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Review

A review and new perspectives for the magnetocaloric effect: New materials and local heating and cooling inside the human body

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ABSTRACT

Nowadays, the magnetocaloric effect (MCE) is considered to be one of the most important fundamental thermodynamic effects to be employed in various technological applications. At present researchers focus mainly on environmentally-friendly magnetic materials and their applications in heating, refrigeration and magnetic energy conversion technologies. However, one must also pay attention to the increasing number of medical applications of the MCE, as e.g. controllable delivery and release of drugs and biomedical substances to defined locations in the human body, and applications of magnetic hyperthermia (cancer treatment). The first method demands local cooling of thermo-sensitive polymers in the body and the second induces local heating by a magnetic mechanism. In the first part of this article the recent progress in magnetocalorics (mainly on materials) is reviewed and the possibilities to increase the effect, e.g. by studying the interactions of magnetic and structural subsystems of magnetic materials in the vicinity of magnetic phase transitions and critical points, are outlined. To determine such and other important phenomena in the MCE, dynamic measurements have been developed. In the second part of the article the applications of the MCE in new methods, developed for applications in medical fields, as briefly mentioned above, are introduced and discussed. It is clear that a comprehensive overview on all important developments cannot be given here. Therefore, only the most important works are cited with a focus on important developments of Russian research. We ask those authors, who have contributed to the MCE and stay unmentioned in this review article, for their understanding.

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Une synthèse et de nouvelles perspectives pour l'effet magnétocalorique: Nouveaux matériaux et chauffage et refroidissement local à l'intérieur du corps humain

Mots clés : Magnétocalorique ; Froid magnétique ; Administration de médicament ; Hyperthermie

Nomenclature

Er	erbium
Gd	gadolinium
Ho	holmium
Tb	terbium
Tm	thulium
RRR	residual resistivity ratio

1. Introduction

The magnetocaloric effect (MCE) manifests itself by an adiabatic temperature change in certain magnetic materials when the external magnetic field is changed (Brueck, 2005; Gschneidner and Pecharsky, 2008; Tishin and Spichkin, 2003). Today the nature of the effect is well explored and understood. The total entropy of the magnetic material is considered to be the sum of three contributions related to the solid's lattice, the electronic system and a magnetic part (Liu et al., 2012; Moya et al., 2015; Tishin and Spichkin, 2002), which is a constant in adiabatic conditions. Obviously, if an external magnetic field is applied, the magnetic and electronic parts of the entropy decrease, and thus, the lattice of the material must counter react by an increase of its entropy to guarantee the constancy of the total entropy. However, a higher third entropy contribution (lattice vibrations) is equal to a higher temperature of the magnetocaloric material. Lowering the magnetic field, vice versa, results in a temperature decrease and cooling process. In many articles the discovery of the magnetocaloric effect was attributed to Warburg (1881), who had observed heat evolution in iron under the application of a magnetic field. However, Smith (2013) made a clarifying review with the conclusion that in 1917 Weiss and Piccard had made the basic discovery of this important physical effect. Up to present, the largest MCE value measured was shown by FeRh alloys, which have been discovered 26 years ago by Nikitin et al. (1990). The behavior of this magnetocaloric alloy was further investigated by these authors, see e.g. Nikitin et al. (1991). A comprehensive overview of MCE values in different materials is graphically presented in Liu et al. (2012). A markstone in the field of magnetocalorics was the discovery of the giant MCE, which was published by Pecharsky and Gschneidner (1997). Even though the MCE is known for such a long time, it still attracts the attention of many researchers and industrialists, also because of the wide range of practical applications where the effect can be employed. It is the progress in new magnetocaloric material development that provides the recent "boom" in MCE studies which was observed for the last two decades (see Fig. 1).

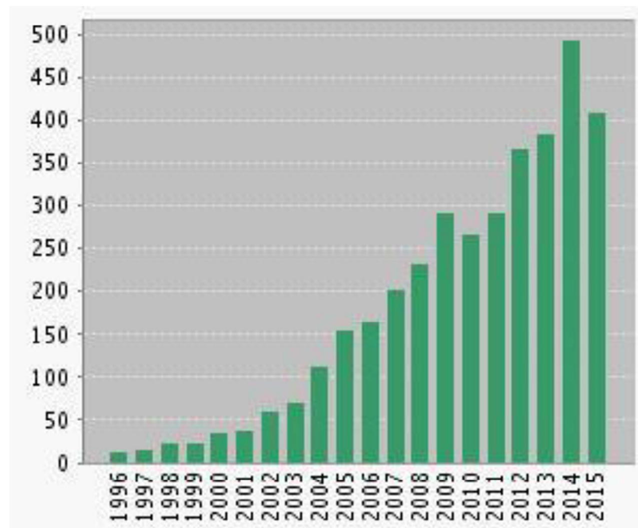

Fig. 1 – The number of publications concerning the "magnetocaloric effect" in the period 1996–2015 (taken from ISI Web of Knowledge).

Despite that the MCE has been studied for more than hundred years, there is no large-scale practical application of the effect so far. Problems to overcome are the high cost of magnetic field sources, not-ready-enough technologies for a manufacturing of the MCE materials, the preparation of appropriate shapes (filigree structures) to be used as working bodies in refrigerators and finally also difficulties to substantially increase the working cycle frequency. In the context of the working party on magnetic refrigeration of the International Institute of Refrigeration (IIF/IIR) a number of promising efforts have been performed (for reviews of innovations, see, e.g. in Kitanovski and Egolf, 2009; Kitanovski et al., 2015; Yu et al., 2010, etc.), which lead us to an optimistic view for the future of this technology. The large refrigeration market led to a decrease of refrigerator costs which makes it challenging in an initial phase to enter refrigeration markets with new MCE-based equipment. However, there exist already companies that are producing market-near prototypes in series of several dozens.

First MCE applications occurred in low temperature physics (e.g. Giauque and MacDougall, 1933), but also here the concurrence, related to applications in certain temperature intervals, by e.g. liquid evaporation, throttling, cryogenic gas expansion, etc. is also remarkable. Meanwhile other effects in