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KISÉRLETI ELRENDEZÉS MAGNETOKALORIKUS ANYA-GOK VIZSGÁLATÁRA
DESIGN OF A TEST STAND FOR INVESTIGATIONS OF MATERI-ALS EXHIBITING THE MAGNETOCALORIC EFFECT

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***Kulcsszavak**: külső hatásra tulajdonságváltozást mutató anyagok, mágneses hűtés, mágneses fagyasztás, gadolínium*

***Keywords:** smart materials, magnetic cooling, magnetic refrigeration, gadolinium*

Abstract

Magnetic cooling is a new way to decrease temperature which is based on the magnetocaloric effect. Although this phenomenon was discovered in the 19th century, no commercial device utilizing a magnetocaloric material as a refrigerant has appeared thus far. This paper shows a design of a laboratory test stand for investigations of the magnetocaloric effect in the materials with a near-room transition temperature. The work also contains the results of investigations of temperature and entropy changes in gadolinium. This material will be the first refrigerant to be used in the designed laboratory test stand.

ÖSSZEGZÉS

A mágneses hűtés, amely a magnetokalorikus hatáson alapszik, egy új módszer a hőmérséklet csökkentésére. Annak ellenére, hogy ezt a jelenséget a 19. században fedezték fel, nincs olyan kereskedelmi berendezés a megnetokalorikus anyagokat, mint hűtést. A publikáció egy olyan laboratóriumi berendezést tervezését mutatja be, amely alkalmas a szoba hőmérséklethez közeli átmenti hőmérsékletű magnetoklakorikus hatást mutató anyagok tanulmányozására. Ez munka foglalkozik a gadolinium hőmérséklet és entrópia változásának vizsgálati eredményeivel. A gadolinium lesz az anyag, amit elsőként fognak megvizsgálni az új készülékkel.

1. INTRODUCTION

The *technological* development within the last years has caused substantial damage to the environment. At present, along with the progress of civilization the ecological consciousness in the general public is increasing, which leads to the growing interest in eco-friendly technologies. That is why there is a tendency to eliminate all the environmentally hazardous substances and to increase the efficiency of devices. One of the areas where special attention should be paid to ecological aspects is refrigerating engineering. The widely used refrigerators significantly contribute to the greenhouse effect because of the utilized cooling agents. Moreover, the efficiency of these devices is insufficient. In recent years, a dynamic development of numerous modern technologies of temperature decreasing has been observed. Magnetic cooling based on the so-called magnetocaloric effect is one of these technologies. Materials which exhibit the magnetocaloric effect belong to a wider material group known as the magnetic SMART materials. This term applies to various materials that change their properties under the influence of external stimuli.

The magnetocaloric effect was first mentioned in literature in 1881. This was the year when E. Warburg noticed that an iron sample placed in a magnetic field changes its temperature [1]. When the sample was placed inside the magnetic field, its temperature increased. When the same specimen was removed from the field, its temperature decreased. The temperature changes were very fast, happening in a split second. The magnetocaloric effect was first used in cryogenics to liquefy hydrogen and helium. This phenomenon made it possible to achieve temperatures below 1 K for the first time. Partially thanks to this achievement W. Giauque received the Nobel Prize for Chemistry in 1949. The possibility of using the magnetocaloric effect in room temperature refrigerators first appeared in 1976 when G. V. Brown built the first device of such type. The device aroused great interest because it did not utilize hydrochlorofluorocarbons (HCFCs) and was therefore environmentally friendly because it did not deplete the ozone layer. The cooling material used by G. V. Brown was gadolinium in the form of thin plates. A superconducting magnet cooled by liquid helium acted as the magnetic field generator. The magnet produced a magnetic field of 7 T. The first magnetic cooler achieved a temperature difference of 47 K [2].

The magnetocaloric effect is a thermodynamic phenomenon which consists in a change of

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a material temperature under the influence of a cyclically variable magnetic field. When a magnetocaloric material enters the magnetic field it becomes magnetized. During this process magnetic dipoles arrange themselves parallel to the field direction while the entropy of the body diminishes. The magnetization process is connected with a rise in the temperature of a specimen. The moment the magnetic field is removed, the demagnetization of the material occurs and the magnetic dipoles lose their ordered state. During this change the entropy of the body increases whereas its temperature decreases. The material temperature change ΔT in the adiabatic process and the entropy change ΔS for the isothermal transformation are both considered to be the measures of the magnetocaloric effect (fig. 1). The ΔS and ΔT values are not equal. The magnetocaloric effect depends on the ambient temperature as well as on the change in the magnetic induction. The effect reaches its maximum value in the temperature of the ferromagnetic-paramagnetic phase transition, also known as the Curie temperature (T_c), which is specific for each material.

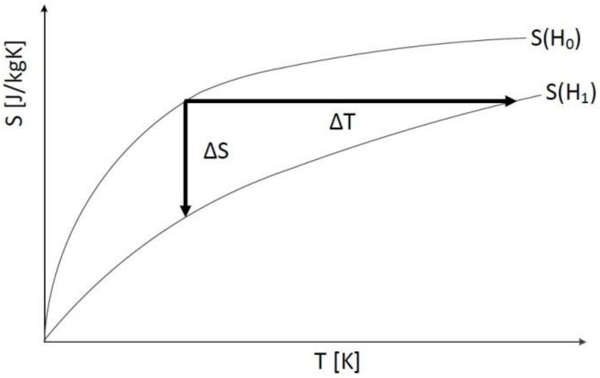


Fig. 1 Magnetocaloric effect as a change in temperature ΔT and in entropy ΔS

Simultaneously with the development of magnetic refrigerator designs, the progress in the investigations of magnetocaloric materials can be noticed. The suitable refrigerant should be characterized by a significant change in its temperature and entropy. As mentioned before, gadolinium was the first material used in a room temperature magnetic refrigerator. This element is still the most commonly used magnetocaloric material, which can be confirmed by the large number of cooling system prototypes which utilize this metal as a refrigerant. Gadolinium is an attractive option for magnetic refrigeration thanks to its Curie temperature T_c, which is 294 K, and owing to its relatively large change in temperature and entropy. Nevertheless, laboratory tests led to the fabrication of new materials which exhibit even larger magnetocaloric effect than gadolinium. In 1997 Pecharsky and Gschneider announced the discovery of a material which exhibits a giant magnetocaloric effect. This material, the $Gd_5(Si_2Ge_2)$ alloy [3], is characterized by ΔS values which are two times larger than in the case of pure gadolinium whereas ΔT rises by about 30% [3]. The increase in the magnetocaloric effect is caused due to the fact that in the $Gd_5(Si_2Ge_2)$ alloy the magnetic transformation occurs along with the reconstruction of the crystal lattice. The material exhibits the first-order phase transition whereas gadolinium is subject to the second-order transition. In the following years several other alloys showing the giant magnetocaloric effect were discovered. These alloys are also subject to the first-order phase transition. An example might be the materials from the $MnAs_{1-x}Sb_x$ [4], $MnFe(P_{1-x}As_x)$ [5] or $La(Fe_xSi_{1-x})_{13}$ [6] group.

This paper proposes a concept of the laboratory test stand for magnetocaloric effect investigations which is currently under construction. This stand is aimed at the investigations of materials in various forms, with a near-room (~ 294 K) transition temperature.

2. STRUCTURE OF MAGNETIC REFRIGERATORS

Even though the first magnetic refrigerator was built over 30 years ago, the basic elements of such devices still remain the same. The cooling systems which operate based on the magnetocaloric effect comprise the following elements: a magnetic bed filled with a magnetocaloric material, a magnetic field source, a transport system for the refrigerating medium, hot and cold heat exchangers and a control system.

On the basis of the overview of prototype refrigerators based on the magnetocaloric effect [7] it can be noticed that the utilized magnetocaloric material appears in several forms such as powders, granules or sheets. The heat transfer medium is usually water with anticorrosive agents. This is because water offers good thermal capacity, eco-friendly characteristics and wide availability. The use of anticorrosive additives is necessary because gadolinium (as mentioned earlier – the most widely used magnetocaloric material) reacts with water. A refrigerating medium in a gaseous form is selected much less often.

Magnetic refrigerators require strong magnetic fields because it leads to the increase in the magnetocaloric effect (growth of ΔS and ΔT proportional to the growth of magnetic field). However, it is also important for the mass and volume of the field generator to remain as low as possible. Values of the magnetic field induced in prototype magnetic refrigerators typically range from 0.8 T to 2.4 T [7].

In order to produce a magnetic field, three types of magnets are used: electromagnets, superconducting magnets and permanent magnets. Currently, the permanent magnets are used most often, however, all the mentioned magnet types have their limitations. Superconducting magnets can generate strong magnetic fields but their main drawback is the necessity for an additional cooling system, essential for these materials to work. The cost of such system is high, which renders the solution uneconomical in the case of household appliances. Electromagnets, similarly to the superconducting magnets, generate strong magnetic fields, but also significant losses. These magnets consume a lot of energy and generate a substantial amount of heat. Permanent magnets do not require an external power source or a cooling system, but their main disadvantage are the limitations in generated magnetic fields (maximum of 2 T).

3. DESIGN OF THE TEST STAND

The designed system for magnetocaloric effect investigations has a modular structure. The modular structure helps to change the system configuration during tests. Fig. 2 shows a 3D scheme and a schematic diagram of the test stand.

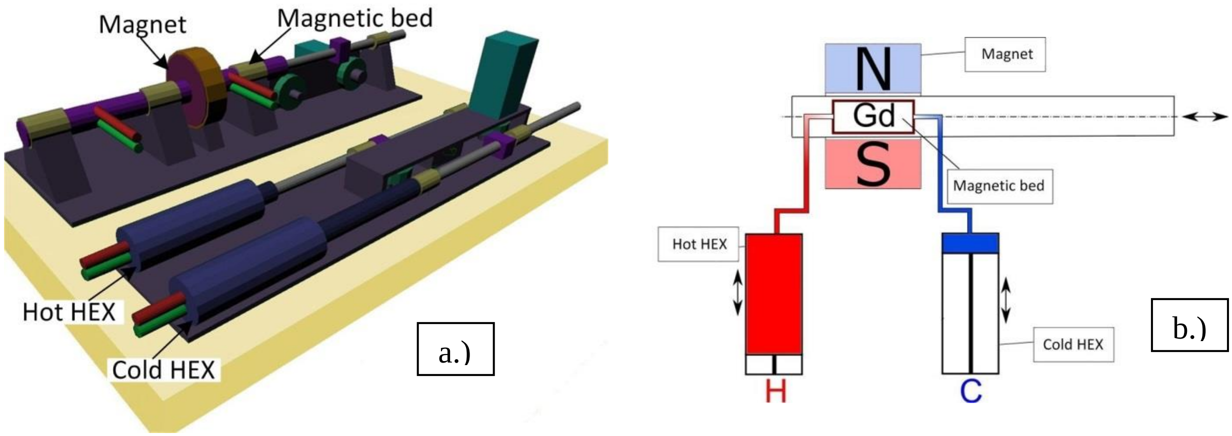
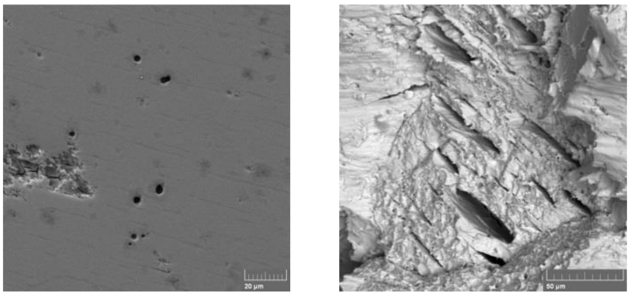


Fig. 2 3D scheme (a) and schematic diagram (b) of the test stand

The magnetic bed has a cylindrical shape. Its diameter measures 25.4 mm while the length is 25 mm. It will be made of a material which provides thermal insulation of a magnetocaloric material from the ambient conditions. In order to cyclically magnetize and demagnetize the material, the magnetic bed will reciprocate relative to a magnetic field concentrator. Gadolinium will be used to fill the bed. The material was purchased in the form of ingots. Fig. 3 shows pictures of gadolinium made using a Scanning Electron Microscope (SEM). In the pictures one can see numerous pores which may have a negative influence on the thermal conductivity of the material. In order to eliminate the pores and because of the large ingot dimensions (leading to the extended time of heat transfer between the magnetocaloric material and the cooling medium) it was necessary to process the material. The purchased material was divided into small particles which would be then utilized in the designed cooling system. The particles measure from 2 to 5 mm (fig. 4).

The presence of the magnetocaloric effect in the purchased material was confirmed using direct and indirect measuring method. The direct method consists in a measurement of the material temperature changes in the real time whereas the indirect method helps to investigate the changes in temperature and entropy of the material with the use of measurements of magnetization and thermal capacity. For direct measurements of the magnetocaloric effect a thermovision camera was used.



a.) b.)

Fig. 3 SEM pictures of the purchased gadolinium ingot (a) and of the metallographic specimen (b)

The measurements were carried out in 0.5 T and 1 T magnetic flux density. Fig. 5 shows pictures from the thermovision camera in which the gadolinium specimen is inside (a) and outside (b) the magnetic field of 0.5 T. The directly measured change in the temperature of gadolinium amounted to 2 K for 0.5 T and 3 K for 1 T magnetic field.

Fig. 4 Gadolinium particles

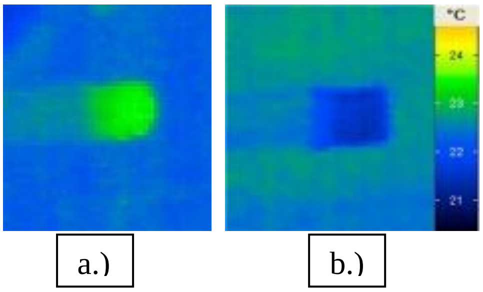


Fig. 5 Pictures from the thermovision camera showing a gadolinium sample entering (a) and leaving (b) a magnetic field

Indirect determination of the magnetocaloric effect was conducted using thermal capacity measurements. The results of these investigations are much more accurate than the measurements with the thermovision camera. The indirect measurements were carried out without the magnetic field and applying 1 T magnetic flux density. Fig. 6 shows a diagram of the thermal capacity of gadolinium depending on the preset temperature. Basing on these data, the changes in temperature (fig. 7 a) and entropy (fig. 7 b) of the material were defined for the magnetic field of 1 T [8]. The maximum obtained temperature difference amounted to 2.5 K while the entropy change was around 4 J/kgK.

To generate the necessary magnetic field, the designed test stand will use a cylindrical Halbach array [9]. This array is a special arrangement of permanent magnets which leads to the concentration of magnetic field inside the cylindrical gap. The Halbach array selected for the constructed system will generate a magnetic field of 1 T.

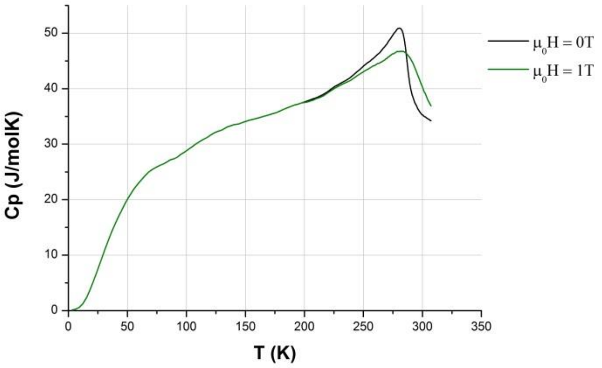


Fig. 6 Relationship between the thermal capacity of gadolinium and its temperature in 0 T and 1T magnetic field (measurements conducted in the International Laboratory of High Magnetic Fields and Low Temperatures in Wroclaw)

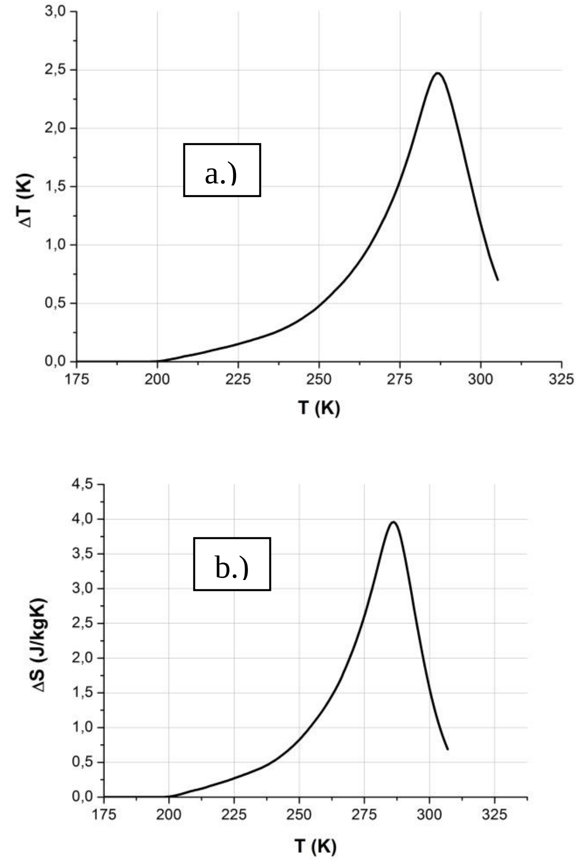


Fig. 7 Changes in the temperature (a) and entropy (b) of gadolinium for 1 T magnetic flux density, depending on the ambient temperature

The medium which recovers and provides the heat to the magnetocaloric material can be used in a liquid or gaseous form. The designed laboratory test stand will use the liquid refrigerating medium. The fluid will be transported within the system consisting of pistons connected to the magnetic bed by flexible pipes. The pistons will not only act as the fluid transportation systems, but also as the hot heat exchanger (hot HEX) and cold heat exchanger (cold HEX).

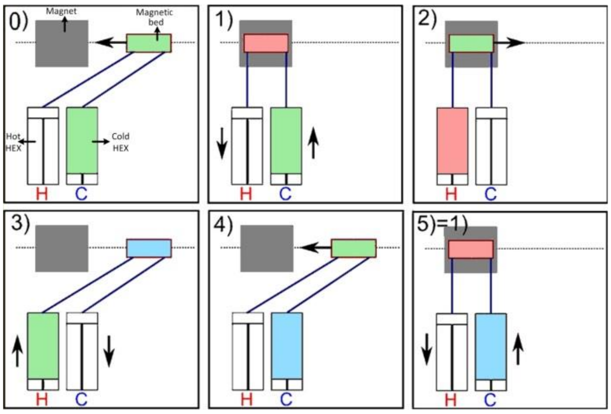


Fig. 8 Working cycle of the test stand

The test stand is designed to work in the AMR (Active Magnetic Regenerator) cycle. In such a cycle the magnetocaloric material not only works as the refrigerant, but also as the regenerator. The AMR cooling cycle consists of 4 stages [10] (fig. 8):

(0) initial state of the system,

(1) adiabatic magnetization of the magnetocaloric material resulting in a rise of the magnetic bed temperature,

(2) constant magnetic field process in which the magnetic bed is cooled by the refrigerating medium flowing from the cold HEX; this medium recovers the heat from the bed and transfers it to the hot HEX,

(3) adiabatic demagnetization of the magnetocaloric material which causes the magnetic bed to cool down,

(4) zero magnetic field process in which the cooling medium is pumped from the hot HEX, provides heat to the bed while the cooled medium from the bed is transported to the cold HEX, thus decreasing its temperature,

(5=1) repetition of the whole cycle.

In fig. 8 the colours of the heat exchangers and magnetic bed illustrate the way in which temperatures change in the system. The green colour denotes an initial temperature, the blue colour indicates a temperature drop ($\Delta T<0$) and the red colour denotes a rise in temperature ($\Delta T>0$).

4. SUMMARY

This paper presents the laboratory test stand for magnetocaloric effect investigations which is currently under construction. Initially the stand will use gadolinium as the refrigerant but it will also provide the opportunity to examine the temperature changes in other magnetocaloric materials, regardless of their form. There are also plans to prepare a numerical model of the system in the near future.

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