The effect of thermal hysteresis on the performance of a regenerative Ericsson refrigeration cycle with MnFe-based composite material

Yan Li¹, Guoxing Lin and Jincan Chen
Department of Physics, Xiamen University, Xiamen 361005, P.R. China
¹Email: YLEEXMU@outlook.com

Abstract. MnFe-based magnetocaloric materials exist a giant magnetocaloric effect so that they can be used as the working substance for room-temperature magnetic refrigeration. But there are two key problems to be solved before employing them as the working substance: one is that for single MnFe-based material, its giant magnetocaloric effect only arise in a small temperature range and the other is that these materials exist generally thermal hysteresis. For these reasons, a novel composite material based on MnFe-based materials is designed optimally, and a regenerative Ericsson refrigeration cycle using the composite material as the working substance is established. Furthermore, the performance of the refrigeration cycle with the composite is analyzed and evaluated. The influences of thermal hysteresis on main thermodynamic parameters of the refrigeration cycle are revealed by numerical calculation. The research results can provide some significant guidances for the parametric design and performance improvement of room-temperature magnetic refrigerators.

1. Introduction
The development and utilization of new energy source with environmental protection have become a hot topic and pressing research project in recent years. Magnetic refrigeration, which employs solid material as its refrigerant, is a new-style refrigeration technology with high-efficiency, energy conservation, environmental-friendly [1, 2]. More and more scholars and engineers have paid their attentions to its research and development. Along with the development of room-temperature (RT) magnetic refrigeration technology, the problems of small refrigeration temperature span and low cooling power emerge. A lot of experimental researches on RT magnetic refrigeration materials and magnetic refrigeration prototypes [3, 4] and some theoretical investigations on magnetic refrigeration cycle performances [5, 6] have been carried out.

Improving cooling power and refrigeration temperature span of RT magnetic refrigerators is an important assignment at present. The key to do that lies in finding more giant magnetocaloric effect (MCE) materials accompanying large refrigeration temperature span and the performance optimization design of RT magnetic refrigerators. Gadolinium (Gd) and its alloys are widely used as RT magnetic refrigeration materials. Due to no large MCE, easy corrosion and high price of these materials restrict the commercialization of the RT magnetic refrigerators. Therefore, it is necessary to explore other RT magnetic refrigeration materials. Sharma et al., present the structural, magnetic, and magnetocaloric data for perovskite TmFeO₃ and establish a magnetic hysteresis cycle for different values of temperatures [7]. Kadim et al., propose the Ho₃Pd₂ compound with large magnetocaloric effect and magnetic and electronic characteristics [8]. Erchidi et al., propose a promising magnetic refrigerant Sr₂FeMoO₆ and SmFe₁₋ₓMnxO₃ [9,10].

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First-order phase changes magnetic refrigeration materials such as Mn (Fe, P, As, Si, Ge) [11-13], La (Fe, Si) [14] and La\(_{1-x}\)Ca\(_x\)MnO\(_3\) [15], Heusler alloys [16] etc., are superior to Gd [17] in MCE performance and production cost. MnFe-based materials belong to hexagonal crystal structure, have large or giant MCE and they are the important candidates of RT magnetic refrigerants. However, the thermal hysteresis and magnetic hysteresis exist in a lot of these materials, which have an adverse influence on refrigeration cycle performance. Exploring the impact of hysteresis on the refrigeration cycle performance is beneficial to the optimum parametric design of RT magnetic refrigerators.

In the present paper, based on the experimental data of heat capacity, entropy temperature characteristic and magnetic entropy change curves of MnFe-based magnetocaloric materials under different magnetic fields are obtained. A new composite material using two kinds of MnFe-based constituent material, (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_1\) and (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_2\), is optimally designed to improve refrigeration temperature span. Then, a regenerative Ericsson refrigeration cycle using the composite material as the working substance is put forward, in which the thermal hysteresis and the non-perfect regeneration are taken into account. Furthermore, the mathematic expressions of the net cooling quantity, coefficient of performance (COP) etc., are derived by thermodynamic analysis method. The influence of thermal hysteresis on the net cooling quantity and COP are revealed. The numerical calculation results indicate that the thermodynamic parameter values of the regenerative Ericsson refrigeration cycles with thermal hysteresis are smaller than those without thermal hysteresis.

2. Optimal mass ratio of MnFe-based constituent to composite material

Using the experimental data of two kinds of MnFe-based magnetocaloric materials, (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_1\) and (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_2\), obtained from Delft university of technology, one can generate the performance characteristic curves of these materials, as shown in Figure 1. The composite based on two kinds of MnFe-based magnetocaloric materials is a layer structural composite. For achieving a near perfect regeneration in regenerative Ericsson refrigeration cycle, the mass ratios of the constituent materials to the composite should be optimally designed. Thus, the composite will not change the MCE properties of materials, but the resultant entropy change of the composite will learn from others’ strong points to offset one’s weakness.

![Figure 1](image)

**Figure 1.** Heat capacity versus temperature curves for (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_1\) (a) and (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_2\) (b) with or without thermal hysteresis, applied fields 0 and 1.5 T; isothermal magnetic entropy change versus temperature curves for (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_1\) and (Mn\(_{1-x}\)Fe\(_x\)P\(_{1-y}\)Si\(_y\))\(_2\) with or without thermal hysteresis under 0-1.5 T field change (c).
The Curie temperatures and mass ratios of each MnFe-based magnetocaloric material are $T_m^1$, $T_m^2$ and $z_1$, $z_2$, respectively. Notice that entropy is an extensive quantity and satisfies the entropy increase principle. Therefore, the magnetic entropy change of the composite material may be expressed as:

$$\Delta S_{\text{com}} = \sum_{j=1}^{2} z_j \Delta S_j (\Delta \mu_\circ H, T)$$  \hspace{1cm} (1)

where $\Delta S_1$, $\Delta S_2$ are the magnetic entropy change of the $(\text{Mn}_{1-x}\text{Fe}_x\text{P}_{1-y}\text{Si}_y)_1$ and $(\text{Mn}_{1-x}\text{Fe}_x\text{P}_{1-y}\text{Si}_y)_2$, $\mu_\circ H$ is the magnetic field intensity ($\mu_\circ H^\prime > \mu_\circ H^\ddagger$) and $T$ is the absolute temperature.

In order to decrease the impact of non-perfect regeneration on the performance of the regenerative Ericsson refrigeration cycle, $(\text{Mn}_{1-x}\text{Fe}_x\text{P}_{1-y}\text{Si}_y)_1$ and $(\text{Mn}_{1-x}\text{Fe}_x\text{P}_{1-y}\text{Si}_y)_2$ should be composited with an optimum mass ratio, which can be calculated based on the following equation [18]:

$$\sum_{j=1}^{2} z_j [\Delta S_j (\Delta \mu_\circ H, T_m^{i+1}) - \Delta S_j (\Delta \mu_\circ H, T_m^i)] = 0 (i = 1, 2)$$  \hspace{1cm} (2)

and

$$\sum_{j=1}^{2} z_j = 1.$$  \hspace{1cm} (3)

Equations (2) and (3) can be simplified into the following matrix equation:

$$\begin{pmatrix} a' & b' \\ 1 & 1 \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$  \hspace{1cm} (4)

where the matrix elements: $a' = \Delta S_1 (\Delta \mu_\circ H, T_m^2) - \Delta S_1 (\Delta \mu_\circ H, T_m^1)$, $b' = \Delta S_2 (\Delta \mu_\circ H, T_m^2) - \Delta S_2 (\Delta \mu_\circ H, T_m^1)$.

According to Figure 1(c) and Eq. (4), the optimum mass ratios can be solved out through numerical calculation, i.e., $z_1 = 0.56$, and $z_2 = 0.44$. In other words, the composite satisfying the optimum mass ratios can make its resultant magnetic entropy change maintain basically a giant MCE over a wider temperature range. This can not only increase refrigeration temperature span but also decrease the non-perfect regeneration in the regenerative Ericsson refrigeration cycle.

3. A regenerative Ericsson refrigeration cycle using the composite as the working substance

Based on Figure 1(a) and (b), Eq. (1), and the optimum mass ratios, the entropy-temperature characteristic curves of MnFe-based composite under different magnetic fields can be obtained by numerical calculation, as shown in Figure 2. From these curves, we may set up a regenerative Ericsson refrigeration cycle (ABCDA), which includes two isothermal processes (A$\rightarrow$B and C$\rightarrow$D) and two iso-magnetic field processes (B$\rightarrow$C and D$\rightarrow$A). $Q_{\text{ei}}$ and $Q_{\text{os}}$ are the heat absorbing from the cold reservoir (or the cooled space) and the heat released to the hot reservoir; $Q_{\text{ws}}$ is the heat absorbed from the regenerator, and $Q_{\text{sr}}$ is the heat transferred to the regenerator during the iso-magnetic field processes. $T_h$ and $T_c$ are the temperatures of the hot and cold reservoirs, respectively; $T_m$ is the temperature at which the maximum magnetic entropy change of the working substance arises.

Based on Figure 1(a) and (b), the entropy of MnFe-based material with definite temperature and magnetic field can be calculated by the following equation:

$$S(\mu_\circ H, T) = \int \frac{C_\mu (\mu_\circ H, T)}{T} dT$$  \hspace{1cm} (5)

and the isothermal magnetic entropy change is expressed as

$$\Delta S(\Delta \mu_\circ H, T) = S(\mu_\circ H^\prime, T) - S(\mu_\circ H^\ddagger, T).$$  \hspace{1cm} (6)
Figure 2. Iso-field entropy versus temperature curves for the composite with 0 and 1.5 T.

By combining with the thermodynamic theory and the regenerative Ericsson refrigeration cycle shown in Figure 2, the exchanged heats of each process in the refrigeration cycle can be, respectively, calculated by the following equations [19]:

\[
Q_{eq} = \int_{C\rightarrow D} TdS = -T_c \Delta S (\Delta \mu_e H, T_c),
\]

(7)

\[
Q_{rh} = \int_{A\rightarrow B} TdS = T_i \Delta S (\Delta \mu_e H, T_i),
\]

(8)

\[
Q_{wse} = \int_{B\rightarrow C} TdS = \int_{T_i}^{T_r} C_H (\mu_e H', T)dT,
\]

(9)

and

\[
Q_{wsr} = \int_{D\rightarrow A} TdS = \int_{T_r}^{T_i} C_H (\mu_e H', T)dT.
\]

(10)

The non-perfect regeneration quantity is given by:

\[
Q_{nr} = Q_{wse} - Q_{wsr}.
\]

(11)

It should be pointed out that the regenerative Ericsson refrigeration cycles may be established on the left, right and both sides of \( T_m \) such that the non-perfect regenerations for different Ericsson refrigeration cycles are generally different. All that matters is that the non-perfect regeneration will affect the performance of the refrigeration cycle such as the net cooling quantity and COP. The net cooling quantity of the regenerative Ericsson refrigeration cycle can be expressed as:

\[
Q_i = Q_{eq} - \delta Q_{nr},
\]

(12)

where \( \delta = 1 \) when \( Q_{nr} \geq 0 \) and \( \delta = 0 \) when \( Q_{nr} < 0 \).

On the other hand, the work input and COP of the regenerative Ericsson refrigeration cycle are given by [20]:

\[
W = -(Q_{rh} + Q_{eq} + Q_{wsr} + Q_{wse})
\]

(13)

and

\[
COP = \frac{Q_i}{W}.
\]

(14)

These equations will be used to calculate and evaluate the performance characteristics of the regenerative Ericsson refrigeration cycle using the composite as the working substance.

4. Results and discussion

On the basis of the above analysis, the effect of thermal hysteresis on the performance of the regenerative Ericsson refrigeration cycle using MnFe-based composite as the working substance will be discussed and evaluated.
4.1. Cooling quantity

From Figure 2, one can find that when \( T_h = 290.0 \) K, increasing \( T_r \) will result in the change of the cooling quantity. The further calculation results show that as \( T_r \) increases, \( Q_{cq} \) first increases and then decreases. Figure 3 shows the cooling quantity \( Q_{cq} \) versus the cold reservoir temperature \( T_c \) curves, where the blue and orange curves correspond to the cases of the cycle with and without thermal hysteresis, respectively. When thermal hysteresis is taken into account, the maximum cooling quantity occurs at \( T'_h = 287.1 \) K and its value is 1333 J kg\(^{-1}\); and when thermal hysteresis is neglected, the maximum cooling quantity appears at \( T_h = 287.9 \) K and its value is 1801 J kg\(^{-1}\). The presence of thermal hysteresis results in decreasing by 25.99% of the cooling quantity.

**Figure 3.** The \( Q_{cq} \) of the regenerative Ericsson refrigeration cycle with MnFe-based composite material versus \( T_r \) curves.

**Figure 4.** The \( Q_{l} \) of the regenerative Ericsson refrigeration cycle using the composite as the working substance versus \( T_r \) curves for different \( T_h \).
4.2. Net cooling quantity
Because of the non-perfect regeneration, the net cooling quantity is smaller than or equal to the cooling quantity for a perfect regenerative Ericsson refrigeration cycle. Figure 4(a)-(c) show that under different $T_m$, the (net) cooling quantity $Q_l$ of the refrigeration cycle versus $T_c$ curves. It can be seen from Figure 4(a) that when $T_c = T_m - 3K$, the net cooling quantity $Q_l$ is not affected by the non-perfect regeneration, but the non-perfect regeneration $Q_{nr}$ will affect COP. In this case, the net cooling quantity is completely the same no matter whether the thermal hysteresis is considered.

Figure 4(b) and (c) show that when $T_c = T_m + 3K$ and $T_c = T_m + 4K$, the non-perfect regeneration quantity has different degrees of influence on the net cooling quantity. In these cases, the net cooling quantity of the present model is always smaller than that of the perfect refrigeration cycle. When $T_c < T_m$, the net cooling quantity increases rapidly with increasing $T_c$. With the further increase of $T_c$, the net cooling quantity becomes relatively flat. When $T_c < T_m$, the non-perfect regeneration of the refrigeration cycle has the large impact on the net cooling quantity. As $T_c$ increases, the difference of the net cooling quantities with and without thermal hysteresis becomes large. For example, when $T_c = 283.0 K$, the difference of the net cooling quantity is 104 J kg$^{-1}$; while $T_c = 286.0 K$, the difference of the net cooling quantity is 136 J kg$^{-1}$. However, when $T_c > T_m$, the difference becomes almost constant, as shown in Figure 4(b) and 4(c).

4.3. Coefficient of performance
Figure 5 shows the COP as a function of $T_c$. It can be seen from Figure 5 that the COP of the refrigeration cycle increases monotonously with the increase of $T_c$. When $T_c$ is equal to 287.1 K or 287.9 K, the COP value without thermal hysteresis is significantly larger than that with thermal hysteresis. As an example, when $T_c = T_m + 3K$ or $T_c = T_m + 3K$, without and with thermal hysteresis, the COP values of the refrigeration cycle are 14.2 and 8.8, respectively, the latter is about 62 % of the former.

5. Conclusions
In the present paper, based on the experimental data of two kinds of MnFe-based magnetocaloric material, $(Mn_{1-x}Fe_xP_{1-y}Si_y)_1$ and $(Mn_{1-x}Fe_xP_{1-y}Si_y)_2$, we design optimally a new MnFe-based composite material that its refrigeration temperature span is larger than that of single MnFe-based magnetocaloric material. The regenerative Ericsson refrigeration cycles using MnFe-based composite material as the working substance are set up, in which the thermal hysteresis of materials is taken into account. Main thermodynamic parameters are derived and the effect of the thermal hysteresis on the performances of the regenerative Ericsson refrigeration cycles are revealed. The numerical calculation results with and
without the thermal hysteresis are compared. The research results can provide some theoretical
guidance for the optimal design of RT magnetic refrigerators.

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