Composite Active Magnetic Regenerators for Hydrogen Liquefiers

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ABSTRACT

This article presents a numerical method for optimizing composite active magnetic regenerators (AMR). Thermodynamic analysis showed that the performance of the AMR cycle depends strongly on the behaviour of the magnetocaloric effect (MCE), as a function of material temperature in the flow direction of the regenerator. Efficient operation of the AMR devices requires the use of composite regenerators. The Gd-Dy alloys have been selected as constitute materials for an AMR bed operating over the temperature range 210-290 K, in hydrogen liquefier stage. The MCE values of different Gd-Dy alloys determined experimentally and analytically are presented. Based on these EMC data a composite regenerator has been proposed. The performance computations of such composite AMR led to thermal efficiency *COP* = 77 % of Carnot cycle which is considerably high value in comparison with a single regenerator composed with pure Gd.

INTRODUCTION

The needs for developing more promising hydrogen liquefiers have prompted a renewed interest in the study of magnetic refrigeration (MR) technology ([1] - [4]). Engineering and economic evaluations indicate that, in principle, MR with its promises of higher efficiencies and lower capital investment costs would create an immediate market niche and new opportunities. The concept of MR is based on the principle of the magnetocaloric effect (MCE) of some materials. The material temperature change induced by external magnetic field changes is called MCE. The magnitude of MCE is about 2 ^{o}C per Tesla of field change for typical ferromagnets near their Curie temperature [5]. Hence, a single working material will not suffice the design requirements of a magnetic refrigerator covering a large temperature span such as liquefaction of hydrogen. Thermodynamic analysis showed that the performance of the AMR cycle depends strongly on the behaviour of the MCE, as a function of material temperature in the flow direction of the regenerator. Efficient operation of the AMR devices requires the use of composite regenerators ([6], [7]).

The design of an efficient magnetic hydrogen liquefier using room temperature as the heat sink would require the development of several composite refrigerants suitable for the temperature range from 20 to 300 K. The most works on the development of magnetic refrigerant materials were done for lower temperature range : 20-77 K.

In this work, a composite material, based on the Gd-Dy alloys, operating over the temperature range 210-290 K is suggested to be used as an AMR in hydrogen liquefier stage. The MCE values of different constitute materials (Gd-Dy alloys) determined experimentally and analytically are presented. The performance of such a regenerator is presented and discussed.

DESCRIPTION OF MR CYCLE

Unlike gas-cycles, an MR devices function according to thermodynamic cycles which involve complex thermofluid interactions within the regenerator. Fig.1 shows a schematic of such an MR device. A complete cycle consists of two isentropic processes (adiabatic magnetisation/demagnetisation process) and two isofield processes (cold and warm blows), which can be briefly described as follows.

(i) *Adiabatic demagnetisation process*: the magnetic refrigerant (regenerator bed) is demagnetised adiabatically by reducing magnetic field from given strength B to zero, with no flow.

(ii) *Cold blow at zero field*: the fluid is then forced by the displacer to move from the hot to cold reservoirs. Going through the cold heat exchanger, the fluid absorbs the amount of heat Q_L .

(iii) *Adiabatic magnetisation process*: the bed is magnetised adiabatically when the magnetic field increases from 0 to B, with no flow.

(iv) *Warm blow at applied field B*: the fluid is then forced from the cold to hot reservoirs. Passing through the hot exchanger, the fluid temperature drops by rejecting the amount of heat Q_H .

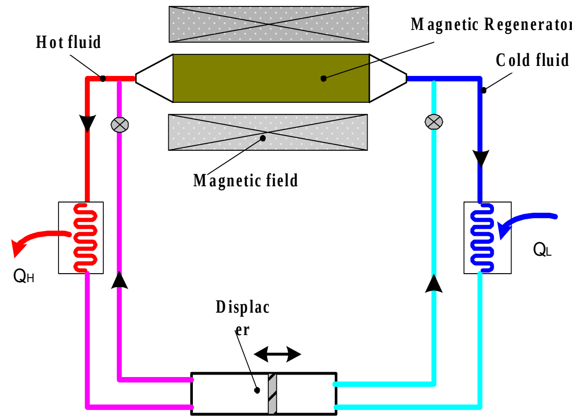

Fig. 1 Schematic of basic operation of magnetic refrigerator

MAGNETOCALORIC EFFECT

To compute magnetocaloric effect (i.e. MCE), ΔT, for a given magnetic material, exposed at magnetic field, B, and temperature T_R, the molecular field theory and Debye model have been used. The calculation procedure is summarized as follows.

$$\Delta T = -T_R \int_0^B \frac{1}{C_R(T_R,B)} \left(\frac{\partial M}{\partial T_R} \right)_B dB \qquad (1)$$

where M is the magnetization of magnetic material given by

$$M = NgJ\mu_B B_J(\chi) \qquad (2)$$

$B_J(\chi)$ is the Brillouin function, and χ according to molecular field theory, is given by

$$\chi = \frac{gJ\mu_B B}{kT_R} + \frac{3\theta_C J B_J(\chi)}{T_R(J+1)} \qquad (3)$$

N is the number of spin per unit mass. J is the total angular momentum quantum number. μ_B is the Bohr magneton. θ_C is the Curie temperature.

The specific heat $C_R(T_R, B)$ can be written as

$$C_R(B,T_R) = C_M(B,T_R) + C_L(T_R) + C_E(T_R) \tag{4}$$

where C_M, C_L, C_E are respectively magnetic, lattice and electronic contributions. The expressions of these properties and more detailed information can be found in Refs ([5], [7]).

MÉTHOD FOR OPTIMISING MAGNETIC REGENERATORS

To obtain optimum composite regenerators, in previous work [7], we developed a numerical method. This approach is summarized as follows. Consider a series of magnetic materials or alloys whose curie temperatures $T_0^1, T_0^2, \ldots T_0^n$ are conveniently positioned over the required temperature range [T_C, T_H]. The total entropy S of the corresponding composite material as a function of magnetic field B and temperature T_R, can be written as

$$S(B,T_R) = \sum_{j=1}^{n} y_j S_j(B,T_R) \tag{5}$$

where y_1, y_2, …y_n are the different mass fractions, n is the number of magnetic materials, and S_j is the total entropy of the j th constitute material.

The MR cycle described above operates under isentropic magnetization / demagnetization conditions, and therefore the following relationship should be satisfied

$$S(B=0,T_R) = S(B>0,T_R+\Delta T) \tag{6}$$

where ΔT is the MCE of the resulting composite material. By combining Eqs. (5) with (6), and rearranging, we obtain

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \cdots & \cdots & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \cdots & \cdots & \alpha_{2n} \\ \cdots & \cdots & \alpha_{ij} & \cdots & \cdots \\ \alpha_{n-11} & \cdots & \cdots & \alpha_{n-1n-1} & \alpha_{n-1n} \\ 1 & 1 & \cdots & \cdots & 1 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ \cdots \\ \cdots \\ y_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ .. \\ .. \\ 1 \end{bmatrix} \tag{7}$$

where the coefficients α_{ij} are given by

$$\alpha_{ij} = S_j(B, T_0^{i+1} + \Delta T(T_0^{i+1})) - S_j(B, T_0^i + \Delta T(T_0^i)) - S_j(0, T_0^{i+1}) + S_j(0, T_0^i).$$

The MR cycle requires a regenerator with continuously increasing MCE, ΔT, thus, let consider those satisfying the following form :

$$\Delta T(T_R) = \kappa T_H \left(\frac{T_R}{T_H}\right)^{\eta} \tag{8}$$

Where, T_H is hot source temperature; κ is a constant to be determined by iteration such that the value of $\eta > 0$.

RESULTS AND DISCUSSION

Figure 2 shows the resulting MCE values as a function of temperature for an applied field of 7 Tesla, obtained for the different Gd-Dy alloys. As it can be seen experimental values are compared with those obtained analytically The analytical curves describe sufficiently well experimental values at higher temperatures (i.e. $T \gg \theta_C$). However, at lower temperatures, pronounced deviation of the analytical curves from experimental ones can be noted. This is can be attributed to the inability of molecular field theory to describe accurately enough the magnetisation in these temperature ranges.

Based on Eq. (7) and the resulting MCE of different Gd-Dy alloys (presented in Fig.2), a composite regenerator has been obtained to operate in the temperature range 210-290 K and for applied field of 7 Tesla. The corresponding mass ratios are presented in table 1. The MCE curve of resulting regenerator is shown in Figure 3. It can be seen that the trend of the MCE consistently fulfills the optimistic behaviour imposed by the Eq. (8).

From a practical point of view the structural properties of the composite are of importance here. If the composite is made from a physical and uniform mixture of different materials, there may be serious entropy generation

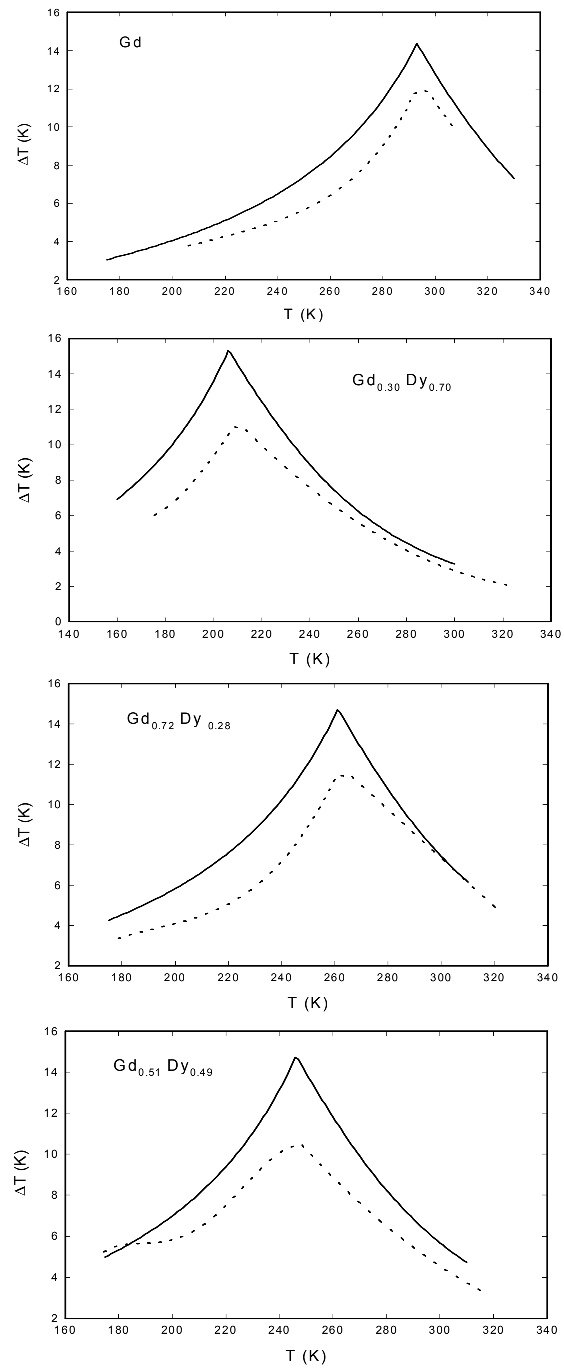

Figure 2 Evolution of MCE as function of temperature; —— **Model,** .... **Experiment**

associated with the temperature differences between adjacent particles that are undergoing different temperature / entropy changes in given magnetic field. Therefore, the resulting entropy generation curve in the composite regenerator is shown in Figure 4. To investigate the impact of the problem of entropy generation on cycle performance, let consider the following example.

The performance of hydrogen liquefier stage operating with the composite Gd-Dy as an AMR in the range 210-290 K, is analysed. Based on numerical simulation presented in our previous works ([7], [8]), the thermal mass ratio, $m_f\, cp\, \tau / M_R\, C_R$, can be estimated to be 0.5, for optimum operation conditions; where, m_f is hydrogen mass flow rate, c_p is hydrogen heat capacity, τ is cycle time period, M_R and C_R are respectively mass and heat capacity of regenerator bed The resulting thermal efficiency *COP* is defined by

$$COP = \frac{Q_H}{Q_H - Q_L} \frac{T_H - T_L}{T_H} \qquad (9)$$

For given cycle operation conditions, it has been found that *COP* = 77 % of Carnot cycle which is considerably high in comparison with a single regenerator composed with pure Gd. Therefore the entropy generation does not seem to affect the cycle performance. However, the end effects of this irreversibility on the overall cycle are not easy to predict without calculating the complete entropy flow through the cycle. This may constitute a topic for further study.

Table 1 The optimum mass ratios (OPR), y_i, of composite AMR

Alloy	$Gd_{0.30}\,Dy_{0.70}$	$Gd_{0.51}\,Dy_{0.49}$	$Gd_{0.72}\,Dy_{0.28}$	Gd
OPR	$y_1 = 0.21$	$y_2 = 0.23$	$y_3 = 0.14$	$y_4 = 0.42$

CONCLUSION

A composite material based on Gd-Dy alloys is proposed as AMR for hydrogen liquefier stage operating over the temperature range 210-290 K. Preliminarily thermal analysis of the resulting AMR cycle showed considerably higher efficiency in comparison with a single regenerator composed with pure Gd.

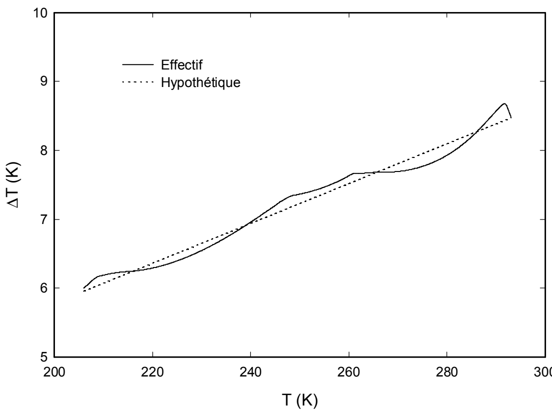

Figure 3 Evolution of MCE as function of temperature for the proposed composite AMR

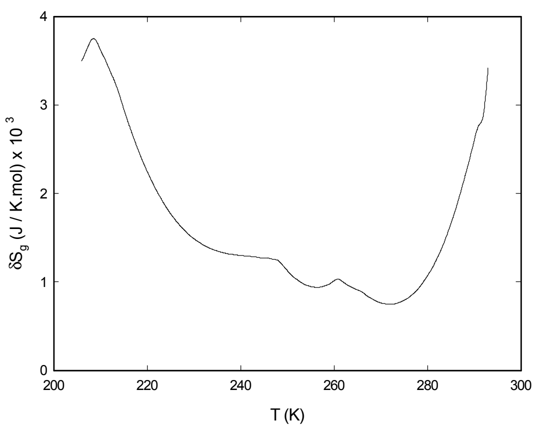

Figure 4 Evolution of entropy generation as function of temperature for the proposed composite AMR

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