Experimental Study of Active Magnetic Regenerator (AMR) Composed of Spherical GdN

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ABSTRACT

An experimental study of an active magnetic regenerator (AMR) employing GdN was carried out. Spherical GdN material was synthesized by the hot isostatic pressing (HIP) method. The specific heat was measured and the magnetic entropy change ΔS and adiabatic temperature change ΔT_{ad} were calculated. The refrigeration with an AMR cycle was tested in the temperature range between 48 and 66 K with the field swinging from 1.2 to 3.7 T at upper side and from 2.0 to 4.0 T at lower side of the regenerator bed filled with GdN spheres. A temperature span, ΔT_{span},was found to develop soon after starting the cycle and became more than 4.7 degree in steady state. This temperature span ΔT_{span} was at least 1.5 times as large as the adiabatic temperature change ΔT_{ad}.

INTRODUCTION

For the hydrogen society expected in the near-future, the high efficiency transport and storage of hydrogen is an important requirement. Liquid hydrogen provides the highest hydrogen densities with respect to both mass and volume. To liquefy hydrogen, it must be cooled down to 20 K. However, the efficiency of conventional cooling systems using gaseous refrigerant generally decreases with lowering temperature, so that much energy is required to liquefy hydrogen. Magnetic refrigeration has thepotential to provide higher efficiency at low temperatures, because it is based on the magnetocaloric effect (MCE) which is associated with an intrinsically small irreversibility. The magnetic entropy change ΔS is extracted by a swinging magnetic field axis externally applied to a ferromagnetic material. The change is lowest in the vicinity of the Curie temperature. This ΔS is converted directly into heat, $Q = T\Delta S$. Application of this concept to a hydrogen liquefaction system has been proposed.[1] To realize the magnetic cooling for hydrogen liquefaction, development of a suitable magnetic refrigerant is absolutely necessary. We have found several rare earth nitrides that are promising candidate materials for the magnetic refrigerant working between 4 ~ 80 K due to some remarkable characteristics.[2-6]

Magnetic refrigeration has been well studied at temperatures, near 20 K[7,8] and at room temperature.[9-12] However, in the temperature range of 20 ~ 77 K, only Matsumoto *et al*.[7] has designed

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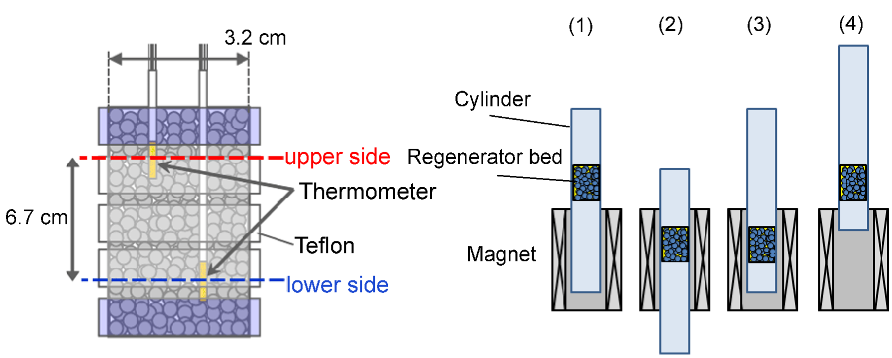
and constructed an Ericsson magnetic regenerator using a 5 T superconducting magnet. They employed $DyAl_{2.2}$ as the magnetic working substance and obtained temperature span of 8.4 degree (58.7 ~ 50.3 K).[13] Active magnetic regenerator (AMR) refrigeration is as alternative cycle proposed for refrigeration and gas liquefaction. This technology is based upon the magnetocaloric effect, a nearly reversible temperature change induced by a magnetic field change. AMR refrigeration devices have the potential to be more efficient than those using conventional refrigeration techniques. In this paper, we report on the magnetic refrigeration test with the AMR cycle employing GdN spheres as the magnetic refrigerant in the 48 ~ 66 K temperature range.

EXPERIMENT

Starting materials of spherical Gd metal (ϕ: 0.85 ~ 1.00 mm, 99.9% purity) were processed in a Hot Isostatic Press (O_2-Dr. HIP; Kobelco Co., Ltd.) at 1873 K in 200 MPa N_2 gas of 99.9999% purity for 2 hour. This condition was allowed the starting materials to be transformed into spherical GdN free from unwanted deformation and/or cracks caused by unbalanced progresses of nitrogen diffusion and nitride formation leading to a density gap. The X-ray diffraction (XRD) pattern of the product was measured with a diffractometer (RINT Ultima+, Rigaku) using Cu-*K*a radiation to examine the resultant phases. The specific heat was measured using a physical property measurement system (PPMS model 6000, Quantum Design, Inc.) at 2 - 100 K under several magnetic fields (0, 1.2, 2.0, 3.8, 4.0, 5.0, 7.0 T). These temperatures and fields are anticipated for the regenerator bed in the present refrigeration test.

The regenerator bed was filled with the GdN spheres with a total mass of 313 g. Two thermometers were located near upper and lower sides of the regenerator bed as shown in Fig. 1(a). Helium gas at 0.13 MPa filled the cylinder as heat transfer fluid. In this apparatus, the AMR cycle was operated by moving the regenerator bed and the gas in a superconducting magnet along its axial direction. The gas flow through the bed was driven by moving the closed cylinder separately.

The present AMR cycle consists of four processes as shown in Fig. 1(b). In the "magnetization process, (1)→(2)", the regenerator bed and the cylinder go into the magnet, then the GdN is magnetized and heated by the magnetocaloric effect. In the "hot-to-cold flow process, (2)→(3)", only the cylinder goes up making the He gas flow upward through the bed and remove heat from the magnetic material whic makes a temperature gradient in the regenerator bed across its lower (cold) and upper (hot) sides. In the "demagnetization process, (3)→(4)", the regenerator bed and the cylinder come out of the magnet, which demagnetizes and cools the GdN. In "cold-to-hot flow process, (4)→(1)", only the cylinder goes down making the He gas flow downward through the bed and gives heat to the GdN. By cycling these processes, a temperature span is obtained in the regenerator bed. The total cycle period was 8 sec, consisting of these four processes (magnetization, hot-to-cold, demagnetization, and cold-to-hot) of 2 sec each. The swinging magnetic field applied to the



(a) Regenerator bed (b) AMR cycle

Figure 1. (a) Inner structure of regenerator bed, (b) Four elementary processes of AMR cycle, (1)→(2); magnetization, (2)→(3); cold-to-hot flow, (3)→(4); demagnetization, (4)→(1); hot-to-cold flow.

bed was 1.2 ~ 3.7 T at the upper side and 2.0 ~ 4.0 T at the lower side of the regenerator bed. These field strengths were indirectly determined from readings of a magnetic sensor attached to the outer surface of the cylinder at its axial positions and magnet currents. The AMR cooling experiment starts after the system has attained a thermal equilibrium at 51 K which is given as a balance between cooling and heating respectively performed by a GM refrigerator and heaters attached to the cylinder.

RESULTS AND DISCUSSION

XRD patterns of the GdN product indicated an NaCl-type structure only and free from that of oxide.[14] Figure 2 shows a photograph of GdN synthesized by HIP which shows a spherical shape (0.986 mm, mean diameter) without unwanted deformation and/or cracks.

Figure 3 shows the specific heats vs. temperature curve of the GdN sample measured under each magnetic field. Note that the curve measured at zero-field exhibits a clear lambda-type peak at 65 K, evidencing occurrence of a ferro-para transition.[15] Increasing the magnetic field, the peak is diminished gradually and the curve at 7 T increases monotonically with temperature.

By substituting these C_H versus T data sets into $S_H(T) = \int_0^T \frac{C_H(T)}{T} dT$, entropy curves as shown in Fig. 4 were obtained for each field. From these $S_H - T$ curves, the magnetic entropy change ΔS and the adiabatic temperature change ΔT_{ad} are obtained graphically. The $\Delta S - T$ curve is thus obtained in Fig. 5(a). Fig. 5(b) is ΔT_{ad} plotted against the temperature at which the demagnetization is given and the cooling starts. It is noticed that these curves have peaks located near the Curie temperature.

At the beginning of the AMR operation, there is no temperature span at 51 K. Figure 6(a) shows time traces of the temperatures measured at upper and lower sides of the regenerator bed

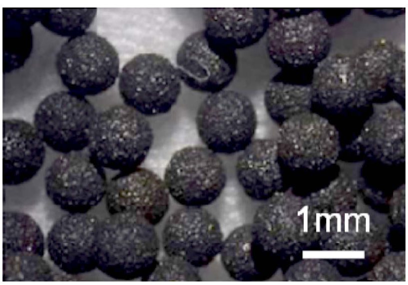


Figure 2. Photograph of spherical GdN particles

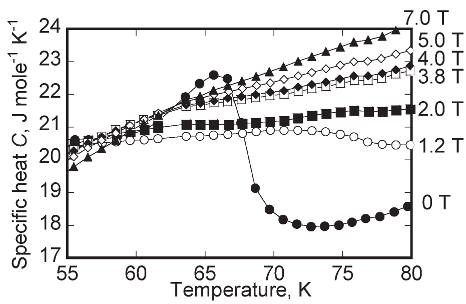


Figure 3. Specific heat, C_H, of GdN as a function of temperature at each magnetic field (0, 1.2, 2.0, 3.8, 4.0, 5.0, 7.0 T).

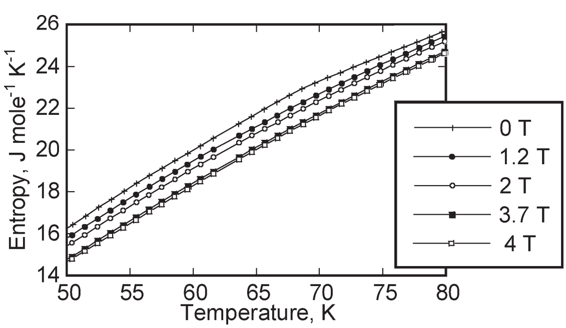


Figure 4. Entropy, S_H, calculated from specific heat measurement data set under magnetic at each magnetic field (0, 1.2, 2.0, 3.8, 4.0 T).

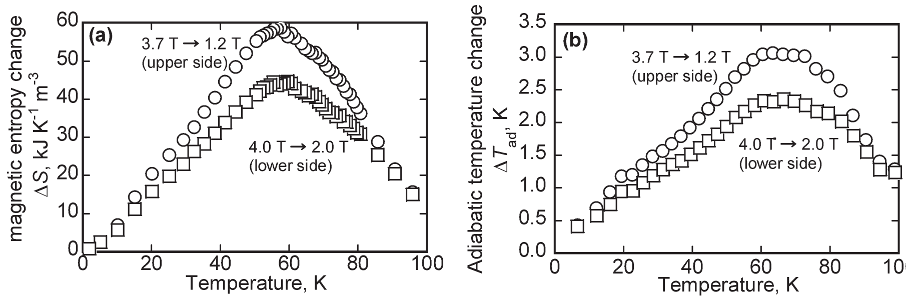


Figure 5. Temperature dependence of ΔS; (a) and ΔT_{ad}; (b) as magnetic field swings from 3.7 to 1.2 T at upper side and from 4.0 to 2.0 T at lower side.

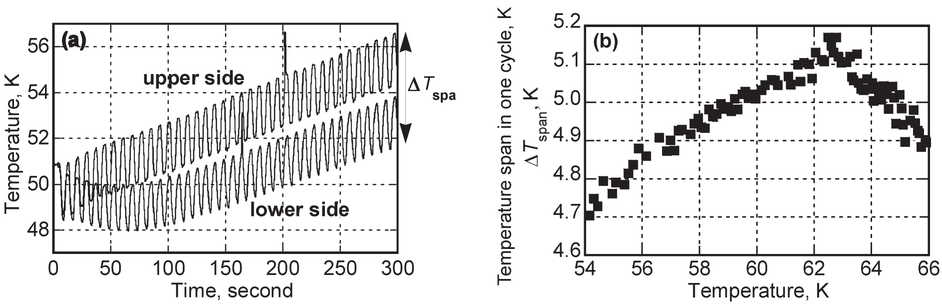


Figure 6. (a) Temperature time traces at upper and lower sides of the regenerator bed filled with GdN in 300 sec. (b) Temperature span ΔT_{span} in each cycle read in Fig. 6(a).

from 0 – 300 sec. As the cycle proceeds, temperature spans develop and attain steady states after 150 sec. The temperature spans observed at the lower and the upper sides are both about 2 degrees. Besides the spans, both of the temperatures are noticed to rise gradually, which is attributed to a heat influx from the shaft which drives the regenerator bed.

ΔT_{span} (= $T_{upper, max} - T_{lower, min}$) in one cycle after steady state is shown in Fig. 6(b). ΔT_{span} is maintained about 4.7 degrees through 54 ~ 66 K, which is 1.5 times larger than the adiabatic temperature change ΔT_{ad} of GdN as shown in Fig. 5(b). These findings directly indicate that the AMR cycle indeed works. Note a peak near 63 K corresponding to the peak in Fig. 5(b), which provides evidence that the temperature spans observed in this test are induced by the magnetocaloric effect of GdN.

SUMMARY

Spherical GdN material without deformation and/or cracks was successfully synthesized by hot isostatic pressing. The refrigeration test of the AMR cycle was performed. The steady state was produced in 150 sec and α ΔT_{span} of more than 4.7 degrees was achieved in the temperature range between 54 ~ 66 K at $\Delta H = 2 – 2.5$ T (3.7 ~ 1.2 T; upper side, 4.0 ~ 2.0 T; lower side). The specific heat, C_H, was measured under different fields (0, 1.2, 2.0, 3.8, 4.0, 5.0, 7.0 T). ΔS and ΔT_{ad} were calculated from the $C_H – T$ curves. A temperature span, ΔT_{span}, was 1.5 times as large as ΔT_{ad} in a wide temperature range (54 K ~ 66 K), proving that AMR cycle works well.

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