Magnetocaloric effect of $RM_2$ ($R$=rare earth, $M$=Ni, Al) intermetallic compounds made by centrifugal atomization process for magnetic refrigerator

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Abstract. $RM_2$ ($R$= rare earth, $M$= Al, Ni and Co) compounds have large entropy change and magnetic transition temperatures can be controlled by change of $R$ and/or $M$ so that are suitable to a magnetic refrigerator for hydrogen liquefaction under development. In order to improve refrigerator performance, spherical powdered HoAl$_2$, DyAl$_2$, and GdNi$_2$ compounds with submillimeter diameter were synthesized by centrifugal atomization process. By measuring the magnetization and heat capacity, we obtained entropy change by magnetic fields and entropy as functions of temperature and magnetic field, which are essential for analyzing the magnetic refrigeration cycle. All samples showed sharp magnetic transitions and had good potentials for use in magnetic refrigeration.

1. Introduction
Magnetic refrigeration has a great potential for highly efficient hydrogen liquefaction since reversible thermal cycle is possible in principle. Magnetic refrigeration makes use of magnetocaloric effect that is the thermal response of a magnetic material to a changing magnetic field. In recent years, magnetic refrigeration study has been expanded below 1 K to room temperature regions [1-3].

Hydrogen energy is considered a good alternative to fossil fuels, because burning hydrogen does not produce greenhouse gases. Liquid hydrogen should be useful for economic transport and storage because of its high gravimetric and volumetric density. Kanazawa University and National Institute for Materials Science (NIMS) have been developing a magnetic refrigerator for hydrogen liquefaction. We have been investigated various magnetic materials that are suitable from 20 K to room temperature. The rare earth garnets, gadolinium doped dysprosium aluminum garnet (DGAG) [4] and Fe-modified gadolinium gallium garnets (GGIG) [5] are shown to suitable to liquefaction stage. Various intermetallic compounds have been studied for higher temperature operation. Rare earth intermetallic compounds are good refrigerant because their large angular momentums of magnetic atoms tend to produce large entropy changes by magnetic field. $RM_2$ ($R$: rare earth, $M$: Al, Ni, Co) is a Laves phase compound. Transition temperature can be controlled by the change of $R$ and/or $M$ [6,7].

Our hydrogen magnetic liquefaction system consists of two magnetic refrigerators: Carnot magnetic refrigerator (CMR) and active magnetic regenerator (AMR) device. The CMR test device succeeded in liquefying hydrogen at 20 K [4]. Regenerative thermal cycles are required as precooling stage of hydrogen gas and active magnetic regenerator (AMR) devices were tested [3]. An AMR is stuffed with magnetic materials, and the regenerator matrix operates the refrigeration cycle by periodically changing magnetic field and fluid flow. In order to improve AMR performance, magnetic

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materials in small sphere shape are preferable for AMR like other regenerators used in gas expansion cryocoolers. In our previous experiments of AMR, small size magnetic materials obtained by crushing from molded compounds were used. Fine powders were created by friction between particles and gave harm the refrigerator because RM$_2$ compounds are brittle. Small particle is better for heat transfer between magnetic material and heat transfer fluid. However, pressure drop due to viscosity increases with decreasing particle size. So, submillimeter diameter spherical materials are appropriate for refrigerator operation condition.

We have made sphered magnetic compounds by centrifugal atomization process and characterized the magnetocaloric effect from magnetization and specific heat.

2. Experiment
HoAl$_2$, DyAl$_2$, and GdNi$_2$ that had stoichiometric compositions were synthesized by RF melting. Centrifugal atomization was used to obtain spherized compounds. The drops of the melt were cooled on a rotating disk to make spherical shape. The distribution of particle diameter was wide. Then, particles were sieved into four fractions, $<355\,\mu m$, $355-500\,\mu m$, $500-850\,\mu m$, and $>850\,\mu m$. Two representative examples of spherized compounds, GdNi$_2$ and DyAl$_2$, are shown in figure 1. The Laves phase was confirmed for each material by XRD analysis.

Magnetization was measured using a commercial SQUID magnetometer (Quantum Design MPMS) at discrete intervals of magnetic field between 0.1 and 5 T in the temperature ranges around transition temperature. Specific heat was measured with Quantum Design PPMS as a function of temperature at various magnetic fields from 0 to 5 T. Measurements were performed from 2 to 100 K for all samples.

Small particles crushed from molded compounds were prepared and measured both magnetization and specific heat for comparison.

3. Results and discussion

3.1. Magnetization
Magnetization in a constant field decreased with increasing temperature for all samples above 2 K. Figure 2 shows the temperature variations of the magnetization for GdNi$_2$ with 500-850\,\mu m diameter and HoAl$_2$ with 355-500\,\mu m one. Magnetization of bulk HoAl$_2$ are also shown in the left figure. As shown in figure 2, magnetization change at the transition temperature is sharp for each sample and magnetization of spherized HoAl$_2$ quantitatively agrees with bulk material. These behaviors show that atomized samples had quality as good as bulk materials.

Table 1 represents effective Bohr magneton and Weiss temperature of atomized and bulk samples. Those were calculated from the magnetization in paramagnetic phase and low magnetic field. Effective Bohr magneton and Weiss temperature of atomized samples coincide with those of our bulk samples and those from literature [6, 8]. No hysteresis was observed for these samples in the magnetization and demagnetization process in a constant temperature.
Figure 2. Magnetization of HoAl₂ with 355-500µm diameter (left) and GdNi₂ with 500-850µm (right). That of bulk HoAl₂ is also shown in the left figure for comparison.

Table 1. Weiss temperature and effective Bohr magneton of sphered samples. Values in parentheses represent those of bulk samples.

|        | Weiss temperature (K) | Effective Bohr magneton (µₜₐₜ) |
|--------|------------------------|---------------------------------|
| HoAl₂  | 31.8 (31)              | 11.2 (10.8)                     |
| DyAl₂  | 58.8 (55.9)            | 10.5 (11.4)                     |
| GdNi₂  | 74.8 (75)              | 8.3 (8.3)                       |

3.2. Specific heat

Specific heat of HoAl₂ with 355-500µm diameter and GdNi₂ with 500-850µm diameter are presented in figure 3. Both materials represent sharp peaks in zero magnetic field, these are ascribed to transition from paramagnetic to ferromagnetic phase. Sharp specific heat peaks for both compounds imply that the sphered samples were homogeneous and good quality, even though the samples were cooled rapidly in centrifugal atomization process. Broadening of specific heat by magnetic field agrees with that occurs for second order phase transition magnetic materials. As for HoAl₂ an additional specific heat peak was observed around 20 K in 0T and the peak was broadened with magnetic field. This peak was also observed in bulk sample [8].

3.3. Magnetocaloric effect

The magnetic entropy change induced by field was calculated using Maxwell relation and the temperature dependent magnetization in constant fields. From the obtained specific heat data, the temperature variation of the entropy in an applied magnetic field was obtained by integration of specific heat divided by temperature.

Figure 4 shows entropy changes of atomized and bulk samples by 5 T magnetic field. Atomized samples have a little smaller entropy changes than bulk samples. Considering that base materials for atomized and bulk sample were made in different lot, atomization process has small effect on magnetocaloric effect. The entropy of the sphered samples obtained from specific heat reasonably agreed with those of bulk compounds.

4. Summary

Spherical HoAl₂, DyAl₂, and GdNi₂ compounds with submillimeter diameter were synthesized by centrifugal atomization process. By measuring the magnetization and heat capacity, magnetocaloric effect was evaluated. All samples showed sharp magnetic transitions and had good potentials for use in magnetic refrigeration.
Figure 3. Specific heat of HoAl$_2$ with 355-500µm diameter (left) and GdNi$_2$ with 500-
850µm diameter (right).

Figure 4. Magnetic entropy change of atomized HoAl$_2$, DyAl$_2$ and GdNi$_2$ by 5 T. Those of
bulk are also plotted for comparison.

5. References
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