Magnetic entropy change of ErAl₂ magnetocaloric wires fabricated by a powder-in-tube method

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Abstract
We report the fabrication of ErAl₂ magnetocaloric wires by a powder-in-tube (PIT) method and the evaluation of magnetic entropy change through magnetization measurements. The magnetic entropy change of ErAl₂ PIT wires exhibits similar behavior to the bulk counterpart, while its magnitude is reduced by the decrease in the volume fraction of ErAl₂ due to the surrounding non-magnetic sheaths. We find that another effect reduces the magnetic entropy change of the ErAl₂ PIT wires around a ferromagnetic transition temperature, and discuss its possible origin in terms of a correlation between magnetic properties of ErAl₂ and mechanical properties of sheath material.

Keywords: magnetic refrigeration, hydrogen liquefaction, intermetallic compounds, powder-in-tube method

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic refrigeration is a cooling technology based on the magnetocaloric effect in which the variation in magnetic entropy (or temperature) of a magnetic material is caused by changing a magnetic field. A well-established applied technique is a cooling by adiabatic demagnetization to achieve ultra-low temperatures below 1 K [1, 2]. Since 1997, the application to room temperature refrigerators has been enthusiastically studied because magnetic refrigeration has the potential to outperform the conventional vapor-compression refrigeration concerning energy efficiency and environmental friendliness [3, 4]. Many great efforts have been made up to date on the development of working materials with a large magnetocaloric effect near room temperature [5–7] (e.g. Gd₅Si₂Ge₂ discovered by Pecharsky and Gschneidner [8]) and efficient refrigeration systems such as an active magnetic regenerator (AMR) [9–11].

A newly attracting potential application of magnetic refrigeration is the hydrogen liquefaction. Hydrogen is one of the cleanest energy sources to replace fossil fuels [12]. For the use in society, it is efficient and economical to transport and store hydrogen in a liquid state because liquid hydrogen is denser than gaseous hydrogen. In this context, high-efficient liquefaction technology is required. One of the authors has confirmed >50% liquefaction efficiency in a test apparatus of the Carnot magnetic refrigerator worked around the hydrogen liquefaction temperature (20.3 K) [13]. On the other hand, in the practical liquefaction process, it is necessary to pre-cool the hydrogen gas from the temperature of a heat sink, such as liquid nitrogen, to nearly 20.3 K by using a multistage AMR cycle [14–16]. What should be noted here is that the
magnetocaloric material must be processed into a specific shape suitable for each refrigeration system. For example, spherical particles or thin plates have been employed for AMR systems to gain better heat exchange efficiency between the working material and the heat-exchanger fluid [17, 18].

Candidate materials for hydrogen magnetic refrigeration are often found in intermetallic compounds containing heavy rare-earth elements. A representative example is the lanthanide (R) Laves phase RT2 (T = Al, Co, and Ni) [19–21], which exhibits a large magnetic entropy change in the temperature range from 20 to 80 K. However, these compounds are difficult to be shaped due to their poor ductility and malleability. Moreover, these materials are quite brittle, leading to a risk of damage by the friction between them during the refrigeration cycle operation. Such mechanical properties prevent these candidate materials from being used as magnetic refrigerants. Besides, they are known to easily absorb hydrogen, which results in the degradation of the refrigerants and their performance. A coating for protection is a typical way to solve this issue, but this takes extra effort in addition to the shaping process for producing magnetic refrigerants.

Very recently, Funk et al reported [22] a way for producing magnetocaloric wire by a PIT method in La(Fe, Co, Si)13, which is a promising material for the room temperature magnetic refrigeration [23, 24]. The PIT method is a conventional and simple technology that has been developed in the field of superconducting wires [25, 26], in which a powdered raw material is filled into a metal tube and then formed into wire-shaped by various metal workings. This approach is attractive owing to many advantages in applying a PIT method to the candidate materials for the hydrogen magnetic refrigeration as follows: (1) this method is available even for difficult-to-process materials since raw materials can be powder. (2) The metal sheath surrounding the magnetic refrigerants protects them from the frictional wear or the hydrogen embrittlement. (3) As Funk et al have pointed out, the wires provide the possibility of various arrangements of magnetic refrigerants. Besides, it should be noted that recent works have focused on wire-shaped magnetocaloric materials because they have been suggested to show superior performance as magnetic refrigerants to conventional spherical or plate-like materials [27–29].

In this paper, we investigate the effects of a PIT process on the magnetocaloric properties in a well-studied compound ErAl2 that exhibits a second-order ferromagnetic transition at \( T_c \sim 14 \) K [19, 30, 31]. We have confirmed that the magnetic entropy change \( \Delta S_M \) is similar in the ErAl2 PIT wires and the bulk counterpart, while it decreases in magnitude for the former due to a reduction of volume fraction of ErAl2 in the wires. We have further found that another effect causes an additional decrease of \( \Delta S_M \) near \( T_c \), which depends on the sheath material. This is the first report to apply the PIT method for fabricating magnetocaloric wire for the hydrogen liquefaction.

### 2. Experimental details

ErAl2 single-core wires were fabricated by an ex situ PIT method without any heat treatment. ErAl2 raw powder with a diameter of less than 50 \( \mu m \) was prepared by a gas-atomization process. The powder was filled into several metal tubes with 50 mm in length, an outer diameter \( (d_o) \) of 6 mm, and inner diameter \( (d_i) \) of 4 or 5 mm (hereafter, referred to 6 \( \times \) 4 tube and 6 \( \times \) 5 tube, respectively). After filling the powder, the tubes were plugged on both sides by cylinders 7 mm in length made of the same material as each tube. Thus-made initial rods were first groove-rolled into wires with a size of 2 mm stepwisely. Then the wires were cut into about 70 mm and further groove-rolled into those with a size of 1 mm stepwisely. The resulting PIT wires were 260–300 mm in length. Cu, Al, and brass were employed as the sheath materials because they are non-magnetic and show relatively high thermal conductivity.

The cross-sectional observations for the fabricated PIT wires were carried out using a JEOL JSM-6010LA scanning electron microscope (SEM) operated at 15 kV. The cross-sectional area was evaluated using an image analysis software Image-J (National Institute of Health, US). Figures 1(a) and (b) show SEM images of ErAl2/Cu PIT wires fabricated from the 6 \( \times \) 4 and 6 \( \times \) 5 tubes, respectively. These images indicate that the
ErAl₂ powder is uniformly filled inside the Cu-sheath as a core material. The cross-section ratios of the ErAl₂ core to the whole wire were evaluated to be 0.437 from figure 1(a) and 0.655 from figure 1(b), which are comparable to the theoretical filling rate, defined as $a_i^2/a_o^2$, expected for each initial tube (0.444 for the $6 \times 4$ tube and 0.694 for the $6 \times 5$ tube). This result implies that the core and the sheath material were deformed at the same proportion during the rolling process. We have found the same features in ErAl₂/Al and ErAl₂/brass PIT wires.

Magnetization measurements were performed by a Quantum Design magnetic property measurement system. Temperature ($T$) dependence of magnetization ($M$) of the ErAl₂ powder and the PIT wires was measured between 2 and 60 K at a temperature sweep rate of 0.5 K min⁻¹ under various magnetic fields ($\mu_0H$) ranging from 0.1 to 5 T in zero-field cooling (ZFC) process. The magnetic fields were applied along the longitudinal direction of each PIT wire with 5–7 mm in length. For the powder sample, field dependence of magnetization was collected between 0 and 5 T in the temperature range of $2 \leq T \leq 40$ K.

The magnetic entropy change is often evaluated from the isothermal magnetization ($M - \mu_0H$) measurements by using one of Maxwell’s relations

$$\Delta S_M(T, \mu_0\Delta H) = \mu_0 \int_{H_i}^{H_f} \frac{\partial M}{\partial T} \, dH,$$

where $H_i$ and $H_f$ is the initial and final magnetic field, and $\Delta H = H_f - H_i$. However, this way requires us to collect lots of magnetization curves at various temperatures for correct evaluation, which is somewhat time-consuming and makes it difficult to obtain in detail the temperature dependence of $\Delta S_M$. So we first examined how to efficiently and accurately evaluate $\Delta S_M$ from the isofield magnetization ($M - T$) measurements in the ErAl₂ powder. Then the validity of this unconventional method was verified by comparing the results obtained from this and the often-used method. In the following, $H_i$ is set to zero.

3. Results and discussion

Figure 2(a) shows the $M - T$ curves of the ErAl₂ powder. One finds the features typical of a second-order ferromagnetic transition with $T_c$ of 12 K, defined as the temperature at which $\partial M/\partial T$ at 0.1 T takes a maximum. The slight discrepancy with the $T_c$ in the literatures may be because the ErAl₂ powder was made by the gas-atomization process where the material is quenched. Similar $M - T$ curves have been observed in all the ErAl₂ PIT wires (not shown). To calculate $\Delta S_M$ correctly from $M - T$ measurements, one should select the measuring magnetic fields properly. As shown in figure 2(b), $|\partial M/\partial T|$ calculated from figure 2(a) exhibit a non-monotonic field dependence, especially around $T_c$: it steeply increases and reaches the highest point below 1 T, followed by a gradual decrease under higher fields. Since $\Delta S_M(T, \mu_0\Delta H)$ at a fixed $T$ is equivalent to the area in the $\partial M/\partial T - \mu_0H$ plane, this peak structure can largely affect the evaluated value of $\Delta S_M$. Accordingly, it is essential to finely collect the $M - T$ curves under magnetic fields in which the peak of $|\partial M/\partial T|$ appears.

Figure 2(c) shows $\Delta S_M(T, \mu_0\Delta H = 5$ T) of the ErAl₂ powder evaluated using equation (1) based on $\partial M/\partial T - \mu_0H$ data calculated from the $M - T$ curves and the $M - \mu_0H$ curves (see the supplementary data), respectively. Two $\Delta S_M$ curves almost agree with each other and peaks at $T_c$. This result indicates that the magnetic entropy change can be correctly evaluated through the isofield magnetization measurements. $\Delta S_M$ of the PIT wires were evaluated in the same procedure.

Figures 3(a) and (b) represent the temperature dependence of $|\Delta S_M|$ for $\mu_0\Delta H = 5$ T per total volume of 1 cm³ in various ErAl₂ PIT wires fabricated from the $6 \times 4$ and $6 \times 5$ tubes. The data for the ErAl₂ powder is also shown for the comparison. The magnetic entropy change of the PIT wires exhibits qualitatively similar characteristics as those of the powder sample.

3 This magnetic field range corresponds to that in which the magnetization at a sufficiently low temperature increases rapidly and approaches saturation in the $M - \mu_0H$ plane (see the supplementary data (stacks.iop.org/JPhysD/53/095004/mmedia)).
while the magnitude is decreased by about 60\%–70\%. This result is not surprising because the volume fraction of ErAl2 is reduced in the PIT wires. In that sense, the data for the powder sample can be regarded as $|\Delta S_M|$ of a hypothetical wire with 100\% ErAl2 core material. Indeed, $|\Delta S_M|$ becomes larger in the case of the PIT wire fabricated from the 6 $\times$ 5 tube, namely, the larger filling rate of the core material. Furthermore, at the temperatures above 30 K, $|\Delta S_M|$ does not depend on the sheath material when the filling rate is the same. These facts suggest that the volume fraction of the ErAl2 core material mainly determines the magnetic entropy change of the PIT wires. On the other hand, we should notice the difference in $|\Delta S_M|$ between the PIT wires at around $T_c$, where the $|\Delta S_M|$ of the ErAl2/brass wire is significantly decreased. A possible origin of which is discussed below.

Here let us evaluate the ratios of the magnetic entropy change in each PIT wire ($|\Delta S_{M\text{wire}}|$) to that in the ErAl2 powder ($|\Delta S_{M\text{powder}}|$), which should correspond to the volume fraction of the core material. Figures 4(a) and (b) show the temperature dependence of $|\Delta S_{M\text{wire}}/|\Delta S_{M\text{powder}}|$ calculated for the PIT wires made from the 6 $\times$ 4 and 6 $\times$ 5 tubes. One finds that the ratios take constant values at temperatures above 30 K. This makes sense because the volume fraction should not change at any temperature. On that account, we employ the mean value of the temperature-independent $|\Delta S_{M\text{wire}}/|\Delta S_{M\text{powder}}|$ as the actual volume fraction of ErAl2 in the PIT wires, being $\sim$0.30 for the wires made from the 6 $\times$ 4 tube and $\sim$0.49 for those made from the 6 $\times$ 5 tube. These values are about 70\%–75\% of the theoretical volume fraction expected from the SEM images assuming no voids. Funk et al have reported that the volume fraction of La(Fe, Si, Co)$_{13}$ core is about 85\% of the theoretical one, even though pre-compacted raw materials were filled into a metal tube [22]. In contrast, ErAl2 powder was filled without any treatments in this study, implying that there can be more voids in our PIT wires compared with the La(Fe, Si, Co)$_{13}$ PIT wire. Accordingly, the obtained values of the ErAl2 core volume fraction seem to be reasonable. With further decreasing temperature, $|\Delta S_{M\text{wire}}/|\Delta S_{M\text{powder}}|$ gradually decreases and exhibits a dip structure near $T_c$, whose characteristic is noticeable with ErAl2/brass wires. This behavior suggests that there is another contribution that affects the magnetic entropy change of ErAl2 itself in the PIT wires, in addition to the decrease in the volume fraction of the core material.

Now we will discuss a possible origin of the extra reduction of $|\Delta S_M|$ around $T_c$ observed in the PIT wires. According to equation (1), a decrease in $\Delta S_M$ results from a decrease in $(\partial M/\partial T)_H$, which occurs when $M$ decreases without changing the temperature dependence and/or when the temperature dependence itself becomes more gradual. To clarify this point, we plot $M/M_{50K}$ at 5 T as a function...
of temperature in figure 5 for the ErAl2 powder and the PIT wires made from the 6 × 5 tube. The magnetizations show the same temperature dependence down to 30 K for all the samples, but the rise in M of the PIT wires is suppressed with further decreasing temperature, the trend is most significant in the ErAl2/brass wire. This mild temperature variation does be the cause of the decrease in \( \frac{\partial M}{\partial T} \) for the PIT wires. The difference in M – T curves observed here resembles those found in ferromagnetic materials with a uniaxial magnetic anisotropy [32–34], in which \( \frac{\partial M}{\partial T} \) becomes smaller in the direction perpendicular to an easy axis of the magnetization. Thus, the extra reduction of \( |\Delta S_M| \) around \( T_c \) suggests that the PIT process induces a magnetic anisotropy in the ErAl2 core material with an easy axis perpendicular to the longitudinal direction of the wire.

It is well known that a rolling process causes a kind of magnetic anisotropy in magnetic materials [35–38]. This magnetic anisotropy is known to increase as the mechanical deformation increases, and the latter usually increases with the stress on magnetic material during rolling. On the other hand, in several studies on superconducting PIT wires [39, 40], it has been pointed out that the higher the hardness of sheath material, the stronger the stress on a core material during cold working. From these facts, the magnetic anisotropy induced by rolling is expected to be large in the use of the harder tube in a PIT process. Since Vickers hardness is indeed higher in the order of Al, Cu, and brass, the expectation is consistent with the result that \( |\Delta S_M| \) around \( T_c \) is most decreased in the ErAl2/brass PIT wires. Therefore, we conclude that the PIT process affects the magnetocaloric properties of the ErAl2 core material through the induced uniaxial magnetic anisotropy. However, the exact nature of the magnetic anisotropy remains unclear at the present stage. To get more insight, it is desirable to investigate the effect of annealing that may control the plastic deformation.

4. Conclusion

We have fabricated the magnetocaloric wires of ErAl2 cladded by non-magnetic metal sheaths by using a PIT method combined with groove rolling. These PIT wires exhibit magnetic entropy changes similar to that of the powder sample, with their magnitude reduced due to the decrease in the volume fraction of the ErAl2 core. We propose that the PIT process affects the magnetocaloric properties of the core material through a kind of the induced uniaxial magnetic anisotropy and causes the extra reduction of the magnetic entropy change around \( T_c \). There is still room for improvement of the magnetocaloric properties in the PIT wires by annealing process and additional processes that increase the volume fraction of the core. We believe that the wire-shaped magnetocaloric materials prepared by a PIT method would be of benefit to the development of magnetic refrigerators for the hydrogen liquefaction.

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