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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).

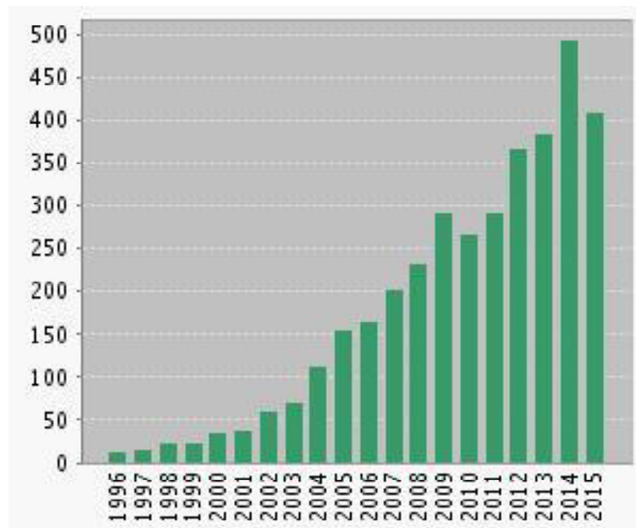

Fig. 1 – The number of publications concerning the "magnetocaloric effect" in the period 1996–2015 (taken from ISI Web of Knowledge).

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 magnetic materials have been developed and widely applied for years:

(1) The technology of permanent magnet's industrial production implies the knowledge of magnetic anisotropy to provide desired magnetic characteristics (see e.g. Gutfleisch et al., 2011; Hrkac et al., 2014; Kuz'min and Tishin, 2007; Thielsch et al., 2012; Woodcock and Gutfleisch, 2011).
(2) Terfenol-D which is the Tb-based alloy with the highest possible magnetostriction properties is produced commercially (Kim and Kim, 2007; Lanza et al., 2011)
(3) The materials which reveal the giant magneto-resistance effect (GMR) are widely used in magnetic memory applications (Bergmair et al., 2012; Daughton, 1999; Wang and Nakamura, 1996).

The authors believe that someday analogous MCE applications, probably primarily in form of some magnetic refrigeration equipment and later on by magnetic heat pumps and last also by magnetocaloric energy conversion machines, may be added to the above list.

Without any intention of criticizing these already classical magnetocaloric developments, it is also highly attractive and important to look into new approaches of MCE applications, which are based on a deep understanding of the physics and engineering in fields where, for example, the cost of the magnetic field source is lower (e.g. because of a smaller size), or even much more advantageous, where the magnetic field source already exists for other reasons (e.g. in MRI apparatuses in hospitals).

In this review article we start with conventional magnetocaloric research and then switch to other future developments, which may also show much potential for practical applications.

2. Magnetocaloric effect: current trends

Note that all current research on the MCE can be roughly divided into two major groups:

The first one is the characterization of new materials, a domain where scientists mainly concentrate on "routine-type" investigations of conventional magnetic and magnetothermal properties of "promising" (new) magnetocaloric materials (Tishin and Spichkin, 2003). This direction of research is extremely important as it covers practically all magnetocaloric materials. The main focus of these studies is the combination of knowledge on well-known substances, which reveals significant MCE values (Annaorazov et al., 1992; Dan'kov et al., 1998; Fujita et al., 2003; Nikitin et al., 1987; Pecharsky and Gschneidner, 1997), with the attempt to discover new materials e.g. with a giant MCE. Important MCE studies in the low temperature region were performed at the Physics Faculty of Moscow State University (Andreenko et al., 1989; Kuz'min and Tishin, 1991, 1993). It must be stated that it is problematic to take the magnetic entropy change as a criterion to judge the MCE's performance in real applications. This choice is doubtful since the magnetic entropy is an indirect and non-measurable parameter, which allows to perform only rough estimates of an MCE quantitative value. In such a case it is recommended to measure the adiabatic temperature change in order to get a direct result of the considered materials' behavior. Moreover, an ideal experimental equipment for such direct measurements is nowadays available (see Franco et al., 2009; Liu et al., 2012). Another interesting activity in this area is the recent attempt to obtain materials with a "smeared out" phase transition region. These materials represent a combination (an artificial alloy) of different magnetocaloric materials with close values of their single Curie temperatures (or temperatures of phase transitions where maximum MCE is observed). By this method one can observe a substantial MCE value that is achieved in a broad temperature range (comparing with the comparatively narrow MCE peaks of the single magnetocaloric materials). Another promising option is to use a series of materials with different amounts of the magnetic component which is responsible for the MCE (Tishin, 1990; Zhang et al., 2013). Unfortunately, at the moment, such attempts are only successfully applied in numerical modeling and in rough estimates of the magnetic entropy change values. It seems reasonable for technologists to concentrate on the preparation of such appropriate samples for further experimental investigations.

The second major direction in the studies of MCE materials is the investigation of "subtle" effects which may play a crucial role in understanding the physics of the phenomenon, and as a result, could then influence its practical applications in the near future. An example of this type, which is rather perspective, are investigations of conventional materials, but of higher chemical purity and perfectness of their crystal structure. The important fact is that a significant MCE value is observed in the vicinity of a magnetic phase transition of the material. As a rule lanthanide metals are a key component of any kind of magnetocaloric material, and it is well accepted that so called "heavy" lanthanides (standing in the rare-earth series after Gd) undergo multiple phase transitions with changing field and temperature. Thus it might be important to design precise magnetic phase diagrams of these metals in order to control their magnetic states and to investigate on the availability of a certain range of temperature and field for practical applications. It was also shown theoretically (Jensen and Mackintosh, 1991; Mackintosh and Jensen, 1992) that heavy rare-earth metals are characterized by several types of non-collinear magnetic ordering (fan, helifan, spin-slip), which are very sensitive to the chemical purity and crystal structure of the material. In the series of experimental works performed by MSU staff in collaboration with the Ames Lab (Iowa, USA) (Chernyshov et al., 2008; Dan'kov et al., 1998; Zverev et al., 2014), the investigation of high-purity single-crystalline samples of Gd, Dy and Tb was performed. For Gd it was shown that interstitials affect the Curie temperature which could also be proven theoretically (Kuz'min and Tishin, 2006). As a result of using the highest ever obtained pure samples (RRR more than 160) the authors managed to find several unreported states in Dy (Chernyshov et al., 2005). The most interesting finding is the existence of a complex magneto-structural transition at ~90 K (Chernyshov et al., 2008), where the MCE value is significant and which found its application in low-temperature magnetocaloric applications (e.g. natural gas liquefaction). For

Tb the authors finally proved the existence of a vast region of the fan phase which has not been previously reported. The location of the tricritical point on the magnetic phase was also refined. In this light all heavy lanthanide metals (Ho, Er, Tm) seem to be very promising regarding some new phase discoveries. For example, in Ho three new phases of spin-slip type and one intermediate phase, which combines the features of ferromagnetic and fan ordering, have been observed (Zverev et al., 2015). The future trend is to prove the existence of non-collinear magnetic phases by non-conventional experimental techniques in experimental studies of magnetocalorics. By using the PCAR (point contact Andreev reflection) technique, the authors (Usman et al., 2011) proved the existence of the cone phase along the *c*-axis in Ho in the low temperature region by observing the anomalies in the Andreev spectrum of an Nb/Ho contact. One of the trends is also to focus on the microstructure of the materials, which can be rather informative in getting knowledge about the magnetic ordering (Lang et al., 2004; Moore et al., 2006; Moretti Sala et al., 2014; Morrison et al., 2009). Thus, using the samples of high purity and perfect crystal structure can substantially refine the location of the critical points (phase transitions) of the material which leads to a clearer understanding of its response on the external magnetic field.

It is noteworthy that not only the inner state (purity and structure) can influence the transition points of the material. Zverev et al. (2011) showed that the experimentally observed Curie temperature depends on the shape of the sample. To avoid any misunderstanding, one should work out the "true" Curie temperature, which is an inherent property of the material; it depends only on the material itself and not, for example, on the shape of a probe. On the other hand, one never works with a kind of abstract and ideal material, but instead with a concrete piece of substance, whose properties turn out to be relevant when trying to determine the "true" Curie temperature. By performing precise and detailed magnetization measurements in the vicinity of the supposed Curie temperature of Gd with two samples with substantially differing demagnetization factors (the samples were in the shape of a plate and an elongated parallelepiped (rod)), the Russian authors revealed a difference of the "experimental" Curie temperatures of ~5 K, a value that is very crucial, for example, for the design of a magnetocaloric working filling of a magnetic refrigerator. To avoid experimental mistakes, one should be aware if one works with external applied or internal magnetic fields, and always correct the obtained value of the Curie temperature taking the demagnetization factor into account (see e.g. Egolf et al., 2015). In this article the transformations of the important magnetocaloric properties (specific entropy, adiabatic temperature change and effective specific heat) from external to internal magnetic field quantities and its physical invariants are outlined.

The appropriate procedure, which represents a modification of the Belov–Arrott method (Arrot, 1957; Belov and Goryaga, 1956), is proposed, which is also very important in the case of a "smeared-out" phase transition region as explained above. It is extremely important to precisely determine the transition point of each constituent. The future trend is to investigate the influence of magnetic anisotropy (which is negligible in the case of Gd but, for example, noticeable in Tb) on the location of the phase transition points. In Tb (Zverev et al., 2014), the difference between the Curie and the Néel temperature is ~10 K, so the mutual shift of both temperatures might be enough for the helix antiferromagnetic ordering (which exists in low fields between 220 and 230 K in Tb) to disappear. Thus, one can control the magnetic state of the material and get the only transition in Tb (where the MCE is large) by handling the anisotropy of the sample (the working body).

Here we have often mentioned the "substantial" value of the MCE, and this is the common trend of the majority of descriptive articles: to get certain values of the MCE and to compare them with "recognized champions", e.g. Gd, $Fe_{49}Rh_{51}$, $Gd_5(Si_2Ge_2)$, etc. The obvious question in this case is what to look for, i.e. what is the maximum possible value of the magnetocaloric effect? In a recent paper (Zverev et al., 2010), the authors theoretically proved that the maximum value of the MCE can never exceed 18 K/T (this result was obtained for the ideal hypothetical binary compound *Ho + nonmagnetic atom*). Any deviation from this ideal case (for real substances) will lead to a decrease of the maximal value, and therefore, it is expected that practical achievable values of the MCE will be in the range of 8–9 K/T. Thus, it is quite reasonable to state that the magnetic refrigerants, which undergo a second-order phase transition (which is used nowadays in single-stage refrigeration cycles) with MCE values exceeding the one of Gd, will be hardly ever found. It is well known that the MCE in FeRh (which undergoes a first-order phase transition) is as high as 6.5 K/T, which can be also used in other practical applications (to be considered below). In a search for highest MCE values, the researchers can spend a large amount of time to measure the properties of materials which might not reveal a significant MCE (e.g. in case of technological investigations or working with absolutely new chemically produced materials). In this case the prediction procedure developed and published by Franco et al. (2009) (Zverev et al., 2010) may help to save a lot of time. A universal curve for the adiabatic temperature change was designed, which is based on scaling laws, and allows to predict the response of the materials in different conditions not available in the laboratory. By applying *Franco's method*, it is possible to reconstruct a reliable MCE dependence as a function of temperature with only a few measurements at some reference points. After these measurements are performed, the rest of the curve is numerically designed by applying scaling laws, a procedure that is very convenient in the case of an investigation of a large amount of similar samples. This procedure was formalized and applied in a form of a program by the first three authors, and exists today as a commercially available experimental setup specially designed for express measurements of the MCE.

3. Magnetic heating, refrigeration and energy harvesting

The most efficient method to increase the efficiency of a magnetic refrigerator, in which magnetocaloric materials are used as working solids (refrigerants), is by an increase of the operational frequency of the linearly or rotationally moving part in the device. At present strong magnetic fields (up to 1.5 T for magnetic field sources based on permanent magnets and up to 5 T for superconductor solenoids) are applied in laboratory prototypes of magnetic heating and cooling devices (see Yu et al., 2010). A certain restriction occurs on the highest value of operation frequency of a magnetic refrigerator. At present it is limited by a level of only a few Hz, because it is difficult to create such strong fields changing with higher frequencies. Furthermore, they may cause an appearance of eddy currents and its related heating. It is possible to apply higher frequencies at lower magnetic fields and, thus, the decrease of the MCE caused by an amplitude lowering of the magnetic field can be counterbalanced or even overcome by a higher operational frequency. Therefore, it is crucial to know the static and dynamic magnetocaloric properties of the materials in low fields in order to apply them adequately in magnetic heat pumps and refrigerators. It is also important to take into consideration the limitations in the heat transfer between the magnetic material and the transfer fluid.

To date, the majority of studies of the MCE were performed for strong magnetic fields (Tishin and Spichkin, 2003), whereas investigations devoted to the MCE at low fields (<0.2 T) are almost absent. It is important to state that magnetocaloric behavior in the low field region can have some peculiarities related to the processes of initial magnetization (transformation of domain structure, rotation of magnetization, etc.) and show form factor effects. The influence of such effects can be especially important in a dynamic mode and can depend on the magnetic field change rate. The only way to investigate these effects is direct measurements in periodically changing magnetic fields (dynamic mode). Besides this, such measurements can give the researchers additional information about the processes of initial magnetization which might be interesting for the fundamental knowledge of magnetocaloric materials and its applications.

4. Medical applications

4.1. *Brief introduction*

In a multitude of books, review and scientific articles, after a discussion of magnetocaloric materials in a first section, usually a second section is devoted to applications of the MCE to magnetic refrigerator applications (e.g. see Egolf et al., 2014; Kitanovski et al., 2015; Tishin and Spichkin, 2003, etc.). Because the research in this applied engineering field is sufficiently reported, in this article our efforts are concentrated – besides Chapt 3, where a few newer remarks on problems with high-frequency refrigerators were described – on a newer field of MCE applications, namely such in the bio-medical field.

4.2. *Targeted drug delivery*

Among other new trends in the MCE domain, there are investigations of microobjects (Hélio et al., 2014; Ilyn et al., 2009; Zhang et al., 2011). Satisfactory theoretical explanations of the effects observed in these materials are so far rather poor. On the other hand, very interesting theoretical papers (Binek and Burobina, 2013; Vopson, 2012) are devoted to the so-called multicaloric effect, where the MCE is observed in a multiferroic material placed into an external electric field region. This topic is promising, but needs some further thorough experimental proofs.

Different types of arthroplasty (vascular surgery with the use of stents, articular prosthetics etc.) are associated with the risk of infectious complications, injuries caused by implants, as well as restenosis. To prevent such complications targeted delivery of biologically active substances (drugs, anti-inflammatory drugs, anti-proliferative agents) is required. In some cases the optimal therapeutic effect is achieved by the periodical change of bioactive substances' concentration in tissues (like a pulsed mode). Thus, the delivery of drugs to a certain place at a certain time, as well as their controlled release under an external action, is the vital necessity for modern medicine in general and for arthroplasty techniques, in particular. The best way to control the state of the implants' coatings with embedded medicine is the impact of low-frequency or a DC-magnetic field, which causes no side effects and easily without any attenuation penetrates through biological tissues.

At the moment the work (Pyatakov et al., 2015; Tishin et al., 2015) is concentrated on the development of functional coatings for controlled release of bioactive compounds in an external magnetic field and methods of its application to the implants. Functional coating consists of a composite material with magnetocaloric properties. Changing the temperature of the magnetic component causes a transition of a biocompatible polymer (which is in thermal contact with the magnetic material) to the hydrophilic state. The composite coating also includes a thermal insulating layer in order to reduce heat transfer to the surrounding tissues. Fig. 2 shows the schematic process of targeted drug delivery from an implant's surface.

A proposed carrier for active substances combines the advantages of accurate delivery provided by using magnetic carriers with the convenience of controlling the retention/release rate of the active substance from the carrier using materials of varying characteristics under the influence of external conditions, such as temperature, magnetic field strength, etc.

4.3. *Hyperthermia methods*

Hyperthermia is the destruction of malignant cancer cells by an internal heating mechanism. Following Egolf et al. (2016), it is categorized by the obtained (steady) temperature level of the tumor: 1) diathermia, leading to a low temperature of $T < 41°C$ (this is not desirable, because of an unwelcome acceleration of the tumor growth rate); 2) apoptosis describes a moderate hyperthermia with a final temperature in the interval of $42\ °C < T < 46\ °C$ and finally; 3) thermoablation by necrosis reaching temperatures of $T > 46\ °C$. Furthermore, a categorization by the size of the cancer region was established: 1) local, 2) regional or 3) whole body therapy. Thermal induction is achieved by various sources, e.g. by irradiation and absorption of light, ultrasound, electromagnetic waves of radiofrequency, microwaves, infrared radiation, etc. Since its first announcement by Gilchrist et al. (1957), intensive research has been conducted in the field of electromagnetically excitable thermoseeds tailored for effective cancer therapy, a technique that is the topic of this section.

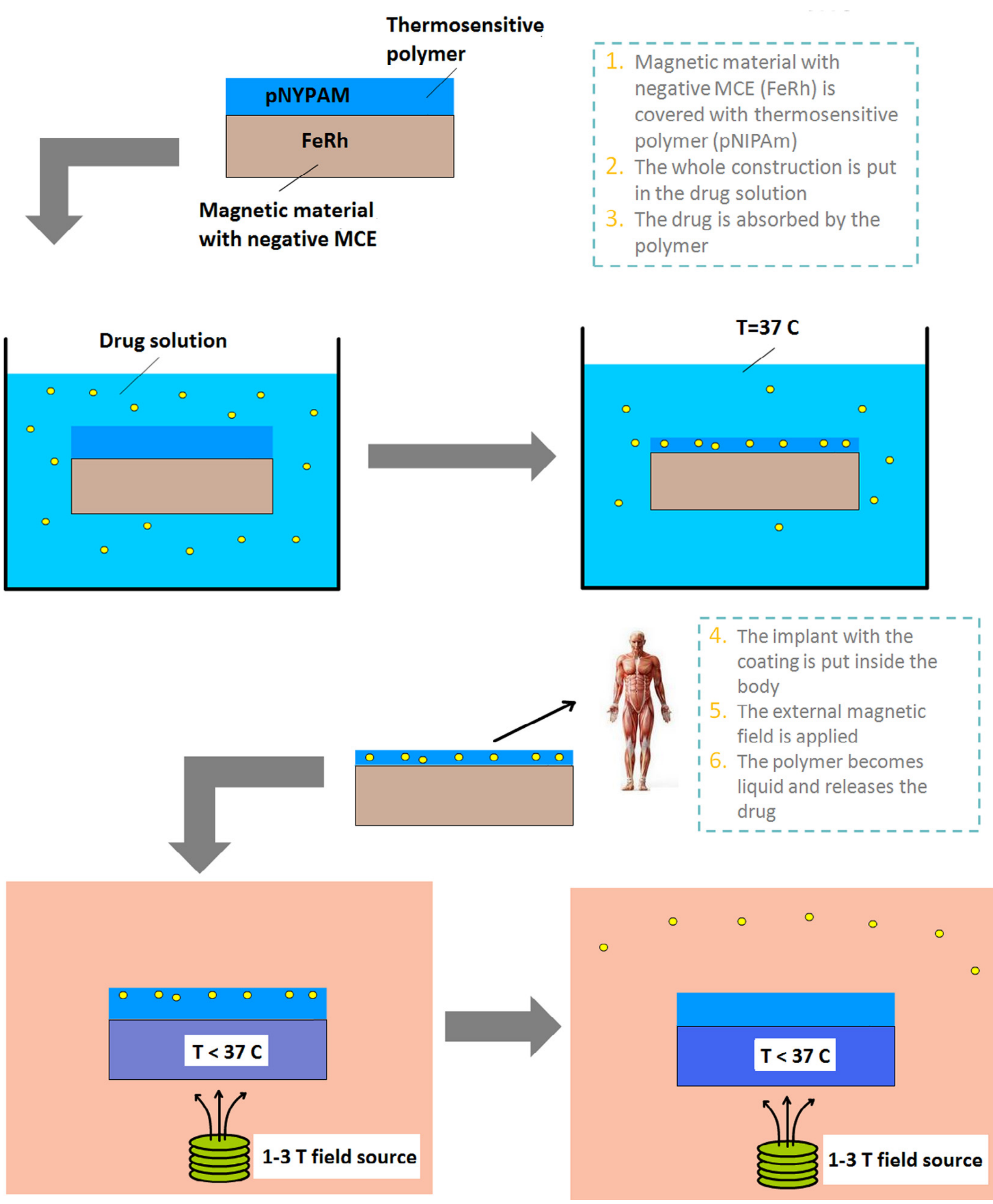

Fig. 2 – The general mechanism of the drug release from the implant's surface. The method is explained in the two frames with three process steps each, which are completely self-explanatory.

There are two new inventions of magnetic hyperthermia methods of the authors of this article which are reported in the next two subsections.

The first invention of the Russian authors (see Tishin, 2016) relates to magnetocaloric material physics and to medicine, in particular to magnetotherapy (hyperthermal electromagnetic therapy) of malignant neoplasms. The inventive method consists of injecting material (nano) particles exhibiting a high-(maximum) MCE into a tumor, wherein the material has a magnetic ordering temperature close (approximately) to the human body temperature and is selected from a group containing precious metals, rare-earth elements (metals) and the alloys or intermetallic compounds. The method makes it possible to destroy cancer cells without damaging healthy cells and is selected such that it is ecologically pure and non-toxic. In a collaboration between the authors of Russia and Switzerland first physical and numerical models have been established (see e.g. (Zatsepina et al., 2009a, 2009b, 2010). In this model it is assumed that a magnetic fluid is injected into and uniformly distributed in a cancer tumor (see Fig. 3).

Like this a large number of heating centers are equally distributed over the tumor domain that is assumed to be spherical. A low concentration of magnetocaloric material particles in the nanosize domain (characteristic radius e.g. 200 nm) is demanded for a characteristic heating of a tumor to approximately 42 °C. For future applications the treatment time is approximately thirty minutes. The method will be applied several times and often in combination with other cancer defeating methods

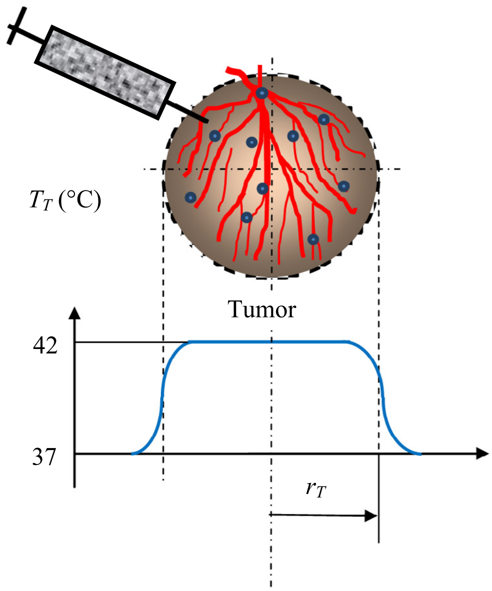

Fig. 3 – A spherical tumor with veins and arteries of radius r_T and its heating by nanowires from, e.g., 37 °C to 42 °C is shown. At the border of the cancer tumor, by heat losses given by heat diffusion, the temperature profile decreases over a certain diffusion length. The red lines show arteries and veins with a blood mass flow and heat transport by fluid convection. Heat production occurs by the application of the magnetic heating method (figure with permission from De Marco (2013, 2014)).

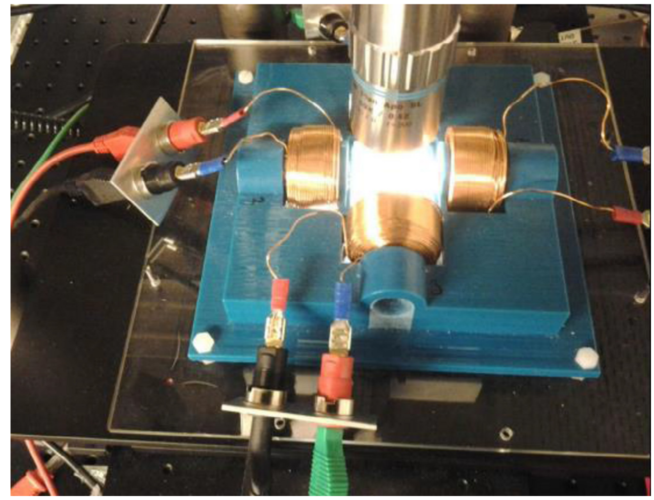

Fig. 4 – The experimental setup to make the physical measurements in a small beaker with a gel containing a nanowire at ETHZ. The frame with integrated camera is shown on the top and four electromagnets surrounding a small beaker (from Tsague, 2015).

as radiotherapy, chemotherapy, etc. Without going into more details, it is reported that the preliminary work of the Russian–Swiss collaboration partners has demonstrated the feasibility of this method that still leaves much space for further more detailed investigations.

The second invention goes back to the last author of this article and is substantially different to conventional magnetic hyperthermia methods, which work by internal magnetic heating mechanisms, like Brown's and Néel's relaxation, eddy currents, hysteresis effect, etc. (see e.g. Rosensweig, 2002).

In this new method, instead of spherical nanoparticles, a large amount of nanowires are homogenously distributed in a biocompatible gel or fluid (Rosensweig, 1997) and then injected into the cancer tumor. By applying a rotational magnetic field, the nanowires are following (like tiny compass needles) the field orientation. In an experimental apparatus of the Institute of Robotics and Intelligent Systems (IRIS) at the Swiss Federal Institute of Technology in Zurich (ETHZ) in a horizontal plane two pairs of magnets are located perpendicular to each other. A sinus and a cosinus magnetic field is produced in the two pairs of magnets. By Pythagoras's law this configuration creates a circular rotating magnetic field (see Fig. 4).

The rotating nanowires could be used as nano scalpels to cut malignant tumor cells, but this kind of application is not evaluated. Instead, by fluid friction in the nanowire's fluid boundary layer, a strong heating effect is produced, which finally leads to an elevated steady-state temperature of the tumor that destroys the malignant cancer cells.

The conventional hyperthermia methods have problems to achieve sufficiently high heating rates. A numerical feasibility study by Egolf et al. (2016) demonstrates that this method responds ideally to the demanded heating rate within the medical tolerated limit $H_0 * f < 5 * 10^8$ Am^{-1}s^{-1}, whereas H_0 denotes the applied external magnetic field and f denotes the rotation frequency of this field. It is clear that the heating rate can be even improved by a simultaneous occurrence of several magnetic heating effects.

The moving nanowires can be tuned to show a variety of different modes, as e.g. oscillation, rotation (compare with Fig. 5), rotation with a certain remaining oscillation, motion with different frequencies of the magnetic field and the nanowire motion, even counterclockwise rotation of the nanowire compared to the magnetic field rotation, chaotic motion, etc. Therefore, it is also possible to design a magnetic field change in the interior of the nanowires and to induce simultaneously additional magnetic heating effects. Notice that it is also possible to induce the MCE. This has the additional advantage of temperature stabilization given by the magnetic phase transition with its elevated effective specific heat and a related higher thermal capacity. A feasibility study, involving a thorough magneto-thermodynamic analysis, of this system is presented in Egolf et al. (2016) and demonstrates excellent heating rates in medically tolerable parameter domains.

5. Conclusions

At the moment there are some obstacles to overcome which prevent the magnetic cooling technology from entering in a short term refrigerator markets. Here are the following reasons for this occurrence:

(1) Conventional cooling technologies are also permanently improved and have after a more than hundred

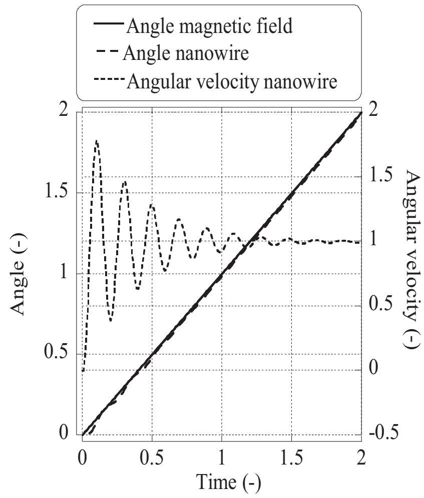

Fig. 5 – The low-viscosity solution where the tumor tissue with injected fluid is not too viscous to allow a nanowire rotation is shown. We observe a linear increase of the magnetic field's angle of rotation (solid line), which agrees with a constant angular velocity. The nanowire follows the magnetic field initially with an oscillation relative to it. This oscillation is damped and after some transition time the movement of the nanowire remains with a small phase shift to the backside of the rotating magnetic field. One may say that the magnetic field pulls the nanowire (Egolf et al., 2016).

years' intensive research and development time still some technical advances compared to new refrigeration equipment that is at present still in an infancy kind of state and far from being at an optimum one. Therefore, more intensive research is required in magnetic refrigeration to improve the promising existing prototypes.

(2) In household refrigerators there is a necessity to obtain a large temperature difference of up to 40 K. Not very high adiabatic temperature changes are no obstacle to obtain such values, which can be realized by cascading and (passive and active) regeneration. However, these methods make the machines larger and also somewhat more expensive, so that the concurrence to evaporation refrigeration is competitive and must involve arguments concerning energy and environment.

(3) The best possible minimization of the magnet's mass is required, because of the elevated cost of the magnet's materials. No satisfying overall optimization simulations of magnetic refrigerators have been reported up-to-date. However, promising research is initiated and ongoing that will overcome this situation in the near future.

However, such arguments are no reason to lose motivation. Environmental considerations are of increasing importance and energy and gray energy considerations will have more appropriate basis in the future, favoring increasingly alternative refrigeration methods.

Realizing such difficulties, Tishin was one of the first researchers who began to alternatively and additionally consider applications where:

(1) the required temperature difference is smaller (e.g. in the 1–5 °C range) and
(2) low price is not the most important argument.

Therefore, attention should be also given to medical applications, as e.g. MCE materials consisting of thermo-sensitive polymers and magnetic materials with large MCE values. Such materials can perform local cooling inside the human body and release drugs, hormones, glues and other substances from the surface of the implant. They can also be used to invent new and innovative magnetic and magnetocaloric hyperthermia methods. Some examples of these two classes of medical applications were given in this article in an overview manner. For more detailed information, in the corresponding sections, accurate references may be found.

Dedication

We dedicate this article to Karl A. Gschneidner, Jr., a pioneer and great expert of rare earth materials and MCE, who passed away early Wednesday morning, April 27th, 2016. We hope that continuation of lanthanide metals studies in our scientific community will be the best monument in the memory of Professor Karl Gschneidner.

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