Cooling Properties of Gd Alloys and La(Fe,Si)$_{13}$-Based Compounds in Active Magnetic Refrigeration for Environmentally-Friendly Cooling Systems

Akiko T. Saito, Tadahiko Kobayashi, Hidehito Fukuda, Ryosuke Arai, and Hideki Nakagome

Abstract—There is currently a global demand for highly-efficient and environmentally-friendly refrigeration techniques. The new concept of active magnetic regenerative (AMR) refrigeration has received much attention as a potential alternative to conventional gas expansion cooling. In the present study, Gd alloys and La(Fe,Si)$_{13}$-based compounds, both of which have been considered as likely candidates for solid magnetic refrigerants, were investigated in terms of their cooling properties in an AMR-cycle system. As a result, features of the cooling properties with both materials were clarified. The Gd alloys are evidently suitable for the generation of large temperature differences, in contrast to the La(Fe,Si)$_{13}$-based compounds, which exhibit good heat-load properties. Numerical calculations support these experimental results and indicate that multi-layered structures composed of the La(Fe,Si)$_{13}$-based compounds with gradually varying Curie temperatures are effective at increasing the temperature difference and also demonstrate good heat-load properties. The optimization of magnetic refrigerants such as these is expected to result in new environmentally-friendly cooling systems.

Index Terms—Environmentally-friendly, magnetic refrigeration, magnetocaloric effect, solid refrigerants.

I. INTRODUCTION

Magnetic refrigeration based on the magnetocaloric effect has received significant attention as an environmentally friendly cooling technique, since the working substance is a solid magnetic refrigerant rather than a gas such as a chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC) or hydrofluorocarbon (HFC), as in conventional gas expansion cooling systems. Solid refrigerants have the advantage of higher energy density and are also retrievable and recyclable without the potential for the environmental release of ozone-depleting or greenhouse gases. Over the last few decades, new magnetic refrigeration systems and magnetic refrigerant materials have been actively investigated [1]-[10] for use in refrigerating and cooling systems for commodities. For practical applications, magnetic refrigerant materials must exhibit suitable cooling performance under the low magnetic fields that can be generated by permanent magnets. Several magnetocaloric materials, such as Gd and its alloys [1], [11] as well as Gd$_3$Ge$_2$Si$_2$ [2], Mn(As,Sb) [12], MnFe(P,As) [13], and La(Fe,Si)$_{13}$-based compounds [14]-[19], have been proposed as candidates for room temperature magnetic refrigeration (RTMR).

Gadolinium (Gd) is well-studied material that was used in the first successful work with RTMR in 1976 [1]. However, Gd is unfavorable for practical use because of concerns regarding sustainability, as it is a rare-earth element. Mn(As,Sb) or MnFe(P,As)-based compounds are also unfavorable for practical use because they contain arsenic and also because of their large thermal hysteresis in the magnetocaloric effect. In contrast, La(Fe,Si)$_{13}$-based compounds contain iron as the major element at more than 80% by atomic ratio, and show little thermal hysteresis [8]. Therefore, La(Fe,Si)$_{13}$-based compounds are considered to be the most-favored candidates for magnetic refrigerants in practical use. Despite this, there has been little research on the refrigeration properties obtained when using La(Fe,Si)$_{13}$-based compounds as the magnetic refrigerant.

To clarify the refrigeration properties of La(Fe,Si)$_{13}$-based compounds, it is important to develop new magnetic refrigeration technologies. In the present study, we fabricated spherical particles of Gd alloys and La(Fe,Si)$_{13}$-based compounds and characterized their magnetocaloric properties and specific heat values. Moreover, the cooling properties obtained from active magnetic regenerative (AMR) refrigeration using particle shaped refrigerants composed of La(Fe,Si)$_{13}$-based compounds were investigated and compared with that obtained when using Gd alloys. The differing characteristics of these materials when applied to AMR were clarified by both experimental study and numerical calculations.

II. EXPERIMENTAL

A. Material Preparations and Method for the Evaluation of Cooling Properties

Fig. 1 presents a conceptual diagram of the AMR-cycle refrigeration process. Magnetic refrigerant particles were packed into a cylindrical container (the AMR unit) filled with heat transfer fluid. The AMR-cycle process consists of the following four steps: 1) a magnetic field is applied to the AMR unit, causing the magnetic refrigerants to warm, 2) the...
heat transfer fluid flows from the cold to the hot end through the magnetic refrigerants, and warm heat is thus transported to the hot side by the flow, 3) the magnetic field is removed from the AMR-unit, causing the magnetic refrigerants to cool down, and 4) the heat transfer fluid flows from the hot to the cold end (in the opposite direction to step 2) through the magnetic refrigerants, and cold heat is transported to the cold side by the flow. After repeated cycles, a temperature gradient is generated in the AMR-unit because of heat accumulation in the refrigerant particles, which are inhibited of thermal flow by their point-contact.

To obtain magnetocaloric materials for use in AMR-cycle trials, spherical particles of Gd alloys and La(Fe, Si)_{13}-based compounds were prepared from their respective mother alloys by means of the rotating electrode process (REP). The compounds were prepared from their respective mother alloys using a one-dimensional model of the heat flow during the AMR-cycle. The resulting particle diameters varied from 0.2 to 1.2 mm in accordance with rotational speed of the mother alloy electrode. In the case of the La(Fe, Si)_{13}-based compounds, the spherical particles were subjected to heat treatment at 1050 °C for 10 days to obtain a NaZn_{13}-type crystal structure by atomic interdiffusion between mutual phases. The crystal structures of the particles were confirmed by X-ray diffraction (XRD) and magnetic properties were identified using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design).

Two g samples of each type of magnetic refrigerant particle were packed into a mini-tube and the temperature changes resulting from the magnetocaloric effects within the mini-tube were measured in dry air under a magnetic field of $\mu_0H_{axl} = 0.8$ T (hereafter referred to as simple magnetocaloric test). In addition, approximately 100 g samples of each type of magnetic refrigerant particle (approximately 12.5 cc in volume) were packed into a cylindrical AMR-unit, after which the cylinder was filled with heat transfer fluid. The heat transfer fluids were either water or a 20% ethylene glycol solution. The La(Fe, Si)_{13}-based compound particles were coated with copper to prevent corrosion by the fluids. The reciprocating motion of the heat transfer fluid was heat controlled by pistons movement attached to the top and the bottom sections of the AMR-unit. The strength of the applied magnetic field was approximately 1.1 T. The temperatures at the hot and the cold ends of the AMR-unit were monitored by type K thermocouples during the AMR-cycle operation. A heat load could be applied to the cold end of the AMR-unit using an electrical heater attached to the tip of the bottom piston. The cooling characteristics during the AMR-cycle were evaluated with magnetic refrigerant particles composed of either Gd alloys or La(Fe, Si)_{13}-based compounds under a variety of conditions, as shown in Table I. The specifications of the AMR-unit are given in Table II.

![Fig. 1. Conceptual view of the AMR-cycle process.](image)

**Table I: AMR-Cycle Operating Conditions**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient temperature $T_i$ (°C)</td>
<td>5 to 35</td>
</tr>
<tr>
<td>AMR cycle frequency $f$ (Hz)</td>
<td>0.3, 0.4</td>
</tr>
<tr>
<td>Heat load input power $Q$ (W)</td>
<td>0 to 3.6</td>
</tr>
</tbody>
</table>

**Table II: AMR-Unit Specifications**

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size ($\mu$m)</th>
<th>Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>710 to 850</td>
<td>Water</td>
</tr>
<tr>
<td>Gd0.96Y0.015</td>
<td>710 to 850</td>
<td>20% ethylene glycol solution</td>
</tr>
<tr>
<td>LaFeSi13</td>
<td>500 to 850</td>
<td>Water</td>
</tr>
<tr>
<td>LaFeSiCoSi13</td>
<td>500 to 850</td>
<td>Water</td>
</tr>
</tbody>
</table>

**B. AMR Model for Numerical Calculations and Method of Evaluating Cooling Properties**

A one-dimensional model of the heat flow during the AMR-cycle is presented in Fig. 2. The governing equations for the magnetic refrigerant and the heat transfer fluid are as follows, respectively:

\[
\rho_f c_f (1 - \varepsilon) \frac{\partial T_f}{\partial t} + \frac{\partial}{\partial x} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial^2 T_f}{\partial x^2} \right) + \frac{\partial}{\partial t} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial T_f}{\partial t} \right) = \frac{\partial}{\partial t} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial T_f}{\partial t} \right) + \frac{\partial}{\partial t} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial T_f}{\partial t} \right) + h P(T_i - T_f) \tag{1}
\]

and

\[
\rho_f c_f A_l \frac{\partial T_f}{\partial t} + \frac{\partial}{\partial x} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial^2 T_f}{\partial x^2} \right) + \frac{\partial}{\partial t} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial T_f}{\partial t} \right) = \frac{\partial}{\partial t} \left( \lambda_f A_l (1 - \varepsilon) \frac{\partial T_f}{\partial t} \right) + h P(T_i - T_f) \tag{2}
\]

Here $T$ is the temperature, $C$ is the specific heat, $S$ is the entropy, $\rho$ is the density, $\lambda$ is the thermal conductivity, and the subscripts $r$ and $f$ indicate refrigerant material and fluid, respectively. The $Nu$ term is the Nusselt number, $m$ is the mass flow rate of the heat transfer fluid, $d_i$ is the diameter of the refrigerant material particles, $A$ is the cross-sectional area of the flow and $\varepsilon$ is the porosity in the AMR-unit cylinder body. The heat flow in an AMR-cycle procedure was calculated in four sequential steps, considering the heat exchange between the refrigerant material and the fluid over a number of small elements along the flow direction. The temperature variations in the AMR-unit were obtained as
functions of time and one-dimensional position. After repeating the calculation of AMR-cycle, the temperature gradient of the AMR-unit was obtained. Moreover, the calculation takes into account the additional effect of heat load.

### III. RESULTS AND DISCUSSION

Temperature dependence of magnetic entropy change, $\Delta S_m$, in spherical particles of Gd, La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ [17] and La(Fe$_{0.86}$Co$_{0.07}$Si$_{0.06}$)$_3$ (these La(Fe$_n$Si)$_m$-based compounds are referred to collectively as LaFeSi) under an external field $\mu_0H_{\text{ext}} = 0.8$ T are summarized in Fig. 3. The magnetic entropy changes were estimated from magnetization curves using the Maxwell relation: $(\partial S/\partial H)_T = (\partial M/\partial T)_H$. Each plot exhibits a peak in the vicinity of the material’s Curie temperature $(T_C)$: 21, 24 and 13 °C for Gd, La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$, and La(Fe$_{0.86}$Co$_{0.07}$Si$_{0.06}$)$_3$. The $\Delta S_m$ peak values in these materials are approximately equal, although the peak widths are different. Fig. 4 shows the results from a simple magnetocaloric test with Gd or La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ particles at various ambient temperatures in an external magnetic field $\mu_0H_{\text{ext}} = 0.8$ T. Both samples exhibit a peak around their $T_C$ value. The peak value of $\Delta T$ in the case of La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ is less than half that generated by the Gd, whereas both materials exhibit approximately equal $\Delta S_m$ peak values. Taking into account the relation $T\Delta S = \Delta C_T$ and the two times greater specific heat of La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ compared with that of Gd (inset to Fig. 4), the lower $\Delta T$ value observed for the La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ is consistent with the $\Delta S_m$ data.

![Fig. 3. Temperature dependence of magnetic entropy change, $\Delta S_m$, in spherical particles of Gd and LaFeSi compounds in an external field $\mu_0H_{\text{ext}} = 0.8$ T.](image)

The refrigeration properties of the different AMR-units listed in Table II were subsequently investigated. Fig. 5 shows the temperature changes at the hot and cold ends of the AMR-unit during AMR-cycle operation with Gd or LaFeSi particles at a cycling frequency of $f = 0.3$ Hz. The steady state temperature difference between both ends is defined as the temperature span, $\Delta T_{\text{span}}$. The variations of $\Delta T_{\text{span}}$ with temperature observed for the various AMR-units listed in Table II are shown in Fig. 6. Broad peaks are observed for each refrigerant material. The $\Delta T_{\text{span}}$ peak values obtained when using the Gd and Gd$_{0.05}$Y$_{0.05}$ refrigerants are almost equal and also significantly larger than those observed when employing the La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ and La(Fe$_{0.86}$Co$_{0.07}$Si$_{0.06}$)$_3$ refrigerant. These represent reasonable results considering that $\Delta T_{\text{span}}$ results from the heat accumulation, $\Delta T$, as measured during the simple magnetocaloric test. As described above, the smaller $\Delta T$ associated with the La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ in the simple magnetocaloric test is attributed to its greater specific heat compared to that of Gd. The higher specific heat should lead to the larger permissible heat load. Therefore, the AMR-cycle properties with heat-load were investigated to clarify the effects of this higher specific heat.

![Fig. 4. Temperature change, $\Delta T$, during simple magnetocaloric tests with Gd or La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$ particles at various ambient temperatures in an external field $\Delta H_{\text{ext}} = 0.8$ T. The inset shows the specific heats of these materials.](image)

![Fig. 5. Temperature changes at the hot and the cold ends of the AMR-unit during AMR-cycle operation with (a) Gd particles at the ambient temperature $T_i=13$ °C, and (b) LaFeSi particles the ambient temperature $T_i=21$ °C where the cycle frequency $f=0.3$ Hz.](image)

![Fig. 6. Temperature span, $\Delta T_{\text{span}}$, as a function of ambient temperature when using Gd, Gd$_{0.05}$Y$_{0.05}$, La(Fe$_{0.86}$Si$_{0.14}$)$_2$H$_{1.2}$, and La(Fe$_{0.86}$Co$_{0.07}$Si$_{0.06}$)$_3$ as refrigerants.](image)
Fig. 7 shows the experimental results obtained from heat load trials during AMR-cycle operations with the Gd$_{0.985}$Y$_{0.015}$ and La(Fe$_{0.86}$Si$_{0.14}$)$_3$H$_{1.2}$ refrigerants along with theoretical results calculated based on the one dimensional heat flow model in AMR cycle. In these trials, the AMR cycle frequency was set to 0.4 Hz. In the case of the AMR-unit with the Gd$_{0.985}$Y$_{0.015}$ refrigerant, the $\Delta T_{\text{span}}$ is seen to decrease sharply with increasing heat load, although the $\Delta T_{\text{span}}$ obtained at no load is about twice as large as that seen for the La(Fe$_{0.86}$Si$_{0.14}$)$_3$H$_{1.2}$ refrigerant. It should be noted that the derivative of $\Delta T_{\text{span}}$ at the intercept (corresponding to the no load point) obtained when using the La(Fe$_{0.86}$Si$_{0.14}$)$_3$H$_{1.2}$ was considerably larger than that seen for the Gd$_{0.985}$Y$_{0.015}$. These results are in good agreement with the model calculation results, indicating that a large specific heat value improves the heat load properties. Precipitous drops are observed in $\Delta T_{\text{span}}$ in the heat load range of 3 to 4 W, derived from the bottleneck in the $\Delta S_{\text{m}}$ decrease arising from its peak shape. The $\Delta S_{\text{m}}$ peak width for the LaFeSi is narrower than that observed in the case of the Gd alloy. Subsequently, we calculated the cooling properties of the AMR-unit assuming the use of multi-layered materials exhibiting gradual variations in $T_C$. The resulting values of $\Delta T_{\text{span}}$ as functions of heat load are shown in Fig. 8(a) and Fig. 8(b) for the Gd-based alloy and the LaFeSi. In the case of the Gd alloy, a slight improvement in the derivative of $\Delta T_{\text{span}}$ at the $\Delta T_{\text{span}}$-intercept (corresponding to the no-load point) was observed when modeling a five-layered structure or when increasing the AMR cycle frequency from 0.4 to 1 Hz.

In contrast, a remarkable improvement in the $\Delta T_{\text{span}}$ derivative was obtained when employing a three- or nine-layered structure composed of LaFeSi at $f = 1$ Hz. Therefore, in the present study, increasing the number of layers is an effective means of increasing $\Delta T_{\text{span}}$ while raising the AMR cycle frequency over the range from $0.4 \leq f \leq 1$ improves the heat-load properties. The significant improvement in the derivative of $\Delta T_{\text{span}}$ in the case of the LaFeSi should be also affected by the high specific heat of this material. Model calculations also indicated the critical $\Delta T_{\text{span}}$ drop down points were extended to 20 W in both multi-layered structures at $f = 1$ Hz.

Fig. 7. Temperature span, $\Delta T_{\text{span}}$, as a function of heat load. Closed circles show the experimental results obtained with Gd$_{0.985}$Y$_{0.015}$ and La(Fe$_{0.86}$Si$_{0.14}$)$_3$H$_{1.2}$ refrigerants. Open triangles show the calculation results.

Fig. 8. Calculation results of temperature span, $\Delta T_{\text{span}}$, for the steady-state during AMR-cycle operation as a function of heat load assuming the 1 kg of refrigerant of (a) Gd-based alloys, and (b) LaFeSi compounds. Triangles show the results with a single refrigerant material layer in the AMR-unit, circles and squares show multi-layered structures. In the case of five-, three-, and nine-layered structures, the Curie temperature of the materials gradually varied by 10 degrees. In the three- and nine-layered structures, the Curie temperature of the materials varied by 10°C, 10°C and 2.5°C, respectively.

### IV. CONCLUSION

Spherical particles composed of Gd alloys and La(Fe$_{13}$Si)$_{13}$-based compounds with diameters ranging from 0.2 to 1.2 mm were fabricated by means of REP and their magnetocaloric properties were characterized. Moreover, the cooling characteristics obtained from the AMR-cycle using particles of La(Fe$_{13}$Si)$_{13}$-based compounds were investigated and compared with the results generated by Gd alloys. It was found that the La(Fe$_{13}$Si)$_{13}$-based compounds generate a AMR-cycle temperature span approximately half that obtained from the Gd alloys. At the same time, the La(Fe$_{13}$Si)$_{13}$-based compounds exhibit better heat-load properties than the Gd alloys. These results are primarily attributed to the greater specific heat of the La(Fe$_{13}$Si)$_{13}$-based compounds. The numerical calculations supported these experimental results and indicated that multi-layered structures composed of the La(Fe$_{13}$Si)$_{13}$-based compounds having a gradual variation in $T_C$ effectively increase the temperature span and demonstrate good heat-load properties. La(Fe$_{13}$Si)$_{13}$-based compounds are thus promising candidates for magnetic refrigeration, and their use may lead to new, environmentally-friendly cooling systems. multi-layered structure by the La(Fe$_{13}$Si)$_{13}$-based compounds gradually-varied $T_C$ are effective to enlarge the temperature span and demonstrate good heat-load properties.
La(Fe, Si)_{13}-based compounds is promising candidate for magnetic refrigeration, and will lead to the new environmentally friendly cooling systems.

**REFERENCES**


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Aikiko T. Saito was born in Tokyo, Japan in December 1964. She received her bachelor’s degree and master’s degree in physics from Hokkaido University, Sapporo, Japan in 1988 and 1990, respectively, and a doctor degree in energy engineering from the Tokyo Institute of Technology, Tokyo, Japan in 1995. She is a senior research scientist at R&D Center of Toshiba Corporation and belongs to Chiba University. Her main research interests are environmentally-friendly techniques associated with the application of new functional materials.