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Magnetocaloric effects of binary rare earth mononitrides, $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$

Takashi Nakagawa [a,*], Kengo Sako [a], Takayuki Arakawa [a], Naoto Tomioka [a],
Takao A. Yamamoto [a], Koji Kamiya [b], Takenori Numazawa [b]

[a] *Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan*
[b] *Tsukuba Magnet Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan*

Abstract

We have synthesized $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ ($x = 0$, 0.25, 0.5, 0.75 and 1) by the carbothermic reduction performed in a nitrogen gas stream. GdN and TbN have been completely miscible with each other as well as TbN and HoN. As x was changed from 0 to 1, the Curie temperature increased monotonously from 18.5 to 43.8 K for $Tb_xHo_{1-x}N$ and from 43.8 to 61.2 K for $Gd_xTb_{1-x}N$. The magnetocaloric effects have been evaluated by calculating the magnetic entropy changes from the magnetization data sets measured at different applied fields and temperatures. In any composition x, the magnetocaloric effects of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ are larger than those of $Gd_xDy_{1-x}N$. Therefore, $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ are promising magnetic refrigerant materials for hydrogen liquefying system working below liquid nitrogen temperature.

Keywords: Magnetic entropy change; Gadolinium; Terbium; Nitride; Magnetic refrigeration; Magnetic refrigerant

1. Introduction

Hydrogen is a promising fuel for energy systems in the near future, because it produces no carbon dioxide. Liquefied hydrogen is suitable for storage and transportation because of its high mass energy concentration and high volume energy concentration. Magnetic refrigeration is one of candidate technologies for the liquefaction of hydrogen [1]. Refrigeration is realized by use of the magnetocaloric effect of solid ferromagnets through frequent magnetization and demagnetization under adiabatic or isothermal conditions [2]. Consequently, the proper selection of magnetic working substances is very important for development of a magnetic refrigerator. A series of materials with gradually varying transition temperatures are needed if the magnetic liquefaction of hydrogen has to be realized, because the magnetocaloric effect of each material is significant only in the vicinity of its transition temperature. Hydrogen liquefaction at atmospheric pressure requires 20 K as the cold sink temperature, and the use of liquid nitrogen as a cheap and readily available heat sink allows the use of 77 K as the upper temperature. Some intermetallic compounds such as $DyNi_2$, $Al_2(Dy, Ho)$ or $Al_2(Dy, Er)$ have been proposed as candidates for the magnetic refrigerants working in this temperature region [1,3,4]. Rare earth mononitrides are also regarded as good magnetic refrigerants for hydrogen liquefaction. The rare earth mononitrides are inert to hydrogen, so that they can work as magnetic refrigerants even in direct contact with hydrogen; it is because they are thermodynamically more stable than the hydrides. In fact, there are a lot of reports on rare earth nitrides prepared by reaction of hydrides with N_2 or NH_3 gas [5–7]. Interestingly, the magnetic transition temperature of $Gd_xDy_{1-x}N$ varies with composition x in a range between the transition temperature of DyN (21 K) and that of GdN (60 K) [8]. Magnetic entropy change ΔS of HoN at 18 K reaches at 291 kJ K^{-1} m^{-3} and that of TbN at 44 K is 196 kJ K^{-1} m^{-3} [9]. These values are larger than those of the intermetallic compounds above mentioned and DyN. Thus, Tb–Ho or Tb–Gd binary nitrides are expected to show larger ΔS compared to $Gd_xDy_{1-x}N$.

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[*] Corresponding author. Tel.: +81 6 6879 7887; fax: +81 6 6879 7889.
E-mail address: nakagawa@mit.eng.osaka-u.ac.jp (T. Nakagawa).

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In this paper, we report on the magnetocaloric effects of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ estimated from the results of the magnetization measurements.

2. Experimental

The Gd–Tb binary nitrides samples ($Gd_xTb_{1-x}N$) were prepared by the carbothermic reduction method performed in nitrogen gas stream. Powders of Gd_2O_3 (99.99%) and Tb_4O_7 (99.99%) and amorphous carbon were thoroughly mixed in the desired proportion with an agate mortar and pestle. The carbon was charged as twice the stoichiometric amount in order to complete the nitriding reaction. Then polyvinyl alcohol was added as a binder and the powder mixture was compacted into a green pellet of 10 mm in diameter and 1.5 mm in height under a pressure of 250 MPa. The pellets were heated at 1773 K in a reaction tube through which 99.9995% purity nitrogen gas flowed during the reaction for 15 h. Five samples were prepared, $x = 0, 0.25, 0.5, 0.75$ and 1, in the chemical formula $Gd_xTb_{1-x}N$. The reaction occurring in this method is expressed as:

$$xGd_2O_3 + \frac{1-x}{2}Tb_4O_7 + (7-x)C + N_2 \rightarrow 2Gd_xTb_{1-x}N + \frac{7-x}{2}CO + \frac{7-x}{2}C \qquad (1)$$

A series of Tb–Ho binary nitrides ($Tb_xHo_{1-x}N$) were prepared in a similar way.

The reaction products were identified by X-ray diffraction patterns measured with a diffractometer (RINT Ultima+, Rigaku Corporation) using Cu Kα radiation. Magnetizations were measured with a superconducting quantum interference device magnetometer (MPMS, Quantum design) under different applied fields H at different temperatures T.

The excess carbon was not removed from the product, so that a certain amount of free carbon remained in it. Judging from the lattice parameters and magnetization data sets of single rare earth nitrides (GdN, TbN and HoN) [8,9], no carbide or carbonitride seemed to be formed in the samples. The residual amorphous carbon is magnetically invisible so that it contributes only to the weight of each product. Therefore, the weight of carbon was taken into account according to Eq. (1) in calculating the specific magnetization. The weight of the free carbon was not more than a few mass percent.

3. Results and discussions

Fig. 1 shows the XRD patterns of $Gd_xTb_{1-x}N$. The XRD profiles of $Tb_xHo_{1-x}N$ are given in Fig. 2. All XRD patterns indicate that the samples are of single-phase materials of mononitrides with NaCl-type structure. GdN and TbN are completely miscible with each other as well as TbN and HoN. It is found from these figures that diffraction peaks shift to the higher angles as composition x decreases. This shows that fcc lattice of mononitride shrinks with decreasing x. In Fig. 3 the lattice parameters determined from the XRD patterns are plotted against x. The lattice parameters of both $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ vary linearly following Vegard's rule. The linearity suggests that the interactions between Gd–N and Tb–N, and between Gd–Gd, Tb–Tb and Gd–Tb are

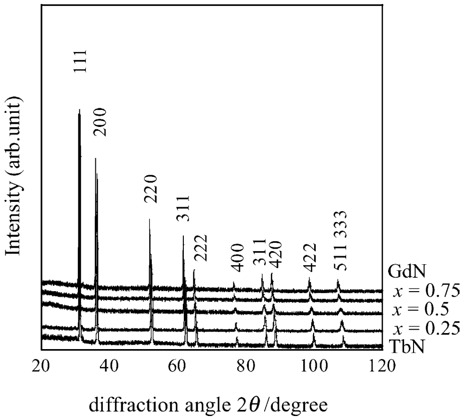

Fig. 1. X-ray diffraction patterns of $Gd_xTb_{1-x}N$.

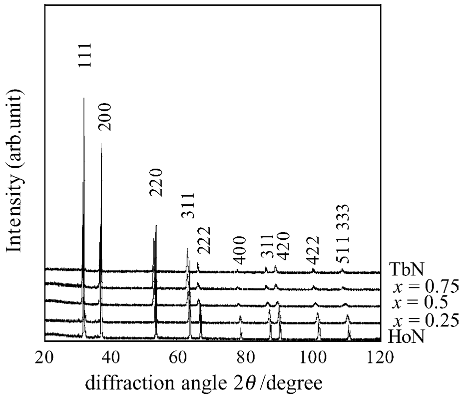

Fig. 2. X-ray diffraction patterns of $Tb_xHo_{1-x}N$.

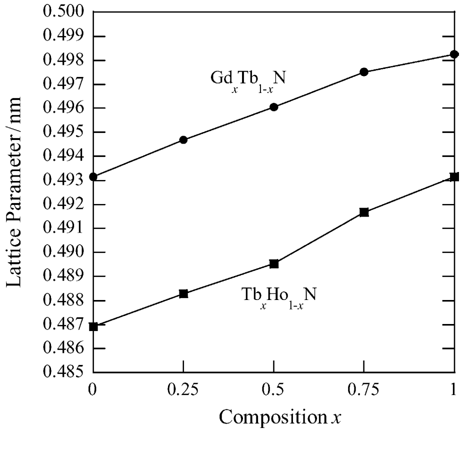

Fig. 3. Lattice parameters vs. composition x plots of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$.

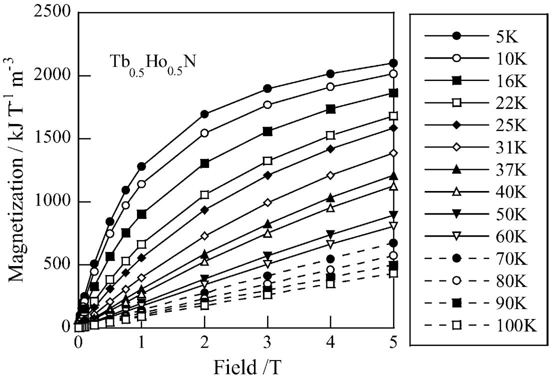

Fig. 4. Magnetization vs. applied field curves at different temperatures for $Tb_{0.5}Ho_{0.5}N$.

very similar. The same can be pointed out for the TbN–HoN binary system. The terminal values (lattice parameters of single rare earth nitrides) well agree with those reported (GdN: 0.4986 nm, TbN: 0.4936 nm and HoN: 0.4877 nm) [10].

A typical data set of magnetization measurements is shown in Fig. 4 for $Tb_{0.5}Ho_{0.5}N$. This figure indicates field dependence of magnetizations M at different temperatures T. At the lower temperature, large magnetic susceptibilities at low fields are observed and magnetizations are almost saturated at 5 T. However, magnetizations increase linearly with applied fields in the higher temperature region. These facts clearly showed that $Tb_{0.5}Ho_{0.5}N$ changes from ferromagnetism to paramagnetism when the temperature is elevated. The other nitrides also show the same magnetic properties. The Curie temperature T_C of each sample is estimated by making an Arrott plot. The obtained T_C values are plotted against the composition x in Fig. 5. In both binary nitride systems, T_C increases monotonously with increasing x. It means that we can obtain the nitrides with the desired T_C between the Curie temperatures of the nitrides with the terminal compositions.

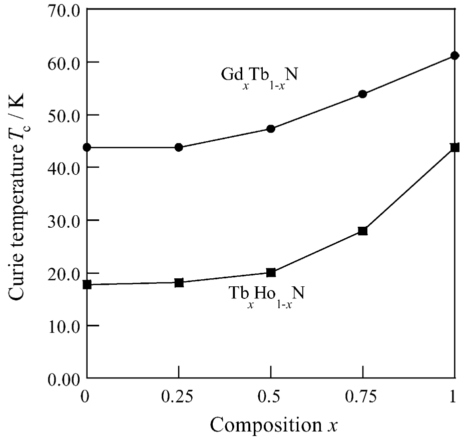

Fig. 5. The Curie temperatures of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ estimated from Arrott plots.

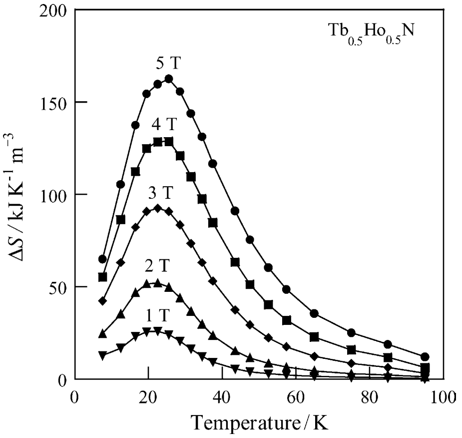

Fig. 6. Magnetic entropy change ΔS vs. temperature curves at different applied fields before demagnetization for $Tb_{0.5}Ho_{0.5}N$.

The magnetic entropy change ΔS is evaluated by executing numerical calculation on the basis of the equation [8]:

$$\Delta S = \int_{H}^{0} \left(\frac{\partial M}{\partial T}\right)_{H} \mathrm{d}H \tag{2}$$

The ΔS versus T curves for $Tb_{0.5}Ho_{0.5}N$ are given in Fig. 6. The curves have peaks at around 22 K regardless of the applied fields. This temperature well agrees with the T_C of $Tb_{0.5}Ho_{0.5}N$. Figs. 7 and 8 show the temperature-dependence of ΔS of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ in the case of demagnetization from 5 T to zero field. The temperatures $T_{\Delta S_{\max}}$ at which the ΔS values are maximized well agree with the Curie temperature T_C of the respective samples. This indicates that we can control the peak position of ΔS of the binary rare earth nitrides by varying the composition x. From the viewpoint of mechanical design, this property is very important.

The maximum entropy change $\Delta S_{\max}$ induced by demagnetization from 5 to 0 T for $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ against $T_{\Delta S_{\max}}$ are shown in Fig. 9, in which plots for $Gd_xDy_{1-x}N$ together. In any composition of x, $\Delta S_{\max}$ of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ are larger than those of

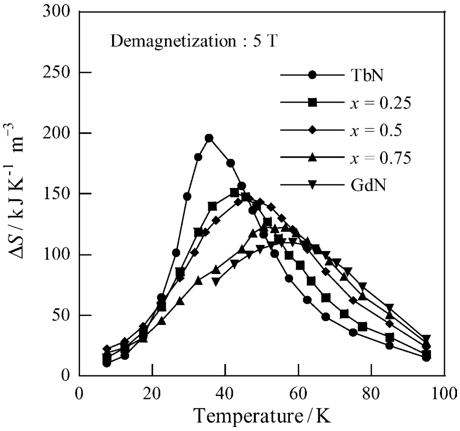

Fig. 7. Magnetic entropy change ΔS of different x in $Gd_xTb_{1-x}N$ as a function of temperature when demagnetized from 5 to 0 T.

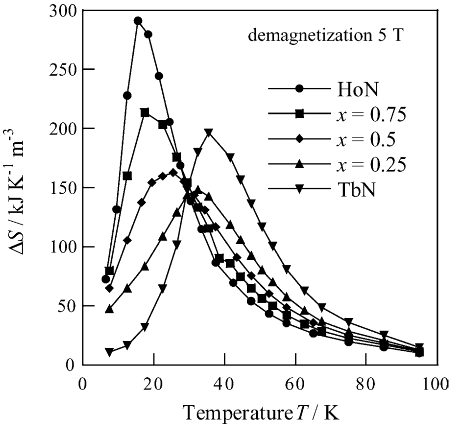

Fig. 8. Magnetic entropy change ΔS of different x in $Tb_xHo_{1-x}N$ as a function of temperature when demagnetized from 5 to 0 T.

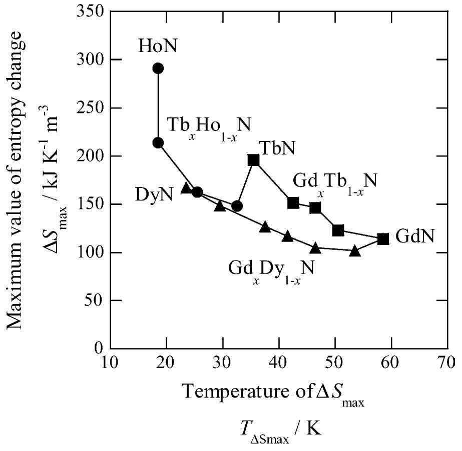

Fig. 9. The maximum value of magnetic entropy change $\Delta S_{\max}$ against the temperature $T_{\Delta S_{\max}}$ at which ΔS is maximized for $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$. For comparison, the plots of $Gd_xDy_{1-x}N$ are shown together.

$Gd_xDy_{1-x}N$. The present results indicate that $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ are promising magnetic refrigerant materials for hydrogen liquefying system working below liquid nitrogen temperature.

The $\Delta S_{\max}$ values of binary nitrides deviate negatively from the tie line of those of single rare earth nitrides with terminal composition. Order–disorder temperatures of the magnetic moments of rare earth atoms in the single rare earth nitride are the same. However, in the binary nitrides, some Gd atoms are surrounded by only Gd atoms, some are by Gd and Tb atoms and some are by only Tb atoms. Different coordination state of an atom results in different transition temperature. Thus, distribution of the different coordination states in the binary system leads to distribution of the transition temperature. This raises decrease in gradient of magnetization change against temperature to reduce the magnetic entropy changes of the binary system.

4. Summary

We have synthesized samples of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ by the carbothermic reduction in a nitrogen gas stream to evaluate their magnetocaloric effect. Their ΔS values have peaks at temperatures varying in a range of 18.5–43.8 K for $Tb_xHo_{1-x}N$ and 43.8–61.2 K for $Gd_xTb_{1-x}N$ depending on x. In any composition of x, the magnetic entropy changes of $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ evaluated from the magnetization data sets are larger than those of $Gd_xDy_{1-x}N$. The present results indicate that $Gd_xTb_{1-x}N$ and $Tb_xHo_{1-x}N$ are promising magnetic refrigerant materials for hydrogen liquefying system working below liquid nitrogen temperature.

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