suggest that \( RT_2 \) compounds are more suitable than \( Dy_3Gd_5O_{12} \) whose thermal conductivity decreases significantly with magnetic fields [4].

The thermal diffusivity \( D = \kappa / \rho \cdot C_P \) and the penetration depth of heat \( L_d = (D / \pi f)^{1/2} \) were calculated from the obtained thermal conductivity, where \( \rho \cdot C_P \) is the volumetric specific heat and \( f \) is the frequency corresponding to a refrigeration cycle [14]. In the case of 1 Hz cycle frequency, it is evaluated that sufficient heat exchange occurs when magnetic materials have sub-millimeter size. We have succeeded in manufacturing sub-millimeter sphere materials [7].

4. Summary

We measured thermal expansion, magnetostriction and thermal conductivity of \( RT_2 \) intermetallic compounds. The thermal expansion in zero magnetic field were almost the same as that of copper. Magnetostriction of the \( RT_2 \) compounds were up to on the order of \( 10^{-4} \). Thermal conductivity were several W/(m \( \cdot \) K), and the magnetic field dependence was small. These results indicate that \( RT_2 \) compounds are suitable as magnetic refrigerants for hydrogen liquefaction in practical use.

Acknowledgments

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Figure 5. Temperature dependence of the thermal conductivity of \( R\text{Ni}_2 \) intermetallic compounds in 0 T. Lines are guide to the eye.

Figure 6. Magnetic field dependence of the thermal conductivity of GdNi\(_2\). Lines are guide to the eye.

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