### TECHNICAL ARTICLE

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# A Brief Review on the Chemical Stability and Corrosivity of Magnetocaloric Materials

# SYDNEY WOJCIESZAK, $^1$ BINYAM WODAJO, $^2$ ANTHONY DUONG, $^2$ RAVI L. HADIMANI, $^{2,3}$ and RADHIKA BARUA $^{2,4}$

1.—Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA. 2.—Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, 401 W. Broad Street, Richmond, VA 23284, USA. 3.—Department of Biomedical Engineering, Virginia Commonwealth University, Richmond, VA 23284, USA. 4.—e-mail: rbarua@vcu.edu

Active magnetic regenerative refrigeration is an energy-efficient and environmentally friendly alternative to conventional vapor-compression refrigeration technology, which is associated with harmful chemical refrigerants and high carbon emissions having high ozone-depleting potential. The core component of AMR is a porous magnetocaloric material that undergoes millions of thermal and magnetic field cycles throughout the device's lifetime, while immersed in a heat transfer fluid. Despite significant research spanning almost four decades, the chemical stability of MCMs continues to pose a critical engineering challenge. In this mini-review, research on the corrosion of roomtemperature MCMs is discussed. Particular attention is given to Gd, Gd<sub>5</sub>Si<sub>2</sub>Ge<sub>2</sub>, and La(Fe,Si)<sub>13</sub> and their compositional variants. Following a brief overview of the wide variety of corrosion monitoring methods used to evaluate magnetocaloric regenerator structures, corrosion inhibition mechanisms are discussed in the context of metallurgical, processing, and environmental factors. Finally, challenges associated with corrosion testing of magnetocaloric structures fabricated via additive manufacturing methods are presented.

# **INTRODUCTION**

Growth in the global population and accompanying environmental challenges, which include a demand for more heating and cooling technologies to offset planetary warming, emphasize the increasing need for viable innovative engineering solutions to enable efficient thermal management. Cooling, described mainly as refrigeration and air conditioning, plays a vital role in several disparate spheres of modern life, such as food preservation and production, climate-controlled residential and commercial buildings, gas liquefaction and energy storage, temperature-controlled cargo carriers, cryopreservation of human organs, vaccines, etc. Unavoidably, cooling technologies are incredibly energy intensive. Currently, 15% of the world's electric power is devoted to vapor-compression cooling, with that value increasing to 30% in developed countries.<sup>1</sup> Associated with this technology are significant carbon emissions and environmentally damaging chemical refrigerants with high ozone layer depletion potential (e.g., chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons).<sup>2</sup> To address this challenge, and in response to strategic global treaties, such as the Montreal and Kyoto Protocols, many countries worldwide, including the European Union, Japan, USA, and China, have begun to unveil new rules to phase out global warming potential gases.<sup>2</sup> These policies have inspired collaborative research efforts to deal with the drawbacks of traditional cooling methods. Among possible alternatives, magnetic cooling devices enabled with the "magnetocaloric" class of functional materials are attractive, as they have the potential for efficiency improvements of up to 50% over conventional vapor-compression systems, which is equivalent to 60% of Carnot efficiency.<sup>3</sup>

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Magnetocaloric effects (MCE) occur when a magnetic field is varied in a cyclic isothermal or adiabatic manner in the physical proximity of a given material, resulting in a temperature change.<sup>4</sup> Although it was discovered way back in 1917 by Pierre Weiss and Auguste Piccard, while studying the temperature-dependent magnetic behavior of nickel,<sup>5</sup> interest in the field of magnetocaloric technologies did not develop until the late 1990s, when the Ames Laboratory, a US DOE laboratory, and the Astronautic Corporation of America unveiled a feasible magnetic cooling device prototype, comprising a room-temperature working magnetocaloric material (MCM).<sup>6,7</sup> Since then, over the last three decades, rigorous efforts have been devoted to the two lines of inquiry: (1) understanding the physics underlying the functional response MCMs, of room-temperature in particular  $Gd_5Si_2Ge_2$ ,  $La(Fe,Si)_{13}$ , MnFe(P,Si), NiMn-based Heusler,  $AlFe_2B_2$ , and their variants; and (2) the development of laboratory/pre-industrial magnetic refrigeration device prototypes.<sup>8</sup> Nevertheless, the gap in going from laboratory samples to a competitive device that meets the market needs remains wide due to several engineering challenges at the system integration level.

To this end, a schematic of a magnetic cooling device is shown in Fig. 1. Depending on the mechanism of application of a magnetic field, magnetic refrigerators may be described as rotary when the magnetic field source moves circularly around the regenerator (or vice versa), and reciprocating, when the magnetic field source or the working MCM material performs a linear motion to create a variable magnetic field on the material. The thermodynamic cycle uses a heat transfer fluid to transport the heat generated or absorbed from magnetizing and demagnetizing the MCM to a hot and cold heat exchanger in both device configurations. The net quantity of the heat exchange depends on several factors, including the physical properties of the fluid, the fluid flow pressure, the porosity of the working magnetocaloric material, the frequency of the magnetocaloric material displacement inside and outside the magnet, etc.<sup>8,9</sup> An overlooked and less frequently studied but critical point to be considered is the *interaction between the* magnetic refrigerant material and the heat exchange fluid, namely, the aging of the material when exposed to prolonged corrosive action. To this end, this focused article aims to review published reports on the chemical stability and corrosivity of magnetocaloric materials.

The manuscript is organized into four sections. First, an overview of the design of the heat exchange system in a magnetocaloric cooling device is provided in "Fundamentals: Design of the Heat Exchange System in a Magnetocaloric Device Prototype" section. Here, we list the most commonly used MCMs and heat exchange fluids used in roomtemperature device prototypes. Salient material



Fig. 1. Schematic of a magnetic cooling device. Depending upon the mechanism to apply a magnetic field, magnetic refrigerators are of two types: (a) reciprocating and (b) rotating. In both configurations, a heat transfer fluid is used to transport the heat generated or absorbed from the working magnetocaloric material (MCM) to a hot and cold reservoir. (c) Different conformations and shapes of the magnetocaloric regenerators.

factors that influence the corrosion of magnetic regenerators are discussed. Second, standard experimental techniques used to evaluate corrosion behavior in the MCMs are discussed in "Experimental Methods for Corrosion Detection & Monitoring" section. Third, strategies to inhibit degradation of the functional response in MCMs due to corrosion are presented in "Corrosion Inhibition Mechanisms" sections. Going forward, the scientific community is leaning towards fabricating regenerators with metal additive manufacturing (AM) schemes. To this end, "Outlook: Corrosion Behavior of Additive Manufactured Magnetocaloric Structures" section offers insight into the chemical stability of 3D printed magnetocaloric structures. Finally, concluding remarks are provided in Conclusion section.

# FUNDAMENTALS: DESIGN OF THE HEAT EXCHANGE SYSTEM IN A MAGNETOCALORIC DEVICE PROTOTYPE

Table S1 in the supplementary material summarizes the room-temperature magnetic refrigerator prototypes that have been conceptualized and fabricated over the last five decades, together with relevant references. Among the MCMs used in these cooling devices, Gd metal and Gd<sub>5</sub>(Si<sub>2</sub>Ge<sub>2</sub>)-based alloys have been most widely used, because their Curie temperatures are close to room temperature, and they are readily available to use, as opposed to other room-temperature MCMs.<sup>5,10</sup> More recently, La(Fe,Si)13-type materials have been used extensively.<sup>10,12,13</sup> Prototypes with lanthanum-based manganites, NiMn-based Heuslers, and Fe<sub>2</sub>P-type compounds have also been suggested.8 For reference, Table I provides a quantitative comparison of the magnetocaloric response of these state-of-art materials, as described by the following figures of merit: (1) magnetic entropy and adiabatic temperature change observed upon application of a magnetic field ( $\Delta S_{mag}$  and  $\Delta T_{ad}$ , respectively), (2) thermal conductivity ( $\kappa$ ), and (3) specific heat capacity  $(C_p)$ .<sup>11</sup>

In an active magnetic regenerative (AMR) device, the MCM is immersed in a heat exchange fluid whose choice is driven by a number of factors: (1) good heat transfer characteristics (high value of the heat capacity and thermal conductivity), (2) low value of viscosity, (3) stability of the thermal and physical properties across the working temperature range of the device, (4) environmental friendliness (low degree of pollution and Environmental Protection Agency approved); (5) non-toxicity (i.e. Food and Drug Administration approved), and (6) low cost.<sup>8</sup> Table S1 in the supplementary material and Fig. 2 provide a comprehensive list of the heat exchange fluids used in the magnetocaloric device prototypes constructed to date. A magnetocaloric regenerator must be shaped to provide a very large heat transfer surface to facilitate efficient convective heat transfer from or to the working fluid. Following the principles of heat transfer, it is understood that, during fluid flow in the magnetocaloric regenerator, the dimensionless Nusselt number is linearly correlated with the heat transfer coefficient, and that the thermal conductivity of the fluid is inversely associated with the characteristic length of the particular fluid void or channel.<sup>12</sup> As such, the porosity of the magnetocaloric regenerator depends not only on the macroscopic properties of the magnetocaloric material but also on the viscosity and thermal properties of the working fluid and the fluid dynamics.<sup>8</sup> This implies that, when liquid water is used as the working fluid, the porosity can afford to be as low as 30-45%.<sup>8</sup> With regard to their shape, magnetocaloric regenerators can be categorized as packed powder beds (crushed, unshaped particles, or spherical gas-atomized powders are used to form the bed, sometimes together with a small mass fraction, 5 wt.%, of polymer binder to fix the position of the particles) and periodically ordered structures (stacked plates, circular or honeycombed microchannels etc.) (see Fig. 2). Depending on the choice of the magnetocaloric material and the heat exchange fluid, as well as the shape and form of the regenerator, corrosion processes in magnetocaloric devices often have complex mechanisms, leading to various forms of localized corrosion, such as pitting, crevice, and galvanic corrosion. The prediction and prevention of corrosion is challenging. Therefore, we present the wide variety of corrosion testing and monitoring methods used to evaluate MCMs, as described in the following section.

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	Gd <sub>5</sub> Si <sub>2</sub> Ge <sub>2</sub> family	La(FeSi) <sub>13</sub> family	LaMnO <sub>3</sub> manganites	NiMn-based Heuslers	MnFe <i>P-</i> type compounds
$\begin{array}{l} \Delta S_{\text{mag}} \text{ at } @ 2 \text{ T } (J/\text{kgK}) \\ \Delta T_{\text{ad}} (\text{K}) \text{ at } @ 2 \text{ T} \\ \text{Thermal} \qquad \text{conductivity} \\ (W_{\text{m}}^{-1} \text{ K}^{-1}) \end{array}$	$8-14 \\ 5-8 \\ \sim 5-6$	$6-22 \\ 2-6.5 \\ \sim 8$	$3-5\ < 1\ \sim 1-2$	8-12 2-5 2	20-25 $2-4$ $4$
Specific heat capacity @ 2 T $(Jkg^{-1} K^{-1})$	124–300	1000-1500	117-250	1000-2000	1500-1800
Data taken from8–26 and all refer	ences therein.				

Table I.	<b>Comparison</b>	of attributes o	of state-of-art	materials for	• magnetocalori	c applications
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Fig. 2. The statistical distribution of the different heat exchange fluids and architectures of magnetocaloric materials used to fabricate magnetocaloric prototypes over the last three decades. Data taken from Refs. 8, 10, and 11 and all references therein

# EXPERIMENTAL METHODS FOR CORROSION DETECTION AND MONITORING

Over the past several decades, various experimental methods have been developed to diagnose corrosion problems, forecast maintenance requirements, and identify the most effective inhibitor and optimum inhibitor dosages. Traditional methods used for corrosion testing and monitoring include the weight-loss coupon test, optical imaging, surface-sensitive spectroscopy, galvanic current detection, and electrical resistance and electrochemical measurements.

The weight-loss coupon test is probably the most widely used and its represents the most direct method for detecting cumulative corrosion damage. It is used to provide the baseline criteria in many corrosion monitoring programs, and simply involves observing the corrosion rate or mass loss of the working material in static or moving heat transfer fluid as a function of immersion/aging time.<sup>13</sup> It is acceptable to use a precision electronic weight balance and a formula along the lines of  $\overline{V} = m/2$ (S t), where m is the change in mass before and after corrosion and S is the exposed surface area with units of  $g/(m^2h)$  or a percent to reflect the mass loss.<sup>14–16</sup> Following Ref. 17, thermal gravimetric analysis can also determine changes in chemical composition or mass loss from corrosion.

Optical methods have been extensively used to examine corrosion in magnetocaloric structures. For instance, in Ref. 15, La(Fe,Mn,Si)<sub>13</sub> alloys displayed pitting corrosion after immersion in distilled water. Pitting is a form of highly localized corrosion that creates tiny holes in the metal. The driving power for pitting corrosion is the depassivation of a small area, which becomes anodic (oxidation reaction), while an unknown but potentially vast area becomes cathodic (reduction reaction), leading to very localized galvanic corrosion, an electrochemical process whereby one metal corrodes in preference to another metal that it is in contact with through an electrolyte. Optical microscopy metallographs of the La(Fe,Mn,Si)<sub>13</sub> samples are shown in Fig. 3a and indicate that the corroded spots appeared simultaneously at grains and grain boundaries of a 1:13 phase. In another example, in Ref. 18, 2D optical microscopy surface images in Fig. 3b show the change in depth and pitting of a LaFe<sub>10.72</sub>Co<sub>1.08</sub>Si<sub>1.2</sub> alloy sample before and after exposure to a 0.5-M phosphate solution. Scanning electron microscopy equipped with back-scattered electron diffraction or energy-dispersive x-ray spectroscopy (EDS) functionality have also been used to analyze surface traits, like grain and pore size or pitting size, as a test for corrosion.<sup>19,33,36</sup> More advanced options include inductively coupled plasma optical emission spectroscopy or inductively coupled plasma atomic emission spectroscopy or xray computed tomography.<sup>20–</sup>

Electron probe microanalysis (EPMA) is another powerful tool for understanding the distribution on overall surface compositional changes during aging. Electron probe micro analyzers may be equipped with multiple different spectroscopy forms, e.g., wavelength dispersive spectroscopy, EDS, and silicon drift detectors, and can provide qualitative analysis on the residual sediment for various pilot set-ups that test corrosion and chemical stability. Surface analysis may include contact profilometric roughness tests to supplement optical microscopy observations. For example, Fig. 3c shows profilograms that provide insight into the roughness profiles of LaFe<sub>10.72</sub>Co<sub>1.08</sub>Si<sub>1.2</sub> alloys before and after exposure to an acidic 0.5-M phosphate solution containing  $Cl^-$  ions (pH = 3).<sup>18</sup> The results for two representative sections (denoted as A and B) indicate a significant local area loss in the material after exposure to a corrosive medium.<sup>18</sup> X-ray photoelectron spectroscopy can also detail the chemical state and specific metal oxide species formed on the surface of magnetocaloric materials.<sup>32,42</sup> This method analysis is based on the phenomenological rule allowing the prediction of relative binding energy positions depending on the degree of ionic and/or covalent character in the bonding of metal oxides, and has been used in Ref. 20 to examine how passive Gd<sub>2</sub>O<sub>3</sub> layers can influence corrosion in magnetocaloric regenerators fabricated for Gdbased alloys.<sup>20,23</sup>

Unfortunately, weight-loss coupon tests, optical imaging, and spectroscopic methods have intrinsic limitations; for instance, they only provides average corrosion rates over extended periods, and do not measure possible shorter-term deviations in the corrosion rate and changes in the corrosion mechanism. To this end, electrochemical methods for corrosion detection are often helpful. The corrosion current is defined as the current produced in an electrochemical cell while corrosion is occurring, and its density is regarded as a more accurate indicator of metal corrosion rate because it is almost directly proportional, which agrees with Faraday's law. A potentiostat can provide polarization curves that illustrate this proportional relationship



Fig. 3. Examples of corrosion testing using optical methods. (a) Optical microstructure metallographs of compounds (a, top) LaFe<sub>11.5</sub>Si<sub>1.5</sub> and (b, bottom) LaFe<sub>11.4</sub>Mn<sub>0.1</sub>Si<sub>1.5</sub> displaying corrosion spots and pitting at the grains and grain boundaries of 1:13 phase after being immersed in distilled water. Reprinted with permission from Ref. 15 (b) 2D optical microscopy surface images showing the change in depth and pitting of a LaFe<sub>10.72</sub>Co<sub>1.08</sub>Si<sub>1.2</sub> alloy sample before and after exposure to a 0.5-M phosphate solution containing 0.03 M Cl.<sup>-</sup> at a pH of 3. (c) Profilograms of the same LaFe<sub>10.72</sub>Co<sub>1.08</sub>Si<sub>1.2</sub> alloys before and after electrochemical measurements; sections *A* and *B* indicate a significant local area loss in the material after exposure to a corrosive medium. Reprinted with permission from Ref. 18



Fig. 4. Polarization curves of  ${\rm Gd}_{100-x}Zr_x$  alloys in distilled water. Reprinted with permission from Ref. 26

between corrosion rate and current density by using a system of 2–4 electrodes, and controlling then measuring the voltage difference between a working and a reference electrode that have constant potential. The cell circuit is completed when the potentiostat measures the current flow between the working and counter electrodes. It can be seen from multiple experimental results that, when corrosion resistance is enhanced, the corrosion potential increases, and the corrosion current density decreases.<sup>24–26,31</sup> Polarization curves can aid with characterizing doping of materials along with coatings. For example, this was demonstrated in Ref. 26 where a Zr-doped Gd alloy promoted the anodic passivation of Gd and accelerated the formation of passive film on the surface of the alloy that raised the corrosion potential and corrosion resistance (Fig. 4), along with the magnetic entropy and the microhardness.

Finally, electrical impedance spectroscopy (EIS) allows users to determine charge transfer resistance, double-layer capacitance, and ohmic resistance. EIS is a method widely applied for coating corrosion property characterization, and for detecting complex interfacial reactions at the open circuit potentials of materials.<sup>40</sup> This characterization method supplies Nyquist and Bode plots indicating film, layer, polarization, solution resistance, and capacitance. In the case of a study that saw cobalt addition to LaFe<sub>11.7-x</sub>Co<sub>x</sub>Al<sub>1.3</sub> alloys, EIS was able to illustrate the improved corrosion resistance that resulted from the higher contents of Co.<sup>13</sup>

### CORROSION INHIBITION MECHANISMS

In a magnetocaloric device, corrosion of the magnetocaloric material upon exposure to the heat transfer fluid is pronounced, and can be repressed by many different strategies, namely, via alloying, passivation, by applying a coating layer, tuning the microstructure, and modifying the environment. Each of these approaches is described below.

#### Passivation

Passivation involves creating an outer layer of a shielding material due to a spontaneous chemical reaction between a base material and the surrounding environment. To this end, it is essential to note that corrosion of the magnetocaloric material upon exposure to the heat transfer fluid is an electrochemical (galvanic) process. For example, consider the case of the Gd regenerators exposed to water. Here, Gd presents a largely negative reduction potential which acts as an anode, while the cathodic reaction is the reduction of oxygen of water:

$$\mathrm{Gd} 
ightarrow \mathrm{Gd}^{3+} + 3\mathrm{e}^{-}$$
  $E^o = -2.5\mathrm{V}$ 

 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^o = +0.4V$ 

The resultant equation is

$$4\text{Gd} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 6\text{Gd}(\text{OH})_3 \quad E^o = +2.9 \text{ V}$$

The thin layer of Gd oxides/hydroxides formed over the sample surface due to the corrosion process reduces the phase fraction of the active magnetocaloric phase, decreasing the magnetization and the caloric response.<sup>23</sup> However, in the long run, the passive film also protects the metallic phase from contact with the environment, thus stabilizing the long-term degradation of the material. In Ref. 20 a core-shell model of oxide layer formation (SiO<sub>x</sub>-Gd<sub>2</sub>O<sub>3</sub>) on the surface of Gd<sub>6</sub>Co<sub>1.67</sub>Si<sub>3</sub> due to corrosion was proposed, based on results obtained from xray diffraction, EPMA, and depth profile by Auger spectroscopy analysis (see Fig. 5). Remarkably, owing to the paramagnetic character of the Gd<sub>2</sub>O<sub>3</sub> passivation layer, the bulk magnetocaloric effect was unaltered even with a micron-thick layer of oxide on the surface.<sup>20</sup> A similar mechanism for

inhibition of prolonged corrosion was also observed in the magnetocaloric borides,  $AlFe_2B_2$ .<sup>27</sup>

In La(Fe,Si)<sub>13</sub>-based alloys, surface passivation and protection is theoretically possible due to the formation of layers of Fe- and La-hydroxides/oxides.<sup>28</sup> Furthermore, Si is known to positively influence the stability of passive layers of Fe-base systems.<sup>28</sup> However, experimental studies indicate that, in actuality, La-Fe-Si alloys have a limited passivation ability as the phase present in the system demonstrates galvanic coupling with differphases > ent corrosion activities: La-rich  $La(Fe,Si)_{13}$ -based matrix > alpha-Fe(Si).<sup>2</sup> <sup>30</sup> This is particularly enhanced in stagnant distilled water, as local fluid acidification enhances corrosion processes, and it is thus understood that laminar fluid flow is beneficial for alloy surface passivation and corrosion protection.<sup>30</sup>

# Coating

Coating refers to a thin layer of an organic/ inorganic material, deposited or applied on a surface of any object, mainly to improve its critical properties and create a protective barrier against deterioration of the surface due to its reaction with its environment. Sputtering and electroless plating are two ways to deposit a protective coating on the



Fig. 5. Depth profile using Auger spectroscopy on: (a) starting, (b) 2 months aged in water, and (c) 3 month-aged material in water. (d) Proposed core-shell model of formation of oxide layer on surface of the material. Reprinted with permission from Ref. 20

surface of the working MCM.<sup>23,29–33</sup> Sputtering is a physical vapor deposition method in which microscopic particles of solid material are ejected from its surface, after being bombarded by energetic particles of plasma or gas, and form a thin film. Electroless plating, also known as chemical plating, is a class of industrial chemical processes that create metal coatings on various materials by autocatalytic chemical reduction of metal cations in a liquid bath.

In Ref. 29 Al coatings with different microstructures were prepared on the surface of Gd using the magnetron sputtering technique. Pure Gd shows a fair amount of surface cracks under water flow conditions, leading to pitting. Compared to a polygonal structure, an Al coating with lamellar structure exhibits a higher electrochemical protection performance and no occurrence of pitting corrosion.<sup>30</sup> Conversely, Au coatings on Gd particles fail to inhibit corrosion, as Au has a much higher potential than Gd and accelerated the oxidation process, as shown in Fig.  $6.^{23}$  When defects appear on the coating surface, both metals are in contact with water, and a potential difference arises between the two metals causing electrons to flow from Gd to Au. For Au coatings to be effective against corrosion, the sputtering process must be cyclically repeated, an impracticable solution for commercial outlook.

Researchers have also attempted to realize corrosion protection of  $La(Fe, Si)_{13}$ -based alloys via phosphate conversion and FeNi or Cu coatings.<sup>30– 32</sup> These coatings are porous and ultra-thin, and, thus, do not provide significant chemical stability. In Ref. 33 the powder-in-tube (PIT) strategy was applied to clad La(Fe, Co,Si)<sub>13</sub> powder by a thin seamless austenitic steel jacket, that could afford good corrosion, protection as well as compensation of local stress from magneto-volume change. How-

ever, due to the large volume of the steel shell of

42%, the magnetocaloric response was reduced by 50% for the as-fabricated PIT wires. Recently, exceptional corrosion protection was observed in La<sub>0.7</sub>Ce<sub>0.3</sub>Fe<sub>11.45</sub>Mn<sub>0.2</sub>Si<sub>1.35</sub> hydride thin plates (diameter of 12.6 mm and thickness of 0.5 mm) coated with continuous Ni–P coatings with columnar microstructure (thickness = 2–6  $\mu$ m).<sup>17</sup> It is proposed that this approach can also be extended to other Fe-based caloric materials.

# Alloying

Alloying (e.g., addition of dopants) and processing (e.g., heat treatments, addition of binders, etc.) typically serve to tune the magnetic phase transition temperature and associated magnetofunctional response of the MCM.<sup>3</sup> However, when carefully selected, dopants can also improve the chemical stability of the working material, particularly in moderately corrosive environments. For example, the standard electrode potential (E) of Gd at 25  $^{\circ}$ C is -2.279 V.<sup>34</sup> Doping with an element that demonstrates a more positive potential relative to Gd promotes the anodic passivation and accelerates the formation of passive film on the Gd surface, thus improving the overall chemical stability of the core working material. Examples of dopants that promote corrosion resistance include: Cr (E = -0.74V), Ti (E = -0.74 V), Co (E = -0.28 V), V (E = -0.28 V)0.26 V), and Zr (E = -1.55 V).<sup>34</sup>

Similarly, in La(Fe,Si)<sub>13</sub>-based alloys, the main corrosion mechanism is also microgalvanic corrosion, where the galvanic current density is controlled by the difference in electrochemical properties between the impurity phases and the desired 1:13 phase.<sup>21,27,31</sup> Conventional microstructures of as-cast alloys indicate  $\alpha$ -Fe dendrites with a few micrometers length and width surrounded by La-rich phases.<sup>35</sup> Formation of La(Fe,Si)<sub>13</sub> requires prolonged heat-treatment conditions involving high temperatures (over 1200 °C) for several days, and



Fig. 6. (a–c) Gd-based samples before and after the different aging processes; (d) mass loss of Gd-based samples upon exposure to water for prolonged periods. Reprinted with permission from Ref. 31

sometimes even weeks. Depending upon the stoichiometric amounts of La, Fe, and Si in the precursor alloy, or addition of dopants such as Co, B, Ni, Nb, and Mn, varying amounts of  $\alpha$ -Fe, La-rich impurities, and La(Fe,Si)<sub>13</sub> phases may be obtained.<sup>13,15,19,33</sup> During the corrosion process, the  $\alpha$ -Fe phase serves as the cathode, while the La-rich phase functions as the anode to be corroded.<sup>31</sup> When the La-rich phase becomes exhausted, corrosion gradually transfers to the 1:13 phase, consequently adversely influencing the magnetocaloric response.<sup>31</sup> Optimizing the phase fractions of the secondary phases via alloying thus provides a route to improve chemical stability.

Alloying also modifies the microstructural features in a magnetocaloric material, subsequently leading to different corrosion behavior. Typically, corrosion process in magnetocaloric alloys initiates at the grain boundaries where the dopants tend to accumulate. The smaller the grain size, the larger the surface area of the grain boundaries, and the greater the propensity of the grain boundaries to corrode. For example, in the Mn<sub>1.05</sub>Fe<sub>0.9</sub>P<sub>0.5</sub>Si<sub>0.5</sub>Cu<sub>x</sub> samples synthesized in Ref. 19 Cu mostly segregates at the grain boundaries of the primary phase, leading to improved mechanical properties, as it acts as a buffer when the volume of the main phase grains changes in the vicinity of the magnetostructural phase transition temperature. Further, it is critical to realize that the corrosion process is aggravated when a corrosive environment is combined with mechanical stresses. The addition of Cu to MnFePSi in Ref. 19 reduces volume change during thermal and magnetic field cycling, thus decreasing the formation of microcracks and minimizing both pitting and crevice corrosion (a localized form of corrosion usually associated with a stagnant solution on the micro-environmental level). Similarly, in Ref. 14 phenolic resins in the La(Fe, Si)<sub>13</sub>-based composite plates filled the voids and boundaries between the particles to varying degrees, increasing its mechanical integrity. When the plates were immersed in water, corroded spots appeared between the resin and the particle gap, and then at the cracks in the grains. Intriguingly, the corrosion rates of the plates containing 5 wt.% and 8 wt.% resin were decreased by 35.06% and 51.54%, respectively, compared with that of 3 wt.%, but the resin had little influence on the magnetocaloric response for stacked regenerator plates.<sup>32</sup>

# MODIFYING THE OPERATING ENVIRONMENT OF THE HEAT TRANSFER FLUID

Modifying the operating environment of the heat transfer fluid provides a versatile means for reducing corrosion of not only the working material but also of the accessories that form a component of the heat exchange system (e.g., pumps, piping, etc.). It is universally acknowledged that water is an almost perfect choice for AMR regenerators because of its superb heat transfer capabilities, low cost, and positive health and safety characteristics. Distilled water (pH  $\sim$  6) is seemingly the most suitable heat transfer fluid for use as the working refrigerant fluid, as it involves de-aerating the electrolyte and removing dissolved oxygen. As evident from Table S1 in the supplementary material, it is the most common option for magnetocaloric prototypes.

Corrosion inhibitors are often added to the heat exchange fluid to improve corrosion control (Fig. 7). $^{36}$  In the water treatment industry, typically, molybdate, orthophosphate, silicate, nitrate, phosphate, phosphonate, or azole is added to the medium to hinder corrosion of various types of metals, like copper, mild steel, stainless steel, aluminum, and iron.<sup>37</sup> Other aqueous heat-carrier media may utilize alcohols, alcohol amines, diols, and polyols, all water-miscible solvents, as anticorrosive agents.<sup>38</sup> In Ref. 37 the authors have examined the corrosion resistance of Gd and LaFeCoSi in demineralized water and a variety of diluted commercial grade heat transfer fluids (Zitrec S<sup>®</sup>, Noxal<sup>®</sup>, now known as ECO10<sup>®</sup>, Sentinel X100<sup>®</sup>, Aquaris K-20<sup>®</sup>, SH-1004<sup>®</sup>, and Aquaris R66<sup>®</sup>). Figure 7 demonstrates that the corrosion rate is lower in LaFeCoSi than inGd, particularly in Noxa-1<sup>®</sup> and Aquaris K-20<sup>®</sup>. The "negative" corrosion rate in Fig. 7 suggests that a chemical reaction between the material and the fluid forms a shielding outer layer, protecting the material and giving a mass gain.

The working refrigerant fluid pH adjustment has been described in multiple studies, with values ranging from 6 pH units to 10 pH units.<sup>26,28,32,38,46</sup> Acidic or basic additions and buffers may include, but are not limited to, NaOH, KOH, NaH<sub>2</sub>PO<sub>4</sub>/ Na<sub>2</sub>HPO<sub>4</sub>, NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub>.<sup>26,28</sup> The BASF patent on corrosion inhibitors for Fe<sub>2</sub>*P*-type magnetocaloric materials in water recommends that the most preferred pH range for room-temperature heat transfer medium is 9–10 units.<sup>39</sup> A conspicuous disadvantage of using water as a heat-transfer medium is its freezing point, which is rather high



Fig. 7. Corrosion rates of Gd and LaFeSi in different heat transfer fluids (according to ASTM 1384-05). The "negative" corrosion rates suggest a mass gain due to the formation of a protective layer on the surface. Data for plot derived from Ref. 37

at 0 °C, so freezing point-depressing salts, like NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, LiB<sub>2</sub>, etc., or anti-freezing solutions, like ethanol (which is safe, stable, and low cost when mixed with deionized water), other alcohols, glycols, mineral oils, and synthetic non-aqueous fluids, may be added to the water to ensure reliability in refrigeration applications. For example:  $Mn_{1.05}Fe_{0.9}P_{0.5}Si_{0.5}Cu_{x-}$ ,  $La_{0.7-x}Eu_xSr_{0.3}MnO_{3-}$ ,  $La_{0.7}Ce_{0.3}Fe_{11.45}Mn_{0.2}Si_{1.35-}$ , and  $Gd_5(Ge_xSi_{1-x})_5$ -based materials have been tested in ~ 3% NaCl solution.<sup>19,25,38,40</sup>

In Ref. 20 Gd<sub>6</sub>Co<sub>1.67</sub>Si<sub>3</sub> was subjected to controlled deionized water (pH = 7) flow to obtain a baseline for electrochemical oxidation corrosion. Following this, the ternary silicide was exposed to passive potassium hydroxide for up to 1 year by using KOH pellets dissolved in water. The results indicated that deposition of oxides was less thick on the KOH-aged sample than the water-aged sample after 3 months, as the KOH solution with a more basic pH effectively improved the chemical stability, and no crystalline Gd<sub>2</sub>O<sub>3</sub> peaks were even found on the 1-year-treated medium sample.<sup>20</sup> In another report,  $LaFe_{10.72}Co_{1.08}Si_{1.2}$  and  $LaFe_{11.00}Co_{0.8}Si$ magnetocaloric alloys were placed in acidified phosphate solutions (0.5 M NaH<sub>2</sub>PO<sub>4</sub> with 0.5 M H<sub>3</sub>PO<sub>4</sub>) at a pH of 3.<sup>18</sup> La(Fe<sub>x</sub>Co<sub>y</sub> $\overline{Si}_{1-x-y}$ )<sub>13</sub> alloys tend to passivate in these specific acidified environments, as well as in the presence of small concentrations of chloride ions, but the passive layer formed was not an effective protective barrier. Instead of shielding against surface corrosion, chloride ions in the passive layer caused a loss in electrochemical stability and exceeded the pitting potential, causing drastic developments of pitting corrosion.<sup>18</sup> These coatings can also encourage thermal barriers, which is undesirable in MCM regenerators, and can lead to cracks due to volume changes. Keeping in mind the galvanic coupling between the various phases and their ideal operating temperatures, the key to corrosion resistance is to change the chemical composition so that the passive layers formed on the surface should be thin, stable, and have better protective properties,

# OUTLOOK: CORROSION BEHAVIOR OF ADDITIVE MANUFACTURED (AM) MAGNETOCALORIC STRUCTURES

It is worth noting that the magnetocaloric community is leaning towards fabricating regenerators with metal AM schemes.<sup>41–47</sup> The basic principle of AM (also known as 3D printing) is the layer-bylayer addition of powders or liquids to produce 3D objects with intricate architectures that would not have been otherwise possible.<sup>48</sup> The existing AM technologies are divided into two main categories: powder-fed and powder-bed systems. The powderfed category includes direct laser deposition (DLD) and laser-engineered net shaping, while the powder-bed category involves selective laser melting (SLM), selective laser sintering, binder jetting, and electron beam melting technologies. In AM methods, the cooling rate is much higher than that for traditional casting methods, with an approximate solidification rate of 273-373 K/s (example: the cooling rate for SLM is usually  $> 10^5$  K/s, while that of DLD ranges from  $10^3$  to  $10^5$  K/s).<sup>49,50</sup> AM is thus characterized by large temperature gradients, high cooling rates, and cycling reheating.<sup>b</sup> Consequently, these solidification conditions can produce microstructures with refined grain structures, dislocation cells, and internal residual stresses, that can significantly affect the corrosion resistance and stress corrosion endurance.<sup>51</sup> These conditions also cause metallurgical defects, including unmelted powders, microcracks, entrapped gas pores, balling, and rough surfaces. The surface morphology and structural inhomogeneities promote an inherent sensitivity of AM materials to localized corrosion and galvanic coupling at different scales. In addition to the inherent defects generated in AM regenerators, MCMs also undergo large volumetric strains when they are cycled in the magnetic field.<sup>52</sup> These many cycles generate microcracks and dislocations in the regenerators, which can further increase the corrosion rate.

It is recommended that, prior to implementation in a device prototype, specific attention should be given to examining the corrosion behavior to AM regenerator parts. To date, only one study has focused on examining corrosion effects in 3D printing magnetocaloric structures. In Ref. 47 regenerators fabricated via laser melting were stable in a normal atmosphere, mainly because the as-printed part mostly consisted of a stable  $\alpha$ -Fe phase, and efforts were made to minimize structural strains during solidification by promoting heat dissipation through the use of support structures during the lasing process. However, after annealing and subsequent quenching of the regenerator blocks to obtain the desired magnetocaloric 1:13 phase, the block ultimately disintegrated in the air over a period of 24 h, and within 1 h in a heat exchange fluid comprising distilled water with 0.1 M Na<sub>2</sub>WO<sub>4</sub> (corrosion inhibitor). The poor chemical stability of the magnetocaloric regenerator was attributed to large temperature gradients during quenching that caused internal strains (enhanced by the presence of the pores) and secondary phase formation. The existing La-rich phases reacted with the heat exchange fluid to form hydrides. In turn, the corrosion caused pits to form, and these served as sites for cracks, which then quickly propagated due to the presence of internal strains.

Going forward, it is recommended that an accurate estimation of residual stresses and distortion in all AM processes is necessary to achieve dimensional accuracy, predict porosity, and prevent premature fatigue failure and corrosion. Since many process variables affect AM, experimental measurements of residual stresses and porosity are timeconsuming and expensive. Following guidelines obtained from Ref. 53 it is recommended that the magnetocaloric community should give specific attention to modeling the corrosion behavior and corrosion endurance of AM regenerator parts using an integrated multiphysics approach that takes into account all the contributing mechanisms for corrosion, including microstructure formation during solidification, materials deformation upon cycling, electrochemical reactions, and fluid dynamics.

#### CONCLUSION

This article presents a general discussion about corrosion of working magnetic materials in roomtemperature magnetic cooling devices. Most magnetic refrigerator prototypes utilize Gdor La(Fe,Si)<sub>13</sub>-based MCMs in the form of a porous regenerator. The relative motion between a heat transport fluid and the magnetocaloric material results in several forms of localized corrosion, such as pitting, crevices, and galvanic corrosion. While passivation due to a spontaneous chemical reaction between a base material and the surrounding environment is the initial indicator of degradation, surface material may be removed by the fluid shear stress, and the motion of the fluid can destroy a protective corrosion film (e.g., formed surface oxides). Predisposition to corrosion can be aggravated, especially when microcracks appear on the surface due to continuous volume change upon thermal and magnetic field cycling, which may further lead to structural failure of the material. Within this context, the metallurgical, processing, and environmental factors that influence corrosion in MCMs have been discussed in detail in this review, and a variety of corrosion inhibition mechanisms have discussed. compositional been namely and microstructural tuning of the working material via processing, coating of the finished regenerator structure, and modification of the environment of the surrounding heat exchange fluid. Finally, given that the magnetocaloric community is now moving towards AM of magnetic regenerators, the challenges associated with the chemical stability of 3Dprinted magnetic components is discussed.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

#### SUPPLEMENTARY INFORMATION

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