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Active and passive magnetic regenerators in gas/magnetic refrigerators

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Abstract

Rare earth materials have found three types of applications in refrigeration technology. One is as passive regenerators in gas cycle refrigerators; the second is as working materials in non-regenerative or in externally regenerated/recuperated magnetic refrigerator cycles; the third is as the combined refrigerant and regenerator in active magnetic regenerative refrigerators. Below 10 K, conventional regenerators in regenerative cryogenic refrigerators lose their effectiveness because the thermal mass of regenerator materials decreases compared with that of the helium gas convected in these cycles. The high specific heat of antiferromagnetic or ferromagnetic ordering transitions below 10 K was suggested for increasing the thermal mass in regenerators over two decades ago. However, it was not until 1987 that Japanese workers made a breakthrough in regenerative refrigerator performance below 10 K with new passive magnetic regenerator materials and by simultaneous modifications of the cycle operation. These new materials are intermetallic rare earth compounds with ordering temperatures below 10 K. The rapid progress that has recently occurred in this area is summarized in this paper. Only a few new references on the application of rare earth materials in Carnot or externally regenerated magnetic refrigerators exist because it has proven difficult to make practical, economical refrigerators using these cycles. Cryogenic magnetic refrigerators using regenerative cycles with rare-earth ferromagnets as the working materials are less established than gas cycle refrigerators. However, there has been significant progress on the active magnetic regenerator (AMR) cycle that combines the magnetic refrigerant and the regenerator in the same material. Demand for improved refrigerants in engineering prototypes using the AMR cycle is driving the search for new ferromagnetic materials with large magnetocaloric effects. Attractive candidates are predominately rare earth elements, alloys and compounds. This paper summarizes past progress and identifies areas where new materials are being sought.

1. Introduction

The annual, global, industrial refrigeration equipment market is estimated at ~US$4–5 billion but the cryogenic refrigeration equipment segment of this market is only a few hundred million dollars. Commercial applications within this cryogenic refrigeration market segment include:

- Production of industrial gases including O_2, N_2, Ar and He;
- Production of cryofuels including liquid petroleum gas (LPG), liquid natural gas (LNG) and liquid hydrogen (LH_2);
- Food preservation including freezing for storage and transportation;
- Biology and medicine including cryosurgery and cryopreservation;
- Cryopumping;
- Industrial applications including metal processing, scrap processing, cryoelectronics, and shrinkfitting;
- Cooling applied superconducting devices including maglev trains, superconducting motors and generators, ore separators, medical diagnostics and superconducting electronics.

Analysis of cooling power as a function of temperature for this list of applications shows that most of the refrigeration is provided by large, centralized refrigerators or liquefiers. Stored cryogens such as LN_2, LOX, LH_2, LNG and LHe are circulated or transported to provide distributed cooling. One exception to this general rule is the distributed refrigeration capacity required for fleet-size liquefiers (tens of kilowatts of cooling capacity) for LNG or LH_2 in refueling infrastructure so essential for alternate fuel use in the transportation sector. Another exception to the use of large, centralized cooling is the use of small cryocoolers (watts of cooling power). The most prominent commercial markets for these units are in cryopumps for the electronic chip processing industry, thermal shield cooling in medical imaging systems, and cooling miscellaneous electronics

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such as infrared sensors. Localized, distributed cooling of applied superconducting devices, especially those using high temperature superconductors, is a promising future growth market for these small cryogenic refrigerators.

The two refrigerator applications of interest in this paper are small cryocoolers that cool superconductive devices to near liquid helium temperatures and fleet-size commercial liquefiers used to liquefy cryofuels. In the first case, inexpensive and reliable regenerative gas cycle refrigerators are being developed to provide watts of cooling power at 4 K for applied superconductive applications. In the second case, practical regenerative magnetic liquefiers with kilowatts of cooling power using rare earth magnetic refrigerants are also under development for the liquefaction of hydrogen and natural gas. Excellent magnetic regenerators must be designed, built and tested for these applications.

A regenerator is a complex thermal device that absorbs heat from the working material on one stage of a regenerative cycle and returns the heat to the working material on the corresponding stage of the cycle. The periodic heat transfer of large quantities of heat compared with the size of the thermal load makes the operation of these devices critical to the performance of the refrigerator/liquefier. Regenerators have been studied for many years and many excellent references are available, *e.g.* [1–3]. Listing some desirable characteristics of ideal regenerators indicates the complexity of regenerator design:

- Infinite thermal mass compared to the working material being cooled or heated;
- Infinite heat transfer (a product of thermal conductance times the contact area) between the working material and the 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 to cold end of the unit.

Trying to achieve these sometimes conflicting characteristics has been and is a challenge to many cryogenic engineers. Real regenerator designs approximate ideal characteristics with the following:

- Finite surface area and finite heat transfer coefficients (conductances); convective heat transfer ($h \geqslant$ 100s of W m^{-2} K^{-1}) through geometries with very high specific areas ($A \geqslant 10\,000$ m^2 m^{-3}) is required. For example, good geometries are: fine particle beds; closely spaced parallel plates with flow between the long dimension of the plates; screens with flow perpendicular to the small dimensions of the screens; and perforated plates separated by porous means with flow perpendicular to the large dimension of the plates;
- Finite thermal mass of the regenerator compared with the working material mass flow; solid regenerator materials with high volumetric density such as stainless steel, bronze, and lead are selected;
- Small longitudinal (axial) thermal conduction in both the regenerator and the working materials is required. Also require good microscopic thermal conductivity to maintain internal thermal equilibrium within regenerator materials and good macroscopic radial thermal conductance; use modest thermal conductors shaped into geometries in which the longitudinal conduction is reduced such as in separated perforated plates;
- Temperature dependent material and fluid properties; must be considered in the designs and are critical when cooling to very low temperatures;
- Pressure drops associated with fluid flow; real friction factors produce pumping power requirements that limit the length of the regenerators and fineness of the internal geometries in the beds (particles $\geqslant$ 100 μm in size depending upon fluid density);
- Finite void volumes associated with porous regenerator geometries; minimized in real designs but actual porosities are generally between 0.3 and 0.7; and
- Parasitic heat leaks from other parts of the refrigerator; careful design with appropriate materials can reduce but never eliminate this effect.

Besides these steady state design goals, there are more complex static and dynamic effects such as eddy diffusivity, heat shuttle effects, flow channeling, etc. which further complicate regenerator operation. In active magnetic regenerators, the addition of eddy currents, hysteretic losses, magnetic force related mechanical stresses, and fatigue add to the design challenges. In spite of these complexities and lack of complete theoretical understanding of these devices [2], excellent regenerators have been built and used in many refrigerators [3].

Direct, isentropic compression/expansion of a gas or magnetization/demagnetization of magnetic materials with reasonable values of pressure or magnetic field ratios will not reach cryogenic temperatures without the use of regeneration. The key characteristic of regenerative cycles is the use of a regenerator to extend the temperature range of the refrigerator beyond that produced by an isentropic process. Types of regenerative cycles include:

- Stirling;
- Gifford–McMahon;
- Vuilleumier;
- Orifice pulse tube; and

- Magnetic types including Brayton, Ericsson, and AMR.

Operational temperature spans range from near room temperature at the hot end to cryogenic temperatures of 150 K and on down to liquid helium temperatures (~4 K) at the cold end. In these cycles, the working material is compressed or magnetized near room temperature, put in contact with a thermal sink to reject heat, and cooled to some lower temperature by the action of a regenerator before being expanded or demagnetized to provide cooling. To complete the cycle, the working material is put in contact with a thermal load to absorb heat, and warmed to near room temperature again by the regenerator.

2. Regenerator design and operation

The performance of a regenerator as a thermal device is measured by its effectiveness, *i.e.* the ratio of the amount of heat that is actually transferred in a regenerative stage of a cycle to the amount of heat that could be ideally transferred. Good regenerators have an effectiveness of ~0.90, excellent regenerators have values of $\geqslant 0.98$, and outstanding regenerators have values of $\geqslant 0.99$ [1]. The importance of the regenerator effectiveness in a typical regenerative cryogenic refrigerator is readily illustrated. For example, assume a regenerative gas refrigerator spans 300–100 K. If the temperature at the hot end of the regenerator is held at 300 K (by heat exchange to a large thermal sink) and the cold end is at 100 K (cooled by gas expansion on previous cycles), perfect regeneration of the working material would deliver compressed cold gas into the cold heat exchanger and expander volume at 100 K. However, if we assume an effectiveness of 0.98, the gas coming out of the cold end of the real regenerator will be 104 K instead of 100 K. The excess enthalpy of the warmer gas caused by the ineffectiveness of the regenerator has to be removed by using part of the cooling produced by the gas expansion at the cold end of the refrigerator (thus reducing the cooling power of the refrigerator). If the regenerator effectiveness decreases to the point where the excess enthalpy flow of the incoming compressed gas equals the cooling power from gas expansion, the refrigerator cannot cool any lower. In regenerative magnetic cycles, the adiabatic temperature changes associated with the isentropic application or removal of a magnetic field are generally smaller than in gas regenerative cycles. For the same refrigerator temperature span, the smaller adiabatic temperature change means the effectiveness of magnetic regenerators must be correspondingly higher than those in comparable gas cycle refrigerators. For highly efficient magnetic refrigerators, thermal effectiveness near 0.99 and higher (~0.998) are required. Such impressive regenerators are possible to design but difficult to build in practical magnetic refrigerators.

3. Passive magnetic regenerator materials

The thermal mass, mC_p, where m is the mass and C_p is the heat capacity, of conventional regenerator materials decreases as their volumetric heat capacity decreases. Below ~20–30 K, the lattice heat capacity is proportional to T^3 and the small electronic heat capacity in metals is proportional to T. In contrast, the thermal mass of high pressure (a few MPa) helium gas increases rapidly below ~10 K because the volumetric heat capacity of helium increases. When the thermal mass of the helium gas in the regenerator exceeds the thermal mass of the regenerator materials, the effectiveness of the regenerator drops rapidly and the cryocooler reaches only about 10 K. This problem with the loss of thermal mass has been recognized for over two decades [4] and many suggestions have been made to solve it. It was recognized early that using the large high heat capacity accompanying a magnetic phase transition in the 4–20 K range might be a good solution. However, for a variety of reasons, none of the early attempts were successful. A three-stage Stirling refrigerator using EuS in the bottom regenerator could not reach 4 K [5]. Furthermore, the $Er_xGd_{1-x}Rh$ intermetallic compounds suggested in 1975 [6] were not successfully used in cryocoolers until quite recently [7,8]. The real breakthrough in this area started in 1987 when the Japanese scientists led by Professor Hashimoto reported the discovery of $Er_{1-x}Dy_xNi2$, $Er(Ni_{1-x}Co_x)2$, Er_3Ni and ErNi [9–11] as suitable replacements for Pb below about 15 K. Er_3Ni was selected as the best initial candidate because it has a broad magnetic ordering transition at ~8 K and has a lattice heat capacity above 15 K that is comparable to Pb. Further improvements came from the development of $Er_{0.9}Yb_{0.1}Ni$ [12] which retains its sharp magnetic transition at a slightly lower temperature than ErNi. Magnetic transition temperatures as low as 4 K were observed when $ErNi_2$ or ErNi was diluted with Yb [12]. There is a corresponding decrease in the peak value of the volumetric heat capacity as Yb is added but the transition remains sharp and the materials are therefore effective. These studies were corroborated and extended by several other groups with interest in using these materials in Gifford–McMahon (G-M) refrigerators to provide cooling at 4 K. The sharpness of the magnetic heat capacity from ordering at these low temperatures requires that two or more materials be combined in the regenerator to provide high heat capacity from 15 K to 4 K. The effects of combining two different materials on the regenerator performance is an example of the analyses that have been done [13–18]. New magnetic materials that are competitive with the ErNi series mentioned above continue to be developed. Examples are Nd [9] and $(Ho_{2.5}Er_{2.5}Ru_2$ [20].

Increasing the thermal mass of the regenerators by use of the magnetic heat capacity was not sufficient to reach 4 K and provide substantial cooling power (1 W) at 4 K. However, the discovery of these materials and their application in two- and three-stage G-M cryocoolers has led to related changes in the operating specifications of the G-M refrigerators that have steadily increased the cooling power and ultimate low temperatures achievable [21–30]. By reducing the speed of operation from 60 rpm to 36 rpm with normal G-M refrigerator pressures (about 2.0 MPa and 0.4 MPa) plus changing the inlet and exhaust valve timing with respect to the compression and expansion strokes, the latest reports show a cooling power of 1.05 W at 4.2 K [31]. This is an impressive achievement because it opens the possibility of cooling superconductive devices without the use of LHe.

The use of the brittle intermetallic materials as regenerators in the second stage of G-M refrigerators presented another interesting problem: how to fabricate these materials into robust, yet inexpensive shapes. The Pb used traditionally in second-stage regenerators has generally been as ~100–200 μm diameter spheres. Early attempts to use arc-melted, crushed and sieved Er_3Ni as the second stage regenerator in a standard G-M refrigerator yielded temporary improved cooling similar to that reported by the Japanese. Refrigerator performance steadily degraded after several days of operation due to a fine distribution of Er_3Ni "dust" throughout the refrigerator [32]. This type of experience led to several efforts to manufacture robust spheres of rare earth intermetallics such as Er_3 Ni and rare earth elements such as Nd [11,19,33–35]. These methods can now produce reasonable quantities of good quality spheres for experimentation. Toshiba is in commercial production of Er_3Ni spheres.

4. Magnetic refrigerants for externally regenerated or non-regenerative cycles

Below about 20 K, the lattice entropy of certain paramagnetic materials is small compared with the magnetic entropy. Thus, it is possible to span from ~20 K to ~2 K with magnetic Carnot cycle devices. Very little recent effort has been done in this area because of the successes with the passive magnetically regenerated G-M cycle refrigerators and the relatively high cost of magnetic stages added onto gas stage refrigerators. Some work has also been done with magnetic refrigerants for magnetic cycles other than the AMR cycle. In these units, the refrigerant must be externally regenerated or recuperated which is difficult to accomplish with large cooling powers and over large temperature spans. Much work has been done and reported in the literature on materials for operation below 20 K but only a few references on investigations for operation above 20 K. Several reviews are included in this paper. They, especially the work by Hashimoto, contain relevant references to studies of rare earth materials as magnetic refrigerants for the cases mentioned above [36–38].

5. Active magnetic regenerator materials

The requirements for the active magnetic regenerative cycle have been developed over the past several years as the unique nature of the AMR cycle has been appreciated [39–41]. The attractiveness of the AMR cycle is its combination of the working material and the regenerator into one unit thus making several practical embodiments of it possible. The large temperature spans which the AMR cycle allows means that the magnetic materials requirements cannot be met with a single material. Therefore, a series of magnetic materials with large magnetocaloric effects in modest magnetic fields that can be combined or blended in some manner is required. Some desirable characteristics of the magnetic refrigerants for the AMR cycle are:

- Simple ferromagnetic order at a well-defined temperature;
- Large magnetic moment per unit volume;
- Easily controllable magnetic entropy in the presence of a modest magnetic field (6–8 T), *i.e.* large *g*-factor;
- Easily tuned Curie temperature so any temperature span can be covered;
- Large adiabatic temperature change upon application/removal of a magnetic field over a modest temperature span (tens of degrees Kelvin);
- High density;
- Medium thermal conductivity;
- Essentially zero magnetic hysteresis;
- Good mechanical strength;
- Chemical stability; and
- Easily fabricated at a modest cost, etc.

The materials investigated and reported are heavy rare earth elements and alloys, rare earth intermetallic compounds with a wide range of compositions, and nanocomposites. For initial magnetic refrigerator design calculations, the heat capacity and adiabatic temperature change as a function of magnetic field and temperature are required. Such measurements have been reported for most of the heavy rare earth elements, Gd, Dy, Tb, Er and Tm [42–48]. The magnitude of the adiabatic temperature change ranges from greater than 2 K per tesla in Gd near its ferromagnetic transition at 292 K to only a fraction of a Kelvin per tesla that may change sign as a function of temperature and field at temperatures in Er. The complex magnetic structures of the rare earth elements other than Gd limit their adiabatic temperature change because all the magnetic entropy is not removed in one transition. However, the rare earth elements have potential use as magnetic refrigerants because they are not diluted by additional non-magnetic elements that reduce the adiabatic temperature change. They are also modestly priced per kilogram of magnetic ion and ductile enough for fabrication into fine geometries required for high performance regenerators.

The need for variable Curie temperatures of the magnetic refrigerants led to a direct extension of the heavy rare earth elements into rare earth metallic alloys with other rare earth elements including Y. These efforts have led to some interesting measurements of the magnetocaloric effect (usually the adiabatic temperature change is measured) as a function of temperature and magnetic field including projections of the effects of very high (50 T) applied fields on the adiabatic temperature change [48–53]. For example, in the Gd–Dy, Gd–Tb and Dy–Tb cases, there is a reasonably systematic, well-defined peak in the adiabatic temperature change as the alloy composition shifts across the composition range. Other cases are more complicated as the magnetic phases change as the compositions change. One interesting result recently reported in the $Er_{0.8}La_{0.2}$ alloy is the significant collapse of several magnetic transitions seen in pure Er into a much sharper transition. There was a corresponding increase in the adiabatic temperature change to the point where this alloy may have some use as a refrigerant [54]. These rare earth alloys definitely offer promise as magnetic refrigerants in AMR cycle designs when appropriate blending is done [41].

The next class of rare earth materials that offer promise as magnetic refrigerants are the intermetallic compounds that are simple ferromagnets. There has been significant work done in this area since about 1980 when the author started developing magnetic liquefiers for LHe and LH_2 with heat rejection at room temperature. These liquefiers required a series of simple ferromagnets with Curie temperatures ranging from about 10 K to near 300 K. Gadolinium compounds were initially chosen because of the lack of orbital angular momentum and small magnetic anisotropy. About 100 possible candidates were identified from the literature on Gd compounds. It was soon realized that near the Curie temperature, magnetic anisotropy constants become small in most ferromagnetic materials. Hence, the number of possible ferromagnetic intermetallic compounds increased as Dy, Ho, Tb and Er compounds were considered. Because most of the transition metal–rare earth compounds have ordering temperatures above 300 K, they were not particularly attractive for cryogenic refrigerants but should have promise near or above room temperature. The results from these studies are showing that there are promising materials with Curie temperatures from below 10 K to nearly 100 K. There is a need for continued work in this area because although the magnetocaloric effect and other related properties of many materials are suitable, the fabrication of these materials into useful magnetic regenerators in working refrigerators remains a major challenge [55–58]. Recent improvements in the adiabatic temperature changes measured in materials with Curie temperatures near 40 K show there is significant promise for future work [59].

Finally, potentially interesting magnetic refrigerants discovered in the last few years are nanocomposites [60–62]. Finely powdered magnetic materials are well known to exhibit superparamagnetism as observed in ferrofluids. In magnetic nanocomposites, it is proposed that superferromagnetism may exist and that appropriate manipulation of the composition of such composites may allow easily adjustable Curie temperatures. The major limitation of this type of magnetic refrigerant is the dilute nature of the magnetic species. On the other hand the removal of the magnetic entropy at a well-defined temperature with a small magnetic field (smaller than for rare earth elements or intermetallic compounds) is attractive. Further research needs to be done in this area.

6. Summary and observations

There has been a steady publication of interesting and new work on rare earth magnetic materials for regenerative refrigerators over the past decade. Obviously, progress is being made towards the realization of commercial G-M regenerative cryocoolers that can provide a watt of cooling power at near 4 K. Steady progress has been achieved with active magnetic regenerative refrigerators and liquefiers, but none have been demonstrated, particularly operating from 300 K to 20 K or below.

There is a need for highly effective magnetic regenerators in AMR-based designs and while the studies reported here show that there are many possible refrigerants with suitable magnetocaloric effects, no fully fabricated, blended magnetic regenerator has been tested and reported. Clearly, a key area for further work is in the fabrication of highly effective designs that meet the demanding specifications of a practical AMR refrigerator.

Finally, in a recent cost analysis of AMR liquefiers [63], it is estimated that the superconducting magnet subsystem will contribute over 40% of the cost of the liquefier (followed by 17% from the magnetic refrigerant). From these analyses, there is a need to develop concentrated magnetic refrigerants that have large magneto-caloric effects in smaller magnetic fields; 15 K in 5 T would be excellent.

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