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International Journal of Refrigeration 26 (2003) 622–636

REVUE INTERNATIONALE DU FROID
INTERNATIONAL JOURNAL OF
refrigeration

www.elsevier.com/locate/ijrefrig

Review Article

Review on research of room temperature magnetic refrigeration

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Received 12 November 2002; received in revised form 25 March 2003; accepted 8 April 2003

Abstract

Room temperature magnetic refrigeration is a new highly efficient and environmentally protective technology. Although it has not been maturely developed, it shows great applicable prosperity and seems to be a substitute for the traditional vapor compression technology. In this paper, the concept of magnetocaloric effect is explained. The development of the magnetic material, magnetic refrigeration cycles, magnetic field and the regenerator of room temperature magnetic refrigeration is introduced. Finally some typical room temperature magnetic refrigeration prototypes are reviewed.

Keywords: Refrigerating system; Magnetic; Refrigerating cycle; Ericsson; Brayton; Performance; Research; Survey

Recherches sur les systèmes frigorifiques magnétiques à température ambiante : la littérature passée en revue

Mots clés : Système frigorifique ; Magnétisme ; Cycle frigorifique ; Ericsson ; Brayton ; Performance ; Recherche ; Enquête

Contents

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0140-7007/03/$35.00
doi:10.1016/S0140-7007(03)00048-3

1. Introduction

Although Montreal Protocol has been restricting the harm to environment of ODS (Ozone Depletion Substance) to a great extent, the greenhouse effect problem is not be solved completely yet. So, in addition to further developing the vapor compression technology, scientists and engineers have begun to explore new refrigeration technology such as thermoelectric refrigeration, thermoacoustic refrigeration, absorption/adsorption refrigeration, and magnetic refrigeration.

The study of magnetic refrigeration was started with the discovery of magnetocaloric effect (MCE) 120 years ago [1]. Then it has been used in cryogenic refrigeration since 1930s. It is maturely used in liquefaction of hydrogen and helium. In 1976, at Lewis Research Center of American National Aeronautics and Space Administration, Brown first applied the magnetic refrigeration in a room-temperature range [2]. By employing rare-earth metal gadolinium (Gd) as the magnetic refrigeration working substance, he attained a 47 K no-load temperature difference in a 7 T magnetic field. Based on the concept of the active magnetic regenerator (AMR), Zimm at American Astronautics Technology Center developed a magnetic refrigerator in 1996, which used approximately 3 kg of Gd as working material and generated up to 500–600 W cooling power in a 5 T magnetic field [3].

Magnetic refrigeration is an environment-safe refrigeration technology. The magnetic refrigeration does not have ozone-depleting and greenhouse effects for employing magnetic materials as refrigeration media. What is more, the magnetic refrigeration unit can be compact, for the magnetic entropy density of magnetic material is larger than that of refrigerant gas. The magnetic field of magnetic refrigeration can be supplied by electromagnet, superconductor or permanent magnet, which have no need for compressors with movable components, large rotational speed, mechanical vibration, noise, bad stability and short longevity. The efficiency of magnetic refrigeration can be 30–60% of Carnot cycle [3], whereas the efficiency of vapor compression refrigeration is only 5–10% of Carnot cycle. Therefore, the magnetic refrigeration is expected to have great applicable prospects.

2. Magnetocaloric effect (MCE)

Warburg first discovered the thermal effect of metal iron when applying it in a varying magnetic field in 1881 [1]. Debye and Giauque explained the nature of MCE later and suggested achieving an ultra-low temperature by adiabatic demagnetization cooling [4,5]. In recent years, magnetic refrigeration on the basis of MCE has been greatly developed in the room temperature range. Whether in the range of room temperature or low temperatures, the magnitude of MCE of magnetic material is the key to cooling capacity.

Entropy of magnet at constant pressure, $S(T,H)$, which is both magnetic field and temperature dependant, consists of the magnetic entropy (S_M), the lattice entropy (S_L), and the electronic entropy (S_E):

$$S(T, H) = S_M(T, H) + S_L(T) + S_E(T) \quad (1)$$

In the above formation, S_M is a function of both H and T, but S_L and S_E are functions of T only. As a result, only the magnetic entropy, S_M, can be controlled by changing the strength of magnetic field.

The magnetocaloric effect, which is intrinsic to all magnetic materials, indicates that the paramagnetic or soft ferromagnetic materials expel heat and their magnetic entropy decrease when the magnetic field is applied isothermally; or otherwise absorb heat and their magnetic entropy increase when the magnetic field is reduced isothermally. Fig. 1 illustrates the MCE (represented by ΔT_{ad} or ΔS_M) of ferromagnetic material in the vicinity of magnetic ordering temperature (Curie temperature T_C). Pecharsky lately pointed out that ΔS_M is not the same as ΔT_{ad} when comparing the MCE of two materials considering the heat capacity differences. He proposed the volumetric magnetic isothermal entropy change as the parameter of the MCE [7].

At the material's magnetic phase transition (PT) point, the MCE peaks strongly and the heat capacity exhibits an anomaly. When the temperature deviates the PT temperature, the MCE decreases greatly. The magnitude of MCE can be obtained both by molecular field approximation (MFA) calculation [8,9] and experimental measurements. Direct MCE measurements of ΔT_{ad} can be conducted using traditional ways with a sensor thermally contacted to the sample [10–14] or by the noncontact thermoacoustic approach [15–17]; indirect measurements are realized by calculation based on the Maxwell relationship after measuring the isothermal magnetization and the field-dependent heat capacity (This method is popular now) [6,18]. Both methods show reasonable agreement [19].

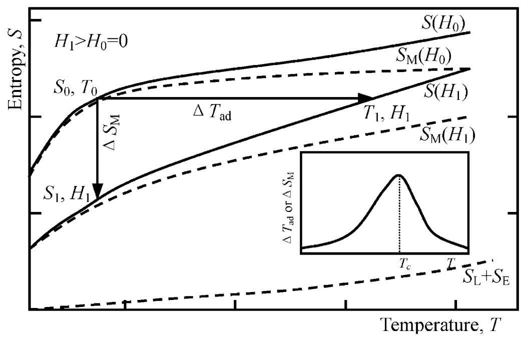

Fig. 1. S–T diagram of MCE.

3. Magnetic material

3.1. Selection of room temperature magnetic material

From the previous entropy analysis of magnetic materials, only magnetic entropy S_M is changeable with the magnetic field change. In the range of room temperature, the influence of lattice entropy S_L is too remarkable to neglect. Therefore, part of the cooling capacity of the magnetic system is consumed for cooling lattice system for the entropy flow from the lattice system, though the temperature decreases to some extent during adiabatic demagnetization. Thus the gross cooling capacity is less than that of the condition of $(S_L + S_E) \approx 0$ [20].

As the core of the magnetic refrigeration, several features of magnetic materials are required for application [21]:

- large total angular momentum number J and Lande factor g of ferromagnetic material, which are crucial to MCE;
- modest Debye temperature (A high Debye temperature makes the fraction of lattice entropy small correspondingly in high temperature ranges);
- modest Curie temperature in the vicinity of working temperature to guarantee that the large magnetic entropy change can be obtained in the whole temperature range of the cycle;
- essentially zero magnetic hysteresis;
- small specific heat and large thermal conductivity to ensure remarkable temperature change and rapid heat exchange;
- large electric resistance to avoid the eddy current loss; and
- fine molding and processing behavior to fabricate the magnetic materials satisfactory to the magnetic refrigeration.

3.2. Research progress of room temperature magnetic materials

Since Brown first applied ferromagnetic material gadolinium (Gd) in the room temperature magnetic refrigerator in 1976, the research range for magnetic refrigeration working materials has been greatly expanded. At first, some ferromagnets concerning the second-order transition were investigated for the large MCE existing in them. Recently the magnetic materials undergoing a first-order magnetic transition become the focus after the giant MCE was found in GdSiGe alloys. Some magnetic materials that are promise to be used in the future are described later.

3.2.1. Gd and its alloys

The prototype magnetic material available for room temperature magnetic refrigeration is the lanthanide metal gadolinium (Gd). At the Curie temperature of 294 K, Gd undergoes a second-order paramagnetic ↔ ferromagnetic phase transition. The MCE [10–12,14,16,19,22–29] and the heat capacity [29–32] of Gd have been studied in many research activities. Its ΔT_{ad} values at T_C are ~6, 12, 16, and 20 K for ΔH = 2, 5, 7.5, and 10 T, respectively; its ΔS_M is about 4.2 J kg^{-1} K^{-1} forΔH = 1.5 T at T_C. Being a metal material, its thermal conductivity and easy-gain are both favorable. It would be the first choice for laboratory research of room temperature magnetic refrigerator so long as the problem of easy oxidization is settled.

Some Gd-based intermetallic compounds have also been proved to possess large MCE. Both $Gd_{0.74}Tb_{0.26}$ [33] and $Gd_{0.5}Dy_{0.5}$ [34] present the MCE equivalent to Gd at ~280 K and at ~265 K, respectively. The ΔT_{ad} values of $Gd_{91.8}Dy_{8.2}$ and $Gd_{89.9}Er_{10.1}$ at a 0.45 T low field are ~1.4 K (at 280 K) and ~1.5 K, respectively, something lower than that of Gd ~2.0 K [16]. Eutectic $Gd_{76}Pd_{24}$ was found two ΔT_{ad} peaks of 8.4 K and 9.4 K at 294 K and 323 K, respectively, and it is favorable to be used in magnetic Ericsson cycle because the adiabatic temperature change is almost constant in the room temperature range [35]. Concerning $Gd_4(Bi_xSb_{1-x})_3$ alloys, although the maximum MCE is nearly 50% of pure Gd at a 10 T field, the width of the peaks at half maximum reaches 60–100 K, which is comparable with that of Gd. So they can provide considerable cooling power over a wide temperature range from ~240 to ~360 K [36].

It was considered to be a milestone of magnetic material research that the reversible giant magnetocaloric effect in a series of GdSiGe alloys was observed in Ames Laboratory [37–39]. Subsequently, plenty of efforts have been devoted to the research on this series [40–48]. These alloys, which have a first-order magnetic transition between ~30 and ~275 K depending the Si to Ge ratio, have peak values of magnetic entropy change 2–10 times larger than that of known prototype magnetic refrigerant materials. It is shown that the ΔS_M values of the series of $Gd_5(Si_xGe_{1-x})_4$ alloys where $0 \leqslant x \leqslant 0.5$, are at least twice that of Gd. Furthermore, by alloying with Ga, the giant MCE temperature increases to ~290 K [37,38].

Table 1 presents the magnetic entropy of some magnetic materials in the range of near room temperature, from which it can be seen that ΔS_M of the GdSiGe alloys are all considerably large in the presence of a 5 T magnetic field and most of those Curie temperatures are

Table 1
Magnetic entropy change of some near room temperature magnetic materials

Magnetic material		T_C (K)	ΔH (T)	ΔS_M (J kg^{-1} K^{-1})	Ref.
Gd		**294**	**5.0**	**~10.2 (ΔT_{ad} = ~12 K)**	28
$Gd_{0.5}Dy_{0.5}$		230	5.0	~10.2	34
$Gd_{0.74}Tb_{0.26}$		280	5.0	~11.5	33
Gd_7Pd_3		323	5.0	ΔT_{ad} = 8.5 K	35
$Gd_5(Si_xGe_{1-x})_4$	x = 0.43	247	5.0	~39.0	
	x = 0.5	276	5.0	~18.4	37
	x = 0.505	280	5.0	~11.7	47
$Gd_5(Si_{1.985}Ge_{1.985}Ga_{0.03})_2$		**290**	**5.0**	**ΔT_{ad} = 15 K**	**41**
$Ni_{52.6}Mn_{23.1}Ga_{24.3}$		300	5.0	~18.0	70
MnAs		318	5.0	30.0	72
$MnAs_{0.9}Sb_{0.1}$		~286	5.0	~30.0	73
$MnFeP_{0.45}As_{0.55}$		300	5.0	18.0	74
Gd			**1.5**	**~3.8**	
		294	**3.0**	**~7.1**	**28**
			6.0	**~11.4**	
$La_{1-x}Ca_xMnO_3$	x = 0.2	230	1.5	5.5	52
	x = 0.33	267	3.0	6.4	62
		~259	3.0	~2.6	49
	x = 0.35	~255	3.0	~5.2	59
	x = 0.4	263	3.0	5.0	53
$La_{0.9}K_{0.1}MnO_3$		283	1.5	1.5	51
$La_{0.75}Ca_{0.15}Sr_{0.10}MnO_3$		327	1.5	~2.8	52
$La_{2/3}(Ca,Pb)_{1/3}MnO_3$		296	7.0	7.5	65

in the room temperature range. Therefore, this series of alloys meet the requirements of room temperature magnetic refrigeration. However, many urgent problems such as easy oxidation, hard preparation, and high price, need to be settled before they are applied in room temperature magnetic refrigeration.

3.2.2. Perovskite and perovskite-like compounds

Large magnetic entropy change has been found in the perovskite manganese oxides in recent years, so that these materials attract more and more attention. The main advantages of this series of compounds over Gd and GdSiGe alloys are low cost, non-active chemical property (no oxidation), little coercive force as well as high electric resistance. Many studies on these compounds are led mainly in China, Spain and United States [49–65]. From Table 1, it is clear that their Curie temperature also can be easily tuned to the needed range by introducing some kinds of metal additions. However, ΔS_M will decrease much in the meantime, lowering their practicability. For instance, ΔS_M of $La_{0.8}Ca_{0.2}MnO_3$ in the presence of 1.5 T magnetic field reaches 5.5 J kg^{-1} K^{-1}, about 1.5 times of Gd, but its Curie temperature is only 230 K. After adjusting Ca ratio to $La_{0.6}Ca_{0.4}MnO_3$, its Curie point increases to 263 K but ΔS_M decreases to 70% of Gd at 3.0 T. To improve the Curie temperatures by adding Sr and Pb, the Curie temperatures reach 327 and 296 K, however ΔS_M decreases obviously. In addition, the behavior of heat transfer of these compounds is incompetent because they are oxides.

3.2.3. Transition metal compounds

Early in 1984, Oesterreicher observed the magnetocaloric effect of rare-earth transition metal compounds whose Curie temperatures are in the vicinity of room temperature, and suggested that it is possible for the series of $Y_2Fe_{17-x}Co_x$ and $Y_2Fe_{17-x}Ni_x$ compounds to be room temperature magnetic refrigerants [66]. Later investigations showed that some other rare-earth transition metal compounds besides GdSiGe alloys mentioned above also exhibit great magnetic entropy change, and their Curie temperatures can easily be tuned by ion doping. The research on $Ce_{2-x}Dy_xFe_{17}$ alloys showed thatΔS_M (in a 1.4 T magnetic field) are ~1.67, 1.41 and 1.18 J kg^{-1} K^{-1} where $x=0.0$, 0.3, and 0.5, and the corresponding temperatures are ~234, ~267, and ~286 K, respectively [68]. Another investigation indicated that the maximum ΔT_{ad} in the series of $Ce_2Fe_{17-x}Co_x$ and $Er_2Fe_{17-x}Ni_x$ ($x=0.3$–2.0) are 4.75 and 4.51 K (in a 2 T magnetic field), and their corresponding Curie temperature values are 294.2 K and 293.5 K, respectively, near metal Gd but much less expensive than Gd [69]. Hence, this series of compounds are benign choices from the view of practical application. The non-rare-earth based Heusler alloys Ni-Mn-Ga undergo a first order transition, which brings about a great magnetic entropy change [70,71]. This has attracted considerable interests. The magnetic entropy change of $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ at 300 K is ~18.0 J kg^{-1} K^{-1}, roughly comparable with that of $Gd_5Si_2Ge_2$ and notably exceeds that of Gd near room temperature [70]. But the width of the peak is only several K and there is a 6 K thermal hysteresis accompanying with the transition, both of which make this alloy unfavorable.

Of the transition-metal-based compounds, MnAs shows a giant MCE. It undergoes a first-order ferromagnetic to paramagnetic transition at 318 K and the magnetic entropy change induced by a 5 T magnetic field is 30 J kg^{-1} K^{-1} at a maximum value, which exceeds that of $Gd_5Si_2Ge_2$ by a factor of 2. However, the magnetic transition is accompanied by a large thermal hysteresis [72]. To tune the Curie temperature to the range below 300 K, $MnAs_{1-x}$ Sb_x compounds have been investigated. The result shows that ΔS_M of $MnAs_{1-x}$ Sb_x for $0 \leqslant x \leqslant 0.3$ in a 5 T field reaches 25–30 J kg^{-1} K^{-1}, and the substitution of Sb for As can tune the Curie temperature between 230 K and 315 K without significant reduction of ΔS_M. Moreover, there is no hysteretic behavior for $0.05 \leqslant x$ and these materials are less cost than other materials so far [73]. Another compound $MnFeP_{0.45}As_{0.55}$ exhibits a giant magnetic entropy change of similar magnitude to the giant MCE material $Gd_5Ge_2Si_2$. Variation of the P/As ratio between 3/2 and 1/2 makes it possible to tune T_C and the optimal operating temperature between 200 and 350 K, without losing the giant MCE [74].

3.2.4. Composite material

Single material, whose temperature range is not so wide enough to be made use of, cannot meet the need of ideal magnetic Ericsson cycle. As a solution, a method of composition was first raised by Brown [75]. The method of composition is that a few ferromagnetic materials with different magnetic phase transition temperature T_C are composed to one new material whose ΔS_M is even in the range of refrigeration temperature. Tokyo Institute of Technology have made experimental trials to make the layer structural sintered material composed of ErAl, HoAl, (DyHo)Al and DyAl alloys in the low temperature range [76,77], which confirmed that the composition of magnetic materials is a future method benign to magnetic Ericsson cycle. In another investigation, two sets of composite materials were obtained over the temperature 240–290 and 210–290 K, respectively from the GdDy alloys. The resultant ΔS_M is practically constant in the required temperature range and amounts to 8.0 and 7.3 J kg^{-1} K^{-1} for the two respective sets [78].

In addition, nanometer-sized magnetic materials may be a useful option for future application [79–83].

4. Magnetic refrigeration cycle

Magnetic refrigerator completes cooling/refrigeration by magnetic material through magnetic refrigeration cycle. In general a magnetic refrigeration cycle consists of magnetization and demagnetization in which heat is expelled and absorbed respectively, and two other benign middle processes.

The basic cycles for magnetic refrigeration are magnetic Carnot cycle, magnetic Stirling cycle, magnetic Ericsson cycle and magnetic Brayton cycle, among which the magnetic Ericsson and Brayton cycles are applicable for room temperature magnetic refrigeration for the Ericsson and Brayton cycles employ a regenerator to achieve a large temperature span and are easy to operate. Fig. 2 shows the Ericsson and Brayton cycles.

4.1. Magnetic Ericsson cycle

Ericsson cycle consists of two isothermal processes/stages and two isofield processes as illustrated in Fig. 3 [20].

1. Isothermal magnetization process I[(A→B in Fig. 2(a)]

   When magnetic field increases from H_0 to H_1, the heat transferred from magnetic refrigerant to regenerator fluid, $Q_{ab} = T_1(S_a - S_b)$, makes the upper fluid increase in temperature.
2. Isofield cooling process II[B→C in Fig. 2(a)]

   In constant magnetic field of H_1, both magnetic refrigerant and electromagnet move downward to bottom and hence heat $Q_{bc} = \int_{S_c}^{S_b} TdS$ is transferred from magnetic refrigerant to regenerator fluid. Then a temperature gradient is set up in the regenerator.
3. Isothermal demagnetization process III[C→D in Fig. 2(a)]

   When magnetic field decreases from H_1 to H_0, the magnetic refrigerant absorbs heat $Q_{cd} = T_0(S_d - S_c)$ from the lower regenerator fluid. After that, the fluid decreases in temperature.
4. Isofield heating process IV[D→A in Fig. 2(a)]

   In the field of H_0, magnetic refrigerant and electromagnet move upward to the top and the regenerator fluid absorbs heat $Q_{da} = \int_{S_c}^{S_a} TdS$.

To make the Ericsson cycle possess the efficiency of magnetic Carnot cycle, it is required that the heat transferred in two isofield processes Q_{bc}, Q_{da} are equal

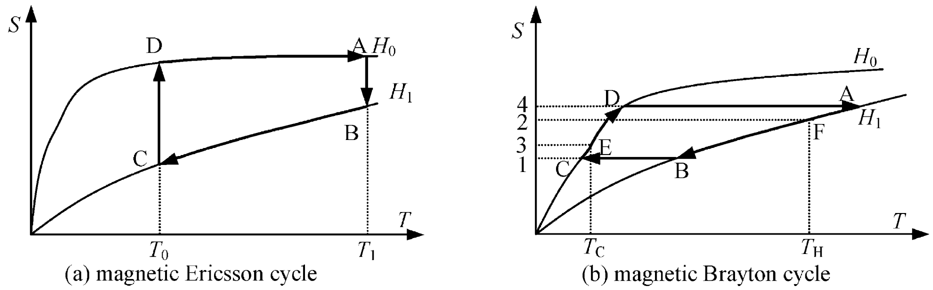

Fig. 2. Magnetic refrigeration cycle.

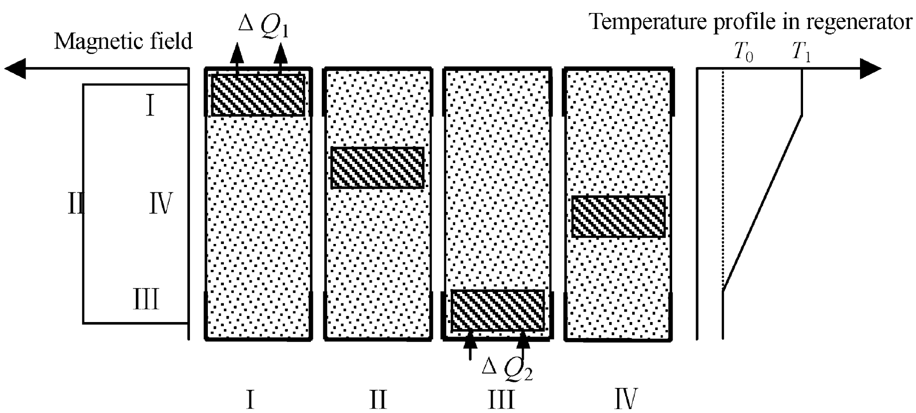

Fig. 3. Principle of magnetic Ericsson cycle refrigerator.

each other. For an ideal Ericsson cycle, 'parallel' T–S curves are optimal, that is, ΔS_M keeps constant in the cooling temperature range. However, the current single magnetic materials cannot meet the requirement; so perfect regeneration of Ericsson cycle can only be realized by composite materials [84–89].

4.2. Magnetic Brayton cycle

Magnetic Brayton cycle consists of two adiabatic processes and two isofield processes as shown in Fig. 2(b). The magnetic refrigerant cycles between the magnetic field of H_0 and H_1, and the temperature of high and low temperature heat source T_H and T_C, respectively. During the isofield cooling process A→B (constant magnetic field of H_1), magnetic refrigerant expels heat of the area of AB14 as Fig. 2(b) indicates. During the isofield heating process C→D (constant magnetic field H_0), magnetic refrigerant absorbs heat of the area of DC14. No heat flows from and out of the magnetic refrigerant during the adiabatic magnetization process D→A and the adiabatic demagnetization B→C process. The Brayton cycle can exhibit optimal performance as well with magnetic refrigerants having parallel T–S curves [84].

5. Magnetic field

5.1. Form of magnetic field

There are two modes to apply magnetic field on magnetic refrigerant: (a) both magnetic refrigerant and magnet are static. Pulsed magnetic field [90] or alternate on-off magnetic field is applied. There is no driving device and the power consumption may be great; (b) there is relative movement between magnet and magnetic refrigerant. The movement fashion may be reciprocating [91] or rotary [92]. In this way, the strength of magnetic field is stable whereas the extra mechanical power is needed due to the great magnetic attractive force.

Because the MCE is induced by magnetic field, the magnetic field strength plays a key role in the magnetic refrigeration. The specific MCE rate change at $T \cong T_C$ is $\sim$3 K/T at lower fields and $\sim$2.2 K/T at a higher 5 T field [28]. It is still a difficulty to apply a high field. Generally, both superconductor cooled by liquid-helium and electromagnet can supply a 5–7 T high fields. Another method of employing NdFeB permanent magnet magnetic field has been focused recently for its compactness and no need for power supply [93–96], despite that its magnetic field intensity is normally no more than 1.5 T. Permanent magnet design is very difficult because solutions for fields of arbitrary configuration are rarely analytic [93]. By design of hollow cylindrical permanent magnet array (HCPMA), Lee gained three permanent magnetic fields roughly appropriate for room temperature magnetic refrigeration (Table 2).

Table 2
Permanent magnetic field designed by Lee

Cross-sectional area (mm^2)	Air gap (mm)	Magnetic field strength (T)	Ref.
23.5	15.2	3	[94]
114×128	12.7	1.9	[95]
3217(Φ64 mm)	5.8	3	[96]

5.2. Design of magnetic field

The magnetic field has a serious influence on the magnetocaloric effect of the magnetic material. The adiabatic temperature change ΔT_{ad} is approximately proportional to the magnetic field $H^{2/3}$ [66]. Moreover, the field experienced by magnetic refrigerant is influenced by its temperature to some extent [67]. Items below need careful consideration in design of magnetic field: (a) to ensure the magnetic field uniformity in the space occupied by magnetic refrigerant and make full use of the effective space in the magnetic field; (b) to avoid the leakage of magnetic flux and increase the ratio of magnetic refrigerant space to the magnetic field space as possible; (c) to reduce the required power consumption for the magnetic field or the relative movement; (d) to shield the strong magnetic field from other electric and electronic devices.

6. Regenerator in room temperature magnetic refrigeration

Since the lattice entropy is too large to neglect in room temperature, part of the refrigeration capacity of the magnetic refrigerant is consumed for cooling the thermal load of lattice system, decreasing the gross cooling capacity of the magnetic refrigerant [20]. By adding a regenerator to the magnetic refrigeration system, the heat expelled by lattice system in one stage of the cycle is restored and returned to lattice system in another stage. So the capacity used for cooling lattice system load can be utilized effectively for the increase of effective entropy change and temperature span. Although a new concept of directly linking the two isofield changes by transferring heat between the two isofield stages through heat paths may realize the Ericsson cycle without regenerators, it is still theoretically feasible by far [97].

6.1. Type of regenerator

There are three types of regenerators used in magnetic refrigerator: (a) external regenerator, (b) internal regenerator, (c) active magnetic regenerator. Heat transfer in external regenerator between the regenerator material (generally solid materials) and the magnetic refrigerant is completed through the intermediate heat transfer fluid. In internal regenerator, the magnetic refrigerant is placed in regenerator as well as the regenerator material, and heat is transferred directly between them so that the regenerator should be in the magnetic field. In AMR cycle, the magnetic material is not only magnetic refrigerant but also regenerator material. Thus the irreversible loss yielded by the second heat transfer in external regenerator or by mixing of the regenerator fluid with different temperature in internal regenerator can be reduced. After the early development [98–100], AMR gradually becomes the main research direction of room temperature magnetic refrigeration regenerator now [101–109].

According to the relative heat capacity, there are two implementation limits between heat transfer fluid and magnetic material. In one limit, the heat capacity of the fluid blown through the regenerator is much larger than that of the magnetic material. The regenerator used in this case is internal regenerator, where the temperature gradient in the regenerator is easily influenced by mixing of fluid. In the other regenerator limit, the heat capacity of the fluid blown through the regenerator is much less than that of the magnetic material. This type of regenerator is commonly active magnetic regenerator, in which the temperature gradient can be kept well and much lower fluid mass flow rates are required for a given cooling power than that of the former case [3].

6.2. Structure and principle of AMR

A single-stage AMR is generally a porous bed of magnetic refrigerant material, which acts as both the refrigerant (coolant) that produces refrigeration and the regenerator for the heat transfer fluid. Flowing through the active magnetic regenerator the fluid carries heat to and from the external heat exchangers.

The working principle of AMR is presented in Fig. 4 [106,110]. Assume that the bed is at a steady state condition with the hot heat exchanger at T_H ($\sim$24 °C) and the cold heat exchanger at T_C ($\sim$5 °C). The AMR cycle experiences four processes: (a) adiabatic magnetization process. Each particle in the bed warms up; (b) isofield cooling process. In a high field, the fluid is blown from the cold end to the hot end, absorbs heat from the bed and expels heat at a temperature higher than T_H in the hot heat exchanger; (c) adiabatic demagnetization process. Each particle in the bed cools again (after the former process); (d) isofield heating process. In a zero field, the fluid is blown from the hot end to the cold end, expels heat to the particles of the bed and absorbs heat at a temperature lower than T_C in the cold heat exchanger. In Fig. 4, the dashed line represents the

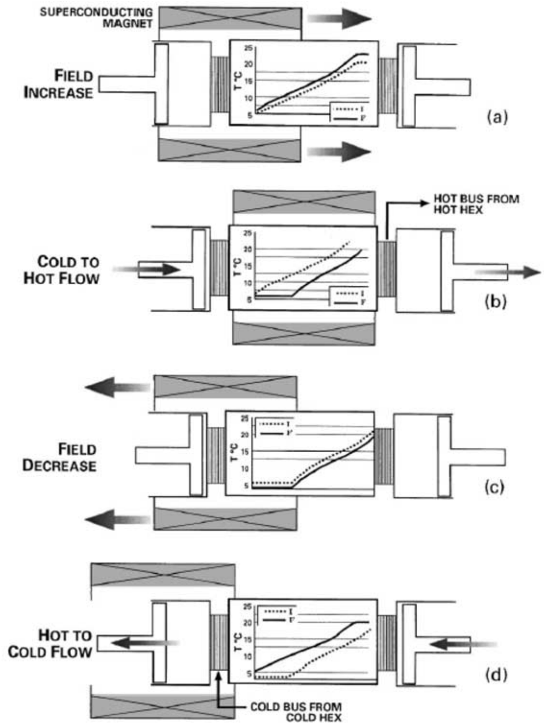

Fig. 4. Four schematic cycles of AMR.

initial temperature profile of the bed in each process, and the solid line represents the final temperature profile of that process. It is useful to predict the performance of magnetic refrigerator by establishing mathematic model about AMR [101,102,107–109].

From previous description it can be concluded that there are several useful features of AMR for practical application in magnetic refrigerator device. The magnetic bed acts as its own regenerator, and the solid particles in a single bed are connected by the convective fluid, so heat need not be transferred between two separate solid assemblies. Each particle in the packed bed undergoes a unique magnetic Brayton cycle and the whole bed undergoes a cascade Brayton cycle, so the temperature span of AMR can greatly exceed the adiabatic temperature change of magnetic refrigerant. Furthermore, the magnetic bed can be made into layers or employs the composite material whose MCE is mean in the cooling temperature range [106,110]. Some researchers studied the behavior of the adiabatic magnetization temperature change (ΔT_{ad}) as the function of material temperature (T) and discussed the selection principle of the composite material [106,108].

6.3. Thermodynamic characteristics of regenerator

There are several desirable characteristics for the perfect regenerator [104]:

- infinite thermal mass compared to the working material being cooled or heated;
- infinite heat transfer (a product of thermal conductance multiplied by the contact area) between working material and regenerator mass;
- zero void volume;
- zero pressure drop for convection of fluid through the regenerator;
- zero longitudinal conduction along the regenerator; and
- uniform, linear temperature gradient from the hot end to cold end of the unit.

The irreversible heat loss of the regenerator has a great influence on the performance of the whole magnetic refrigeration system. Chen analyzed the effect of thermal resistances and regenerative losses on the performance of magnetic Ericsson cycle qualitatively [111]. Main irreversible heat losses are:

- loss of finite heat transfer between regenerator material and heat transfer fluid;
- loss of pressure drop yielded by flow resistance;
- thermal conduction along the magnetic material. This is a significant loss mechanism [105];
- loss of mixing of regenerator fluid in the internal regenerator;
- loss of heat leakage;
- losses of magnetic hysteresis and eddy currents;
- loss caused by viscous dissipation in the regenerator fluid; and
- loss of "dead volume".

In a reciprocating AMR, some amount of the heat transfer fluid is always in the connecting lines between the beds and the heat exchangers and never cycles both through the beds and the heat exchangers. This trapped heat transfer fluid, commonly referred to as the "dead volume," is a significant source of inefficiency in active magnetic regenerators [112].

There are several characteristics of flow and heat transfer in AMR:

- Porous media flow. Magnetic refrigerant is generally packed into the bed as porous particles or screens.
- Oscillating flow. The fluid flows periodically reversing direction during the operation of magnetic refrigerator, so the heat transfer coefficient and flow resistance coefficient are dependent on the kind of fluid media, flow frequency, flow rate and porosity, etc.
- Heat transfer with internal heat source. There are temperature and heat changes periodically in AMR.
- Heat regeneration. Heat is regenerated in the mixture of magnetic material and fluid media as regenerator material is also the magnetic refrigerant. The regeneration process will certainly influence the transformation between magnetic energy and heat energy.
- Dynamic process. The flow and heat transfer in AMR is a dynamic process during which the local thermodynamic equilibrium cannot be maintained.

7. Magnetic refrigeration system

Since the lattice entropy of the magnetic refrigerant is large in the range of room temperature and the magnetic entropy change is relatively large only in the vicinity of Curie point, effective entropy change will consequently be small if no measurement is adopted to fetch lattice entropy. In addition, the supply of adequately strong magnetic fields is limited by many factors. As a result, the development of room temperature magnetic refrigeration falls far behind that of cryogenic magnetic refrigeration. However, after Brown constructed the first room temperature magnetic refrigeration system in 1976, researchers all over the world began to lay emphasis on the research on room temperature magnetic refrigeration and developed some guidable magnetic refrigeration systems sequentially.

7.1. Brown magnetic refrigerator

The magnetic refrigerator developed by Brown in 1976 is a reciprocating type and employs an Ericsson-like cycle [2]. The magnetic field is supplied by a water-cooled electromagnet, whose maximum strength is 7 T. The magnetic working body immersed in the regenerator consists of 1 mol Gd plates (1 mm thick) separated by stainless-steel screen wires at interval of 1 mm to allow the regenerator fluid to pass in the vertical direction. The adiabatic regenerator is full of a vertical column of fluid (0.4 dm^3, 80% water and 20% alcohol).

The working body is held stationary in the magnetic field while the regenerator tube containing the fluid oscillates up and down. The 7-T field is turned on and off at appropriate time during the cycle to complete the demagnetization cooling, isofield (zero field), magnetization heating and isofield (strong field) processes sequentially. Under condition of no load, as shown in Fig. 5, either of the demagnetization and magnetization process deviates from the isothermal process of ideal magnetic Ericsson cycle. And then the temperature span is gradually enlarged with the cycle operation. After about 50 cycles the temperature at the top reaches 46 °C and the temperature at the bottom reaches −1 °C, obtaining a global temperature span of 47 K.

Nevertheless, the cooling capacity is unremarkable as a result of a larger temperature span. Moreover, the cycle could not be operated quickly and the temperature gradient decreased both for the easy mixing between high- and low-temperature fluid in regenerator.

7.2. Steyert magnetic refrigerator

An alternative system of a rotating refrigerator in accordance with the Brayton cycle was designed and constructed by Steyert [98]. In this system a ring-shaped porous magnetic working body rotates across high- and low-field regions. The heat exchange fluid enters the wheel at a temperature T_{hot}, and leaves the wheel at a temperature T_{cold} after expels heat to magnetic refrigerant in low-field. Then, the fluid re-enters the wheel at temperature $T_{cold}+\Delta$ after picking up refrigeration heat load Q_{cold}. In the thermal exchange with the wheel which is at temperature $T_{hot}+\Delta$, the fluid warms to $T_{hot}+\Delta$. Finally it deposits heat Q_{hot} in the high temperature heat sink, completing the cycle as it re-enters the wheel at T_{hot}. The whole system is schematically demonstrated in Fig. 6.

7.3. Kirol system

This system was designed by Kirol [113] as a rotating machine, obeying magnetic Ericsson-like cycle. The magnetic field is supplied with NdFeB permanent magnet and a maximum 0.9 T field could be obtained in an air gap. The rotor is constructed of flat disks group of gadolinium with narrow spaces between them. Thickness of each disk is 0.076 mm and spaces are 0.127 mm wide. One hundred and twenty-five disks, 270g in total weight, are epoxy bonded together to form a rotor. Rectangular flow ports are positioned at magnet edges so that inlet and outlet fluid (water) could flow across the field change regions. Four complete thermodynamic cycles are completed during one circle of the rotor and an 11 K temperature lift is acquired.

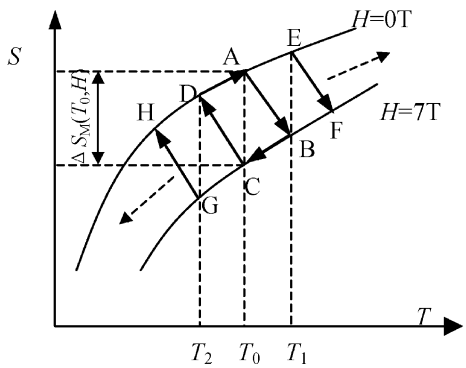

Fig. 5. Sketch of Brown system cycle.

7.4. Zimm magnetic refrigerator

This magnetic refrigerator developed by Zimm [3] is reciprocating type in accordance with the magnetic Brayton cycle. Four processes of the cycle are shown in Fig. 4 as described previously. A maximum 5 T field is achieved with NbTi superconductor. The concept of AMR cycle is adopted in the regenerator. Approximate 3 kg Gd spheres, 0.15–0.3 mm in diameter, are packed in two magnetocaloric beds. The heat transfer fluid is water (added with antifreeze). The total cycle time of 6 s is composed of magnetization/demagnetization of 1 s each and a fluid flow time of 2 s in each direction. The results show that in a 5 T field, it can generate up to 600 W of cooling power and its efficiency approaches 60% of Carnot with a COP approaching 15. But with a maximum 38 K temperature span the cooling power decreases to approximate 100 W. It can still generate about 200 W cooling power in a 1.5 T magnetic field. Furthermore, the device has been operated for more than 1500 h and 18-month period without any major maintenance or any breakdowns.

In addition to those above magnetic refrigerators, Green [114] developed a reciprocating magnetic refrigerator whose active magnetic regenerator consists of 1/3 Gd, 1/3 a mixture of Gd and Tb and 1/3 Tb, and obtained a 24 K (292–268 K) temperature span with little capacity. Bohigas obtained a 1.6 K difference between hot and cold regions through a rotating machine under a 0.3 T permanent magnet magnetic field [115]. Zhang built a reciprocating magnetic system based on Brown system, but only get a 1.1 K temperature lift in a 0.8 T field [116].

It was reported lately that American Astronautic Corporation combined with Ames laboratory developed 'the world's first room temperature, permanent magnet, magnetic refrigerator' in September 2001. It has just been applied for US Patent [117]. With a custom-designed permanent magnet it can produce a magnetic field strength nearly twice as high as the general permanent magnet field. A powder of element Gd is stuffed in pockets inside the ring-shape regenerator. The regenerator, roughly the diameter of a compact disk, rotates powdered magnetic material in and out of a gap in the

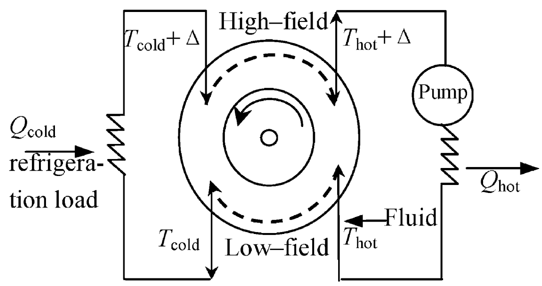

Fig. 6. Sketch of Steyert magnetic refrigerator.

powerful magnet at rear. The refrigerator is schematically shown in Fig. 7.

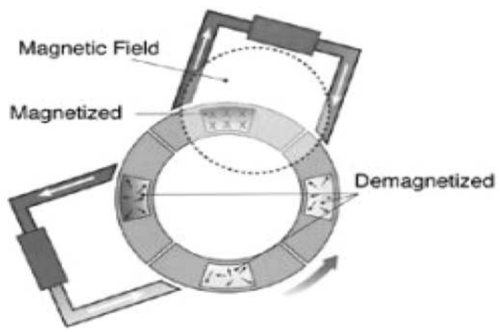

Fig. 7. Schematic representation of the new magnetic refrigerator.

8. Future perspectives of room temperature magnetic refrigeration

It can be seen from the earlier description that main progresses have been made in America. However, with the continual phasic progresses of room temperature magnetic refrigeration, the whole world has accelerated in the research. Nevertheless, it is notable that main work is concentrated on investigations of magnetic materials, lack of experimental explorations of magnetic refrigerator. From the former results achieved by researchers, it can be seen that there is still a great performance difference between magnetic refrigerator and vapor compression refrigerator in terms of cooling capacity and temperature span. Main difficulties lie in:

8.1. Large MCE of magnetic material is required

Magnetic materials available for room temperature magnetic refrigeration are mainly Gd, GdSiGe alloys, MnAs-like materials, perovskite-like materials. Though their MCE are large comparable to other materials, there are still some disadvantages such as narrow temperature region applicable (MCE decreases quickly when deviates T_C), unsatisfactory magnitude of peak values of MCE and a high magnetic field (5–7 T) required for remarkable effect. In addition, the impurities and structural imperfections significantly affect their magnetization, heat capacity, and other properties [118]. Generally, these materials are something far from extensive applications.

It has been verified in the investigations on magnetic materials in the room temperature range that composite materials can yield large MCE in a wide temperature region. But it has not been applied in magnetic refrigerator, partly depending on the level of processing of magnetic material. The MCE of magnetic materials is so important in magnetic refrigeration that most work is directed to investigating and searching for new magnetic materials of large MCE. Once magnetic materials of high performance are found, the breakthrough of magnetic refrigeration will be achieved.

8.2. Strong magnetic field is required

Up to now the magnetic field can be supplied with superconductor, electromagnet, or permanent magnet. Superconductor and electromagnet can produce 5–7 T strong fields. But the superconductor available is only the very expensive and structure-complicate low temperature superconductor, which needs to be cooled by liquid-helium of extreme low temperature. The electromagnet needs great electric power to produce high magnetic field, which makes it cumbersome and hard to maintain. In general, these two methods are impractical for the room temperature magnetic refrigeration in the future commercial application. On the other hand, despite of low cost, easy fabricating and good availability, the NdFeB permanent magnet can only produce a magnetic field no more than 1.5 T now. The supply of magnetic field is also a great obstacle of room temperature magnetic refrigeration development.

8.3. Excellent behavior of regeneration and heat transfer is required

Theoretical analysis indicates that the practical efficiency of magnetic refrigeration system is dependent on the behavior of the regenerator and heat exchanger. In addition to employing regenerator material to meet the requirements of ideal regenerator, there are still space for improving in mechanical design, structural design (porous packed particles, thin plates, wire-screens, and so on) and processing of materials. What is more, the behavior of heat transfer and flow characteristics such as oscillating flow frequency, flow rates, flow media, porosity of porous media, and internal heat source is essential to the capacity of refrigeration. In conclusion, heat transfer in regenerator and external heat exchanger should be enhanced to let the heat generated by magnetic material be transferred as soon as possible.

9. Summary

Progresses of room temperature magnetic refrigeration have been made worldwide. However, the development of room temperature magnetic refrigeration is not in mature status yet. Room temperature magnetic refrigeration will be a new refrigeration method with extreme potential on account of high efficiency and environment-safe. However, wide application can be achieved indeed only after the breakthrough in the fields of material science and refrigeration technology.

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