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Review

Review on the role of metals in the field of phase change materials: From their use for thermal energy storage to multifunctional applications

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ABSTRACT

The recent energy crisis has driven the research community attention toward the development of new strategies for managing available resources. Phase Change Materials (PCMs) offers the possibility of storing a large amount of thermal energy at almost constant temperature. PCMs include different classes of materials: organics, inorganics and eutectics. Among the inorganic PCMs, metallic materials—despite the high energy density and thermal conductivity—have attracted less attention, mainly due to challenges related to their management. Indeed, the issues related to their ease of reaction with the surrounding environment threaten the cyclic performance stability of its response.

This review presents the distinctive features of metallic PCMs as well as the strategies developed for their effective management. In addition to these aspects, the present review work explores the role of metals in combination with other classes of PCMs for the development of Composite PCMs (C-PCMs) with enhanced properties. In particular, the review focuses on the impact of the introduction of metallic phases in C-PCMs on the heat transfer performance of other PCMs. After this focus, the literature survey concludes with the discussion of metal potential in enabling the creation of multifunctional C-PCMs, which operate on principles beyond those of conventional PCMs.

1. Introduction

1.1. Thermal energy storage and phase change materials

The energy crises occurred in recent years, coupled with the depletion of carbon-based sources and the implementation of global decarbonization plans, have driven scientific research toward the development of new strategies for a more efficient management of available resources, capable of meeting global energy demands [1]. Although their full potential has yet to be realized, renewable technologies—which currently operate alongside conventional energy sources—are strongly affected by the unpredictability of environmental conditions. In this context, the concept of Thermal Energy Storage (TES) has gained significant attention. This approach involves storing thermal energy that would otherwise be wasted, allowing it to be used later when needed [2].

TES rely on three different mechanisms: thermochemical storage, sensible heat storage, and latent heat storage [3]. The first exploits the heat associated with reversible chemical reactions and is highly dependent on the reaction's conversion rate. Conversely, the potential of sensible and latent heat storage is directly proportional to the thermophysical properties of the materials, particularly specific heat and latent heat of transformation, respectively. The materials thus represent the 'core' of sensible and latent heat storage. Sensible heat storage enables the accumulation and release of thermal energy within a specific temperature range—wider operational ranges correspond to higher storage capacities. On the other hand, latent heat storage enables the storage of significant amounts of thermal energy at a constant temperature (or within a narrow temperature range), i.e., during the material's phase transition (or close to it). Heat is stored during the transformation upon heating and released during the reverse transformation. Latent heat storage materials can undergo various types of transformations [4,5] but the most exploited is the solid–liquid transition, as it offers the best compromise between storable/releasable energy and manageable volume change.

A prominent example of Latent Heat Thermal Energy Storage (LHTES) is represented by Phase Change Materials (PCMs) [6–8]. Generally, PCMs are defined as materials that exhibit abrupt changes in

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at least one physical property as they undergo a phase transition, occurring under specific conditions. The storage potential of PCMs based on a reversible solid-liquid transition occurring at a specific melting temperature, for example, can be quantified using the following energy balance, described by the sum of the terms in Eq. (1):

$$Q = \int_{T_i}^{T_m} mC_{p,s}dT + m\Delta H_m + \int_{T_m}^{T_f} mC_{p,l}dT \quad (1)$$

Here, T_i [K], T_m [K], and T_f [K] represent the initial, melting, and final temperatures over which the PCM is thermally cycled. The letter m denotes the mass of the PCM used in the TES/TEM process [8], while ΔH_m [J kg^{-1}] is the latent heat of fusion per unit mass associated with the solid–liquid transition. $C_{p,s}$ [J kg^{-1} K^{-1}] and $C_{p,l}$ [J kg^{-1} K^{-1}] are the specific heat capacities at constant pressure (specific heat) of the solid and liquid PCM, respectively. The Q [J] is generally referred as the total storable energy of the material. High ΔH_m, combined with T_i and T_f close to T_m, makes materials suitable for Latent Heat Thermal Energy Storage (LHTES) system. Fig. 1a visually describes heat storage during heating while Fig. 1b describes its release during cooling. While for fully reversable transformation the activation temperature is the same in heating and cooling, the actual presence of extensive supercooling in certain material classes leads solidification temperature (Ts) toward lower values with respect to the melting temperature T_m.

The definition of this latter, as stated in [9,10], is fundamental for the determination of the temperature service range of the PCM, allowing the full exploitation of its latent heat ΔH_m. This quantity, together with PCM sensible heat contributions in both solid and liquid state, is of relevant importance, determining the absorption/release potential of the device, as also stated by Eq. (1).

Although not often experimentally evaluated as these latter, Xu et al. [11] claims as another key point for energy storage evaluation the efficiency in storing energy. In this view, Mesalhy et al. [12] identifies thermal conductivity as the material property determining the rate of heat storage and extraction, and, consequently, the power related to the phase change and making it worth to be investigated [13].

PCM materials are often categorized into three main groups based on their nature: organics, inorganics, and eutectics [14–16].

Organic PCMs offer high latent heat per unit mass, accessible transition temperatures (generally below 100 °C), and high specific heat at constant pressure in low-density materials. They are also inexpensive and non-toxic, but some are highly flammable [17,18]. The relevant properties, reported in several literature works [2–7,17–22] are summarized in Table A1 (in appendix) and in Figs. 2 and 3. In general, Fig. 2a presents PCM transition temperatures, Fig. 2b refers to the latent heat of fusion, given as usual in terms of energy per unit mass (kJ/kg) and Fig. 2c refers to the 'energy density', calculated multiplying latent heat of fusion by material density (where available) and measured in MJ/m^3 (corresponding to kJ/dm^3 and to J/cm^3). The energy density is a suitable way to evaluate the storable energy in cases where static applications of PCM are considered. The comparison between the two plots shows that while most of organic materials have higher latent heat than metals, the energy density is typically in favour of metals. However, the performance of organic PCMs —especially in terms of charging/discharging rates—is limited by low thermal diffusivity, strictly related to the aforementioned thermal conductivity. This latter property defines the non-stationary thermal transport phenomena and can be derived as the ratio between thermal conductivity and the product of specific heat and density. However, although its higher relevance during transient with respect to the thermal conductivity, thermal diffusivity is not often included nor calculable from literature data (see Tables A1-A4 in appendix). Thermal conductivity indeed, simply allows the evaluation of the heat which flows through a unit area in a unit time, whereas thermal diffusivity is related to the temperature change in unit volume of material due to a specific heat flow.

On these bases, notwithstanding the major resonance of the thermal conductivity, in the literature it is worth mentioning the importance of properly estimating thermal diffusivity for a more comprehensive knowledge of the thermal response behaviour of the PCMs. In particular, thermal diffusivity gives an indication about the temperature fastness change within the material. For this reason, although not experimentally defined, the authors, where possible, provide thermal diffusivities in Tables A1-A4 on the bases of the other physical quantities experimentally estimated. The reported values in the Tables refer to the values on the graph shown in Fig. 3c. The following equation is adopted for the calculation (Eq. (2)):

$$\alpha = \frac{\lambda}{\rho C_p} \quad (2)$$

α [m^2 s^{-1}] represents the thermal diffusivity, λ [W $m^{-1}K^{-1}$] the thermal conductivity, ρ [kg m^{-3}] the density and C_p [J $kg^{-1}K^{-1}$] the specific heat. In the case of Phase Change Materials, the temperature-dependence on specific heat C_p often considered included the latent related to phase transition. By using this approach, a reduction of thermal diffusivity of PCMs during the transition can be quantified.

Nevertheless, as clearly shown by Salazar [23] for (homogeneous) condensed matter, including metals, ceramics, polymers, glasses and liquids, there is a substantial proportionality between thermal diffusivity and thermal conductivity since the product of specific heat and density lies in a quite narrow range (from 1 to 4 10^{-6} J m^{-3} K^{-1}). Due to this reason, thermal conductivity is often considered instead of thermal diffusivity to sort materials for thermal storage in terms of potential fastness of charging/discharging (even if for PCM the phase transition adds complexity to this simplified approach). Data of thermal conductivity, thermal diffusivity for organic and other PCM classes are illustrated in Fig. 3a and b, respectively. Fig. 3a and b clearly show the advantage of using metallic PCMs when superior thermal conductivity and diffusivity are needed. The linear correlation between thermal diffusivity and diffusivity in fully solid (and in some cases liquid) PCMs

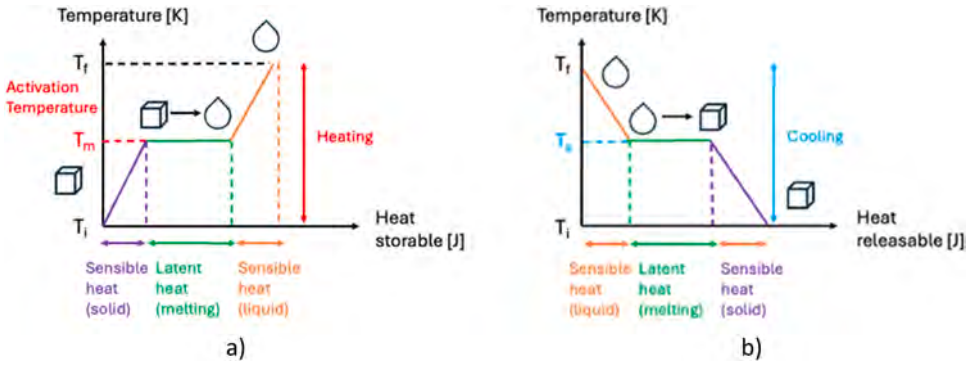

Fig. 1. Schematic description of the thermal energy storage (a) and thermal energy release (b) processes.

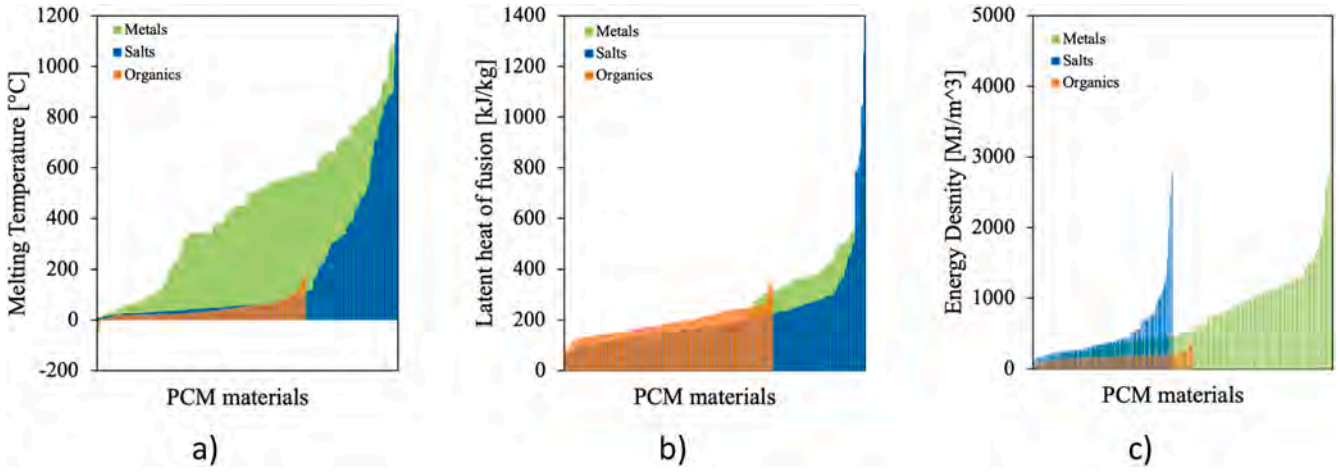

Fig. 2. Relevant PCM properties for organic, salt and metal material classes: melting temperature (a), latent heat of fusion per unit mass (b), energy density (c).

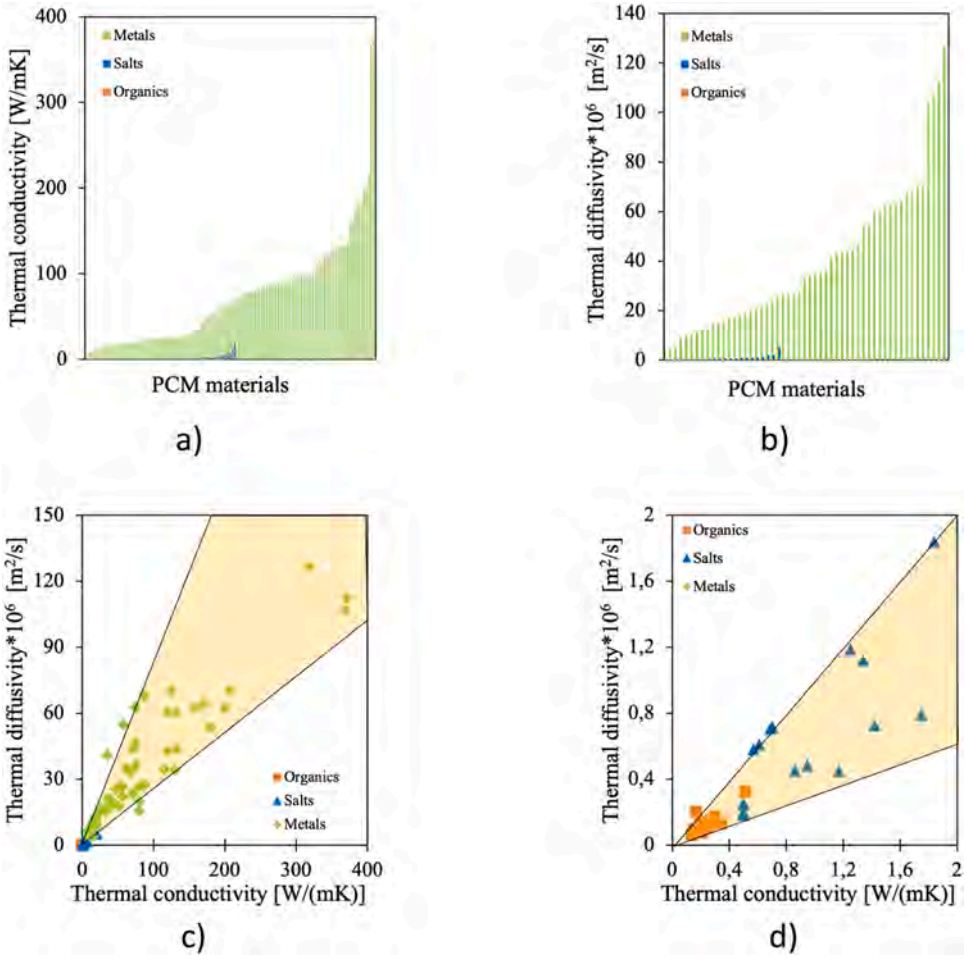

Fig. 3. Relevant thermal properties for organic, salt and metal material PCM classes: thermal conductivity (a), thermal diffusivity (b) and their correlation (c), also at low values (d).

is clear from Fig. 3c, the common trend for various material classes being within the range proposed by Salazar.

Inorganic PCMs are further classified into salts and metals.

Focusing at first the attention on salts, a summary of their relevant data as PCMS published the scientific literature [2,3,6–8,14,19,20,22,24–28] is presented in Table A2 (in appendix) and summarized in Figs. 2 and 3. Like organics, salts provide similar latent heat per unit mass but offer greater flexibility in transition temperatures, ranging from room temperature up to over 1000 °C, making them suitable for various applications. On the other hand, with respect to organic PCMs, salts typically have higher thermal conductivity (often an order of magnitude greater) and smaller volume changes during phase transition. However, their performance is sensitive to the efficiency of phase transition process and nucleation behavior. Issues such as phase segregation and

supercooling can negatively affect their storage capacity [28], and their corrosivity and toxicity must also be considered [29].

Metallic PCMs, while having a lower latent heat per unit mass than organics or salts, boast a significantly higher energy density, i.e., heat stored per unit volume, - nearly the double [28] - making them particularly attractive from a volumetric standpoint [5,24,30,31]. Also, for the metallic PCMs, a summary of properties relevant for their use as PCMs is presented in appendix (Table A3) as well as in Figs. 2 and 3, where data are taken from several scientific literature papers [3,20,24,28,32–35]. They can span a wide range of phase change temperatures—from low-melting-point metals like Ga (close to room temperature) to high-melting-point metals like Cu (above 1000 °C). Metals also possess extremely high thermal conductivities, often up to two-three orders of magnitude greater than those of organic and salt-based PCMs. Their drawbacks include relatively low specific heat and challenging liquid phase handling due to high reactivity and corrosiveness. Key properties of metallic PCMs are shown in Table A3.

Metallic PCMs generally cover a broader range of transition temperatures (Fig. 2a) with respect to organic and salts, especially from 200 °C onward. While organic PCMs rarely exceed 200 °C, and salts can reach up to 1200 °C, the availability of metallic PCMs in the 200–1200 °C range is significantly higher. Metals also provide advantages in terms of volumetric energy density and thermal conductivity (Figs. 2c and 3a).

The last main class considered in literature for PCMs, eutectics. They are mixtures of two or more components (organic or inorganic) resulting in specific transition temperatures (eutectic temperatures) rather than in transition temperature ranges. The transition temperatures are typically lower than those of the individual components. This enables the design of new materials with tailored thermal and operational properties [36,37]. Due to their potentially fully organic or fully inorganic nature, following alternative classifications, eutectic PCMs can also be considered as 'organic', 'salts' or 'metallic' PCMs. A summary of eutectic PCMs reported in literature [2,3,5,14,20,27] and of their relevant properties is given in Table A4.

The approach followed in the present paper is to consider as PCM classes those of 'organic', 'salts' and 'metallic' PCMs. Thus, eutectics are categorized based on their base components (organic, salt, or metal), as exhibited also in Figs. 2 and 3. To allow a direct comparison between these classes, histograms related to the main properties for PCMs are presented Figs. 2 and 3.

1.2. Widening the concept of thermal energy storage and phase change materials

While the interest on PCM is pushed forward by the abovementioned Thermal Energy Storage needs from the energy sector, their perspective applications are far wider. Due to their heat absorption capabilities, PCMs are also attractive for Temperature Management (TEM). Actually, PCMs are exploited to collect and manage heat when integrated with operational systems, to improve their overall efficiency or to avoid the achievement of excessively high/low temperatures, heating and cooling rates, or by 'simply' adjusting heating and cooling stages to specific needs.

Their phase transitions, associated with endothermic events, absorb heat from surrounding devices, buffering temperature increases. PCMs for TEM applications span various everyday uses, including building temperature regulation, where they help buffer daily temperature fluctuations and maintain comfortable indoor climates [38,39]. In this role, PCMs absorb heat during the day and release it at night, contributing to lower energy consumption and reduced environmental impact—an important contribution given that the building sector is responsible for approximately one-third of global greenhouse gas emissions [18]. Additional PCM enhancements, such as the inclusion of metallic nanowires [40], improve TES/TEM performance by leveraging superior thermal and electrical conductivities. PCMs are also being integrated into smart textiles for temperature regulation [41], with potential applications in electronic and medical wearables that adapt to environmental changes [42]. PCMs also support food preservation by extending shelf life [43,44] and are useful in healthcare and medical therapies where precise temperature control is crucial [45–47]. TEM is also critical for safety, particularly in systems prone to overheating—such as batteries [48,49] and electronic devices [50]. Integrating PCMs in these systems helps dissipate excess heat and prevent operational failure. The same principle applies to industrial machinery with high heat dissipation [46,51].

The use of PCMs is quite affected by their tendency to interact with the surrounding environment. One of the 'major concerns' is the potential oxidation of the metallic PCMs, in their solid or liquid stage, which reduces the amount of material undergoing phase transition and thus reduces the storable energy [52]. On the other hand, when high melting materials are used for PCM confinement and form stability (containers, capsules) their interactions with the container should be carefully considered. Actually, in the case of metallic PCMs several forms of liquid metals corrosion of the container and of PCM composition ad properties modifications induced by partial dissolution of the confinement material are reported in literature [53–57]. Due to these reasons, studies on PCMs are sometimes joined to those on their interactions with environment and various potential container materials.

The short analysis of pros and cons of various PCM classes clearly shows that single PCM materials are often not able to meet all the performance requirements for specific applications. Consequently, combining PCMs with other materials to form composite PCMs (C-PCMs) has emerged as a promising approach in recent years [58], with the goal of developing TES/TEM systems with enhanced properties. Widely explored strategies include improving thermal conductivity of organic or salt-based PCMs by incorporating highly conductive materials [59]. Integrating PCMs with containers [60,61], or structural frameworks to manage volume changes during phase transitions [62]. The same capsules [63] could be considered as composite PCMs, and the capsule material and geometrical features affect the behaviour of encapsulated PCM.

Research has investigated second-phase materials across all scales—from macroscopic foams to nanoparticles [64,65].

To fully exploit PCM potential, these C-PCMs materials should be considered during the early design phases of operating systems—especially those constrained by volume [66]. Their addition to such systems, possibly already functioning, however, can be cost-effective. For this reason, more recently, C-PCM are designed also in order to offer functionalities beyond the bare TES/TEM, able to make its role outstanding. Accordingly, PCMs are increasingly being integrated for multifunctional use, adding significant value to system design [67–71].

This present review work is related to the status and role of metallic materials —traditionally the least explored PCM class [30] —in both standalone and composite PCM applications (here, as the PCM or added phase). The aim is to highlight the unique properties imparted by metals to PCMs, encouraging their applications and stimulating new ideas for their use.

The review is structured in three parts: the first describes various PCM classes, focusing then on metallic PCMs (Chapter 2), on the role of metals as heat transfer enhancers of PCMs in TES/TEM applications (Chapter 3), and on PCM contribution to multifunctional C-PCM systems (Chapter 4).

2. Metals as PCMs

The present section aims to provide an overview of the use of metals as Phase Change Materials (PCMs). The first studies on this topic were published by Farkas and Birchenall in the late 1970s, who also proposed the use of eutectic alloys as a viable solution for Thermal Energy Storage (TES) and Thermal Energy Management (TEM) applications [72]. The unique properties of metallic PCMs stem from the nature of metallic bonding, where atoms share a sea of delocalized electrons that form

electronic clouds. These clouds are responsible for heat (and also electrical) transfer. This mechanism, in which electrons are nearly free to move, is significantly more efficient than the molecular motion that governs heat transfer in materials such as water, oil, and organic fluids [3], which dominate the transport processes in other classes of PCMs. These different dominant mechanisms result in significant differences in the thermal transport properties among various PCM classes, as thermal conductivity and diffusivity data listed in Tables A1–A3 and summarized in Fig. 3a. Thermal transport properties are critical in the field of PCMs, as they determine how quickly a system can respond to thermal changes. As previously said in Section 1, although in transient regimes diffusivity is of higher importance with respect to conductivity, the PCM fastness response is evaluated on the basis of this latter, due to the lack of data on the former. However, in the majority of the cases, high diffusivities recall high conductivities. Thanks to their inherently high thermal diffusivity and conductivity, metallic PCMs typically do not require the addition of secondary phases to enhance heat transfer—an extra processing step often necessary for other PCM types [24,73]. Low thermal diffusivity and conductivity, in fact, can lead to slow heating and cooling rates, thereby reducing the rates of melting and solidification, corresponding to heat absorption and release [25].

Fig. 4 provides an overview of the key properties of various metallic PCMs, presented both as pure metals and alloys, and categorized by their major elemental component. Specifically, Fig. 4a shows the latent heat of fusion, while Fig. 4b presents thermal conductivity, Fig. 4c energy density, i.e., latent heat of fusion per unit volume, and Fig. 4d specific heat at constant pressure. All the mentioned physical quantities are plotted against the melting temperature of the metallic PCMs.

Fig. 4a highlights the high energy storage potential of Al-based alloys (black squares) and Si-based alloys (red circles), though their use is generally limited to high-temperature applications. Fig. 4b, on the other hand, demonstrates the thermal conductivity advantage of Al-based alloys, which offer faster heat transfer compared to other PCM classes—except for a few pure metals such as Cu and Ag at elevated temperatures. Figs. 4c and 4d further state Al-based alloys performances, both in terms of energy density and specific heat at constant pressure.

2.1. Classification and examples of metallic PCMs

As previously stated, metallic PCMs offer the possibility to cover a wide range of transition temperatures that reflects on their potentiality in pursuing efficient TES/TEM performances in different applications. In the literature indeed, a classification in the metallic PCM field is performed, depending on their transition temperatures: low- (−40 °C-120 °C), medium- (120 °C-500 °C), high- (500–900 °C) and ultra-high (>900 °C) melting point [74,75].

2.1.1. Low-temperature metallic PCMs

The most representative example of the first class is gallium (Ga), due to its attractive transition occurring at 29,76 °C, slightly above room temperature; [30]. For this reason, its pure form and its related alloys

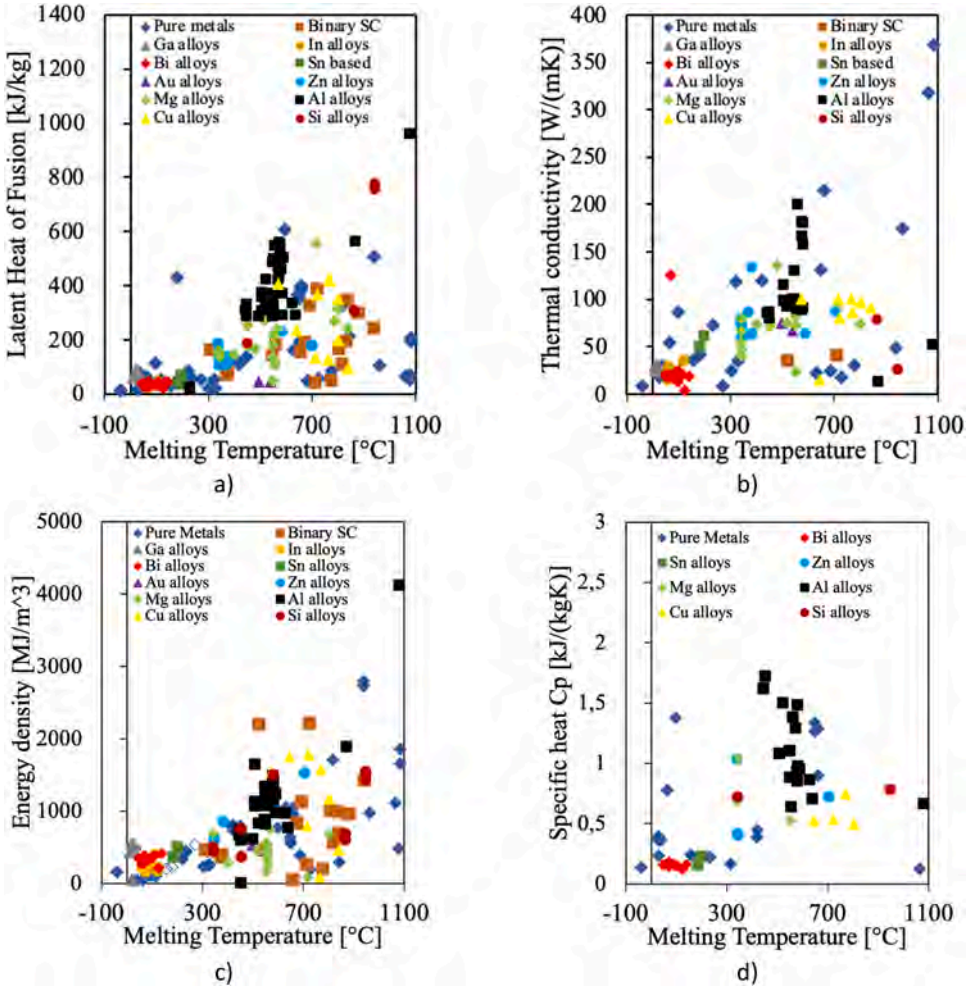

Fig. 4. Relevant PCM properties for pure metals and metallic alloys: latent heat of fusion per unit mass (a) and thermal conductivity (b) with respect to the melting temperature.

can substitute organic PCMs in specific application, especially in the electronic fields, due to the advantage of the higher thermal conductivity at similar transition temperatures [14,76]. For example, Ga offers better TEM performances with respect to dielectric gels if coupled with electronic chips at the same power level [20]. In addition to thermal management on electronic devices, Ga is widely employed as PCM in terms of solar energy, thermal comfort maintenance and building heat storage [7]. However, its liquid form is corrosive and may cause liquid metal corrosion issues [77,78]. For this reason, systems involving the use of this latter PCM should be properly designed. Ga is usually combined with other elements with low melting point in order to propose new PCMs with tailored transition temperatures. Wang and co-workers [66] for instance, proposed the use of fluidic GaInSn ternary system for heat dissipation purposes. Thermal characterization of the low-melting point metal established a latent heat of transformation of 111.5 J/g and thermal conductivity of 20.3 W m^{-1} K^{-1}.

Mingear et al. [79] reported the use of Ga-In nanoparticles as Phase Change Materials for thermal fluids, addressed toward the increment of the whole thermal diffusivity and the use of heat sinks for power electronics.

2.1.2. Medium-temperature metallic PCMs

Moving to medium melting point metallic PCMs, this includes Bi, In, Pb and Sn in their pure form. As far as the alloys with medium melting point, several contain Ga. They are widely employed in general as liquid metal coolants and solder alloys, due to their low transition temperatures and the possibility to form eutectics with even lower melting points. Sn-Pb-Bi and In-Sn-Bi ternary systems potential are explored also in terms of thermodynamic databases, in order to quantify their properties of relevance in the field of PCM purposes [80]. In this view, however, Pb is now banned from the market due to its environmental and health concerns [81].

Lincu et al. [82] employed high volume fractions of Bismuth (50–70 %) with silica matrix or silica shells, setting up composite materials, granting 22–32 J/g and showing good stability and reliability.

Zhu et al. [83] obtained via boehmite treatment and calcination Sn encapsulated by Al_2O_3, starting from SnO_2. The synthesized composites, whose dimensions range from 60 to 2000 nm, demonstrate to have high PCM content, i.e., 92.37 %, and a good shape stability even after 100 thermal charge/discharge cycles.

Another example of **medium-melting point metal** is Zn (melting temperature of 419.5 °C), either used as itself or in combination with other elements, especially Mg and Al, classified instead as high-melting temperature PCMs. Nieto-Maestre et al. [84] suggested the use of the novel eutectic alloy $Mg_{49}Zn_{51}$ for direct steam generation applications. The suitability of the alloy was established after ThermoCalc simulations addressed toward the identification of the metallic system able to meet the following requirements: melting temperature between 285 and 330 °C (under the working conditions of 79 and 145 bar), and latent heat of fusion per unit mass of 150 and 170 J/g. More recently, Blanco-Rodriguez et al. [85] characterized thermophysical properties of eutectic Mg-51 %Zn from room temperature up to its melting point, in view of concentrated solar power. The system demonstrates to be suitable for high pressure and high energy steam processes. In another scientific paper the authors also tested the efficiency of the proposed PCM also experimentally on lab scale [86].

The same research team also studied metallic Mg-Zn-based alloys as PCM in the Zn-rich corner of the phase diagram [87]. In particular, the addition of Al to Zn-based system was explored. $Zn_{84}Al_{8.7}Mg_{7.3}$, $Zn_{88.7}Al_{11.3}$ and $Zn_{92.2}Mg_{7.8}$ (atomic percentages) were characterized in the view of TES purposes. More specifically, they exhibit transition temperatures of 344 °C, 382 °C and 371 °C, associated with latent heat of 132 J/g, 118 J/g and 106 J/g, respectively. Thermal conductivity of the aforementioned metallic systems ranges from 66 to 139 W m^{-1} K^{-1} in solid state, and from 33 to 58 W m^{-1} K^{-1} in their liquid state. Their research by the same team also involved eutectic compositions; $Mg_{70}Zn_{24.9}Al_{5.1}$ and $Zn_{85.8}Al_{8.2}Mg_6$ [88] are characterized in terms of thermophysical properties and their thermal stability, tested and verified after 700 cycles across phase transition. Moreover, the chemical compatibility of $Mg_{70}Zn_{24.9}Al_{5.1}$ with commercial stainless steels, a potential container material, is checked as well.

2.1.3. High and ultra-high temperature metallic PCMs

As far as the **high-melting point metals** are concerned, Al, Mg are the main metals employed for TES/TEM applications, alloyed among themselves of with other elements, such as for example Si, Zn, Cu. However, the strong oxidation issues associated with the above listed metals severely hinder their applications. For instance, Al is reported to be encapsulated with capsules of different size ranges. Xu et al. [89] proposed mixed sintering method for the production of centimeter-sized form-stable Al_2O_3 backbones, hosting pure Al as PCM. 400 MPa and 5 min were found out to be the optimal conditions for their production. The maximum performances were granted employing 60 % of Al mass fraction, which offers 194.2 J/g and 2.15 W m^{-1} K^{-1} of storable latent heat and effective thermal conductivity of the whole composite, respectively [89]. Al-Si is another combination widely explored in the literature also with different compositions, as in the work of Gokon et al. [90]. The authors in this case, cyclically tested different eutectic/hypereutectic Al-Si alloys (Al-12wt %Si, Al-20wt %Si, Al-25wt %Si, Al-30wt %Si and Al-35wt %Si) in terms of compatibility with graphite-carbon containers and response stability under 20 charging/-discharging cycles. Sun et al. [91] proposed to study the thermal reliability and the corrosion behaviour of Al-34 %Mg-6 %Zn in contact with stainless steel (SS304L) and carbon steel (C20). Shimizu and Nomura [92] proposed the study, supported by thermodynamic calculations, of Al-5.9 %Si-1.6 %Fe alloy for the energy supply of Carnot batteries. The experimental results show the alloy undergoing phase change at approximately 620 °C, with a storage capacity of 375–394 J/g. Furthermore, the alloy grants high thermal conductivity, i.e., 160 W m^{-1} K^{-1}.

While, as seen before, the use of pure Al has been considered as PCM material, the use of Mg-based PCM always considered Mg alloyed with various elements. An example is provided by the results presented by El Karim et al. [93] who investigated $Mg_{84}Cu_{16}$ and $Mg_{59}Cu_{41}$ binary eutectic compositions. The authors characterized them from the microstructural point of view and evaluated their PCM performances. These latter exhibited melting point of 488 and 550 °C and latent heat of fusion of 232 and 144 J/g, respectively. The element combination also grants high thermal conductivity, i.e., 107 and 97 W m^{-1} K^{-1} for $Mg_{84}Cu_{16}$ and $Mg_{59}Cu_{41}$ in turn. The authors performed also corrosion tests between the selected systems and SS304 and SS316, employed as containers, in order to check the compatibility in the combinations of the materials.

Similar material combinations has been explored by Sun et al. [94] They studied the feasibility of employing Mg-24 %Cu, Mg-31 %Cu and Mg-45 %Cu as PCMs for TES purposes. The alloys were microstructurally characterized and then, a functional investigation was conducted. DSC tests reveal 485 °C, 486 °C and 485 °C as transition temperatures and 152 J/g, 215 J/g and 91 J/g of storage potential, respectively. Moreover, high thermal conductivity and low coefficient of thermal expansion suggested them to be ideal candidates for TES purposes.

Even more complex combinations were taken into account, i.e., Mg-25Al-15Zn-14Cu [95]. In this work, the alloy thermal stability under repeated cycles was investigated. The system demonstrated to be reliable even after 1000 cycles with the storage of 190.4 J/g at the transition temperature of 415.5 °C.

In the view of ultra high-temperature PCM on the other hand, Gokon et al. focused their effort on the characterization of a set of Cu-Si alloys and their suitability with graphite-carbon capsules. The performances of Cu-20wt %Si, Cu-25wt %Si and Cu-30wt %Si are tested under charging/discharging cycles with DSCs test [96].

Encapsulation approach was applied also to pure Cu as PCM, as

described by Zhang et al. [97]. In this work, millimetric-sized Cu spheres are covered with a thick Cr-Ni bilayer, resulting from a chromium periodic-barrel electroplating and nickel barrel-plating method. The spheres exhibit 71 J/g thermal energy storage at 1077 °C.

Also Zhao et al. [98] worked on the same topic, adopting in this case alumina capsules on pure Cu, with a buffer inner cavity related to a sacrificial layer of paraffin. The capsules, whose sizes range from 9.5 to 21 mm, exhibit in the temperature span 1000–1100 °C a storage potential of 222 kJ/kg, which coincides with 745 J/cm^3 of energy density. The resulting capsules also show high shape, thermal and chemical stability.

Violidakis et al. [99] developed a numerical model for the study of the thermal profiles and the related charge/discharge rate for Si as phase change material to be integrated in solar photovoltaics for the production either of heat or electricity for domestical applications.

Datas et al. [100] experimentally investigated Si as PCM. The analysis reveals high latent heat, 1800 J/g, at 1410 °C and combined with 25 W m^{-1} K^{-1} thermal conductivity. In this sense also Si-B are explored [101].

2.2. Issues related to the use of metallic PCMs

Metals for PCM purposes should be properly chosen in order to avoid phenomena that under repeated thermal cycles can modify their properties. This phenomenon may cause the modification of the chemical composition of the designed metallic system and, consequently, change its thermophysical properties, including storage potential.

2.2.1. Segregation

One of these critical issues is chemical segregation, i.e. the local change of chemical composition, which may affect the performances of the PCM itself [30,102]. In a multielement metallic PCM local change of chemical composition can occur as a result density differences [103].

In metallic PCMS chemical segregation can result from non-equilibrium solidification of alloys, specifically of those characterized by wide compositional differences between solid and liquid in the solidification temperature range [104].

For this reason, metals with congruent melting or eutectic melting behaviour have to be selected. Pure metals indeed can offer a reliable solution, as well as alloy with known eutectic compositions. Furthermore, on the bases of thermodynamic considerations, Birchenall and Riechman [105] suggested the use of eutectic alloys in the TES field as advantageous in terms of storable heat. Another solution involves the use of intermetallic compounds [106] as PCMs. Moreover, possibly, numerical tools such as CALPHAD-based calculations can offer the possibly of predicting and quantifying latent heat of fusion, allowing the design of new targeted alloys with precise composition [107]. In this sense, lots of metallic systems with complex compositions still remain unexplored. They could also help modelling non-equilibrium solidification and predicting chemical segregation.

2.2.2. Confinement

Another concern that needs to be taken into account dealing with metals is related to their corrosivity issues and reactivity with the surrounding environment.

For this reason, proper confinement strategies have to be taken into consideration when dealing with PCMs which rely on phase transition involving liquid or gaseous states.

In this view, a confinement structure able to efficiently store PCM and consequently, avoiding leakage when it undergoes phase transitions [108,109], has to be provided to the PCM as a support (Figs. 5a and 5b). The structure, generally solid in the temperature range of interest (in other words, having a melting temperature higher than the PCM), can offer also form stability, i.e., no modification of the PCM shape after the phase transition, as the PCM is in the molten state (Fig. 5c). Confinement structures are generally considered as 'container' when they are of various shapes and contain relatively large amount of PCMs, while they are referred as 'capsule', generally spherical, as they confine small amounts of PCMs [108,110]. A representative example of the container is provided by the scheme in Fig. 5, where the grey part is considered as the confinement structure itself, containing the PCM (orange domain in Figs. 5a and 5b). Both containers and capsules should have the following features [108]:

- Good mechanical strength
- Resistant to corrosion
- Good thermal stability according to the operating temperature
- Good thermal conductivity
- Good chemical/structural stability
- Should not react with PCM core
- Easy to handle

2.2.2.1. Container. Properly designing suitable containers for metallic PCMs can represent an added value for the stability of this latter. Indeed, they have to contain the desired PCM during charging/discharging cycles without causing any possible leakage, which may also lead to damages to the surrounding devices. Moreover, the reaction between PCM and its container may occur as well. This latter may change the composition of the PCM itself, consequently modifying the thermophysical properties and hence, its thermal response [111]. In this sense, some attempts have been performed in the literature addressed toward the compatibility between PCM and the related container material.

Rawson et al. for instance studied the corrosion behaviour and established the compatibility of either alumina, iron or graphite container with the eutectic Al-25 %Cu-6 %Si PCM alloy for the provision of heat in electric vehicles [112]. In particular, an example of the reaction occurring between the container and the PCM itself is provided in Fig. 6.

Fukahori et al. studied the compatibility of containing units for Al-Si alloys, exploring ceramic structural materials such as Al_2O_3, AlN, Si_3N_4, SiC and SiO_2 [113]. In particular, the first three listed ceramic materials demonstrate to be suitable for hosting Al-Si PCM due to the higher corrosion resistance with respect to the remaining ones.

Although focused on the mere compatibility between the metallic liquid PCM and the containment unit, to the authors' best knowledge, none of the proposed studies take into account the study of the performances decrement of the resulting system due to the development of the corrosion layer. In the simplest case, i.e., considering only one corrosion reaction which leads to a uniform corrosion layer, this latter indeed can cause the growth of the conduction thermal resistance within the whole system, proportional to its thickness (Eq. (3)) in the case of the heat

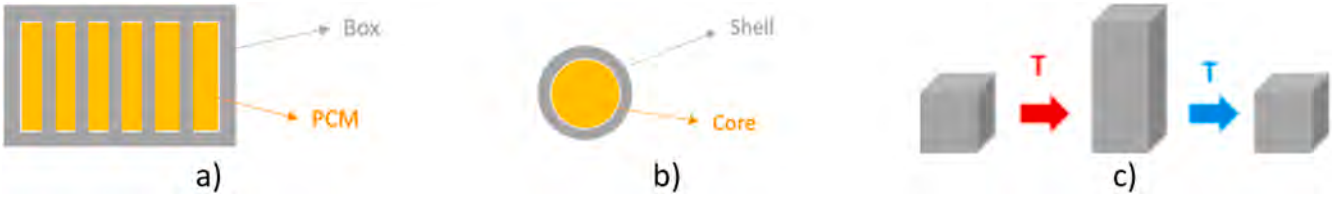

Fig. 5. Schematic representation of the metallic PCM confinement techniques: box container (a), shell encapsulation (b) and form-stable basics (c).

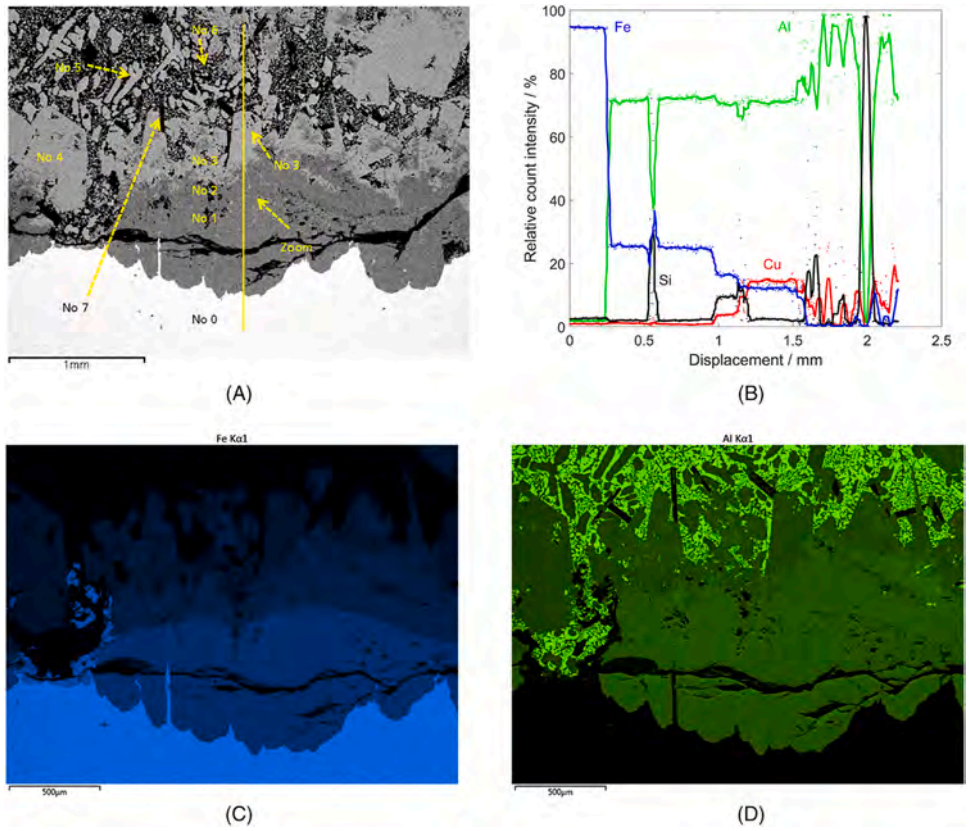

Fig. 6. Images of the reaction occurring between the iron container and the Al-25 %Cu-6 %Si PCM: original SEM image (a), materials composition along the line (b), Fe EDX map (c) and Al map (d). Reproduced from [112], under Creative Common CC BY license.

exchange for a plane geometry.

$$R_{cond} = \frac{L}{\lambda A} \tag{3}$$

In this case, L [m] is considered as the thickness of the corroded layer, λ [W m^{-1} K^{-1}] as the thermal conductivity of the corroded layer and A [m^2] as the surface exchange. Eq. (3) highlights the strict correlation between the thermal resistance and the kinetics in the growth of the corrosion layer, mainly dependent on the boundary condition and the material involved in the system. A qualitative analysis in any case can be derived, considering the simplest case in the reaction of corrosion [114,115].

In the first stages of the reaction, a linear growth of the corrosion layer can be observed due to the direct contact between the container and the liquid PCM. When the layer reaches a certain thickness, the corrosion reaction is mainly driven by the diffusion of the liquid corrosive metal through the corrosion layer. In this case, the regime turns out to be a parabolic drop rather than linear [116]. The development of the conductive thermal resistance is represented in Fig. 7.

Eq. (3) also highlights the importance of the geometrical factor. Indeed, if the development of the corrosion layer remains limited with respect to the dimension and the thickness of the highly thermally conductive domains (only some percentages), the corrosion layer thermal resistance can be considered negligible, although the limited k.

It is worth mentioning that possible deviations with respect to the presented trend may arise due to the occurrence of other phenomena, among which the spalling of the corrosion layer, or due to the features of the layer itself (porosities, cracks, discontinuities,…). These latter may lead to the direct exposure of the container to the liquid metal PCM, causing a step growth in the development of the corrosion layer. Moreover, within the context of corrosion phenomena the PCM metal reaction product can further directly abandon the interface moving inside PCM or dissolving into it.

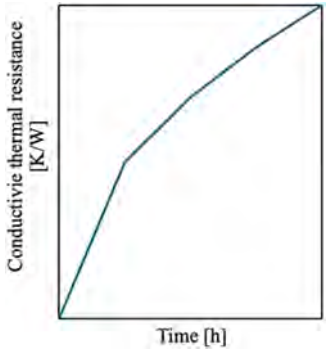

Fig. 7. Trend of the conductive thermal resistance growth with respect to the exposure time between the liquid metallic PCM and the metallic container.

At the same time, the potential dissolution of the corrosion layer into the liquid metal PCM can cause also the drop in the thermal conductivity of the PCM layer itself. In this sense, the literature offers analytical models for the effective thermal conductive estimation of the metallic solutions [117], as well as composite material [118], which works when the PCM is completely solidified. A more detailed explanation about these latter will follow in Section 3. Also, this phenomenon may affect the thermal resistance of the high thermally conductive material, lowering the thermal conductivity. Within this context, a case-by-case analyses is necessary to fully comprehend the impact of the corrosion phenomena on the heat transfer effectiveness.

2.2.2.2. Encapsulation. On the other hand, encapsulation technique involves the growth on the PCM surface of a shell material, resulting in

the obtainment of a composite PCM (C-PCM). The size of the capsules ranges from the macro to the nano [119–123]. Examples are provided in Fig. 8. Encapsulation techniques offer reduced reactivity with the surrounding environment and control on the volume changes associated to the phase change [27]. In addition, encapsulation techniques are useful for alleviating leakage and avoiding phase separation [124]. In this view, under repeated thermal cycles, encapsulation approach may also give to shape stability to PCM [125], a topic that will be treated in more detail in the next sections.

Moreover, the adoption of capsules causes a strong reduction in thermal resistance, granting an efficient heat transfer toward the PCM itself [126]. In particular, thermal resistance is lowered when the diameter of the capsules is reduced, and, consequently, the surface area of the C-PCM capsules increases [25]. The beneficial role of encapsulation in protecting the inner PCM from environment and favouring heat transfer toward PCM center can be established achieving the thermal stability of capsules. Indeed, the cyclic expansion and shrinkage of the PCM contained inside the shell, that behaves in a different magnitude, can cause the development of stresses, which may lead to cracks and the consequent failure in this latter [25]. Stresses are size-dependent and can be reduced by the presence of porosity indise capsules themselves which can accommodate the volume change of PCM during its transitions without posing any geometrical constrain. In this sense, proper mechanical testing should be designed for the characterization of their reliability, as suggested by Peng et al. for microcapsules [126]. The authors also suggested their application dispersing them in textiles, industrial slurries for heating and cooling of the devices, concrete mixtures, thermal insulation foams, thermal conversion devices and biomedicine [126]. For this reason, PCM shells should be mechanically tough and not reactive with the PCM itself [27]. This latter point was on the focus of Fukahori et al.'s work [127]. The research group proposes a macro cup-cap-based Al_2O_3 encapsulation for a hypereutectic Al-25wt %Si alloy, which has a transition temperature of 577 °C, 432 J/g of latent heat and 167 W m^{-1} K^{-1} of thermal conductivity. The macro capsule demonstrates to be effective in hosting the metallic PCM, also due to the void inside it, which can accommodate the thermal stresses related to the expansion/shrinkage of the metallic PCM itself.

The same combination of materials, in this case employing the eutectic Al-12wt %Si composition, was studied when covered by **macro** alumina shell. Powder formation route and in-situ powder alloying were employed for the shell achievement [128], . The designed capsules endure up to 1300 cycles, offering storage density performances of 496 J/g in the 500–700 °C range.

The research group also worked on other material combinations. They indeed combined pure Al, acting as PCM, and alumina, which works as the container, still in the order of millimeters, as presented by Zhao et al. [129]. The study demonstrates the reliability of the alumina capsules, whose diameter size ranges between 4 and 25 mm, over 3000 thermal cycles, without showing any leakage. This latter statement, coupled with the 348 kJ/kg latent heat, makes them appealing for the inner cavity applications in high-temperature TES system.

In this view, numerical simulations, validated by experimental activity, can offer an added value in terms of PCM behaviour evaluation during its charging/discharging cycles, as in the work of Gimenez-Gavarell and Fereres [130]. The authors employ the production of a borosilicate shell on either Pb or $NaNO_3$ as core PCMs, testing the resulting products both experimentally and numerically, simulating the convective heat transfer and analyzing the resulting freezing time.

Zhou et al. [131] successfully proposed the adoption of Alumina-based shell in the order of some mm, filled with Cu-Al atomized powders. The set-up demonstrates to sustain also 400 h of air exposure at 1100 °C.

Moving from the macro-encapsulated metallic PCMs to **the micro-encapsulated** ones, the combination of PCM and capsule material can remain the same, even if the processing steps can be very different with respect to what previously showed. A relevant example in the range of the micro size is provided by Nomura et al. They proposed the production of microencapsulated PCM, employing α-Al_2O_3 capsules hosting Al-Si alloy, via two-step technology. The first one involves the formation of the Alumina shell precursor AlOOH on the PCM via boehmite treatment, whereas the second one consists in the formation of the effective shell via oxidation treatment. The Al-25 %Si alloy (mass %) PCM exhibits 573 °C as the transition temperatures, whereas 247 J/g is its related latent heat [123].

The same materials were tested in terms of structural stability under repeated thermal cycles between room temperature and 1000 °C [132]. After 20 thermal cycles a decrement in the storable heat is quantified. The development of cracks at the core-shell interface due to the materials thermo-mechanical properties mismatch, can lead to the loss of sealing effect as shell cracking under stress of thermal origin.

Another technique involved in the production of encapsulated PCMs is the Chemical Vapor Deposition (CVD) method. The adoption of this latter technology allows Zhang et al. to successfully encapsulate Fe, which in this work plays the role of the active PCM for high temperature applications, with pyrolytic carbon and silicon carbide SiC [133]. Encapsulated PCM offers a double transition in both solid-solid state (48.85 J/g at 686 °C) and solid-liquid (128 J/g at 1136 °C) state. Moreover, the resulting core-shell products displays good cyclic behaviour and corrosion resistance.

Less investigated for metallic PCMs is the dimensional range of

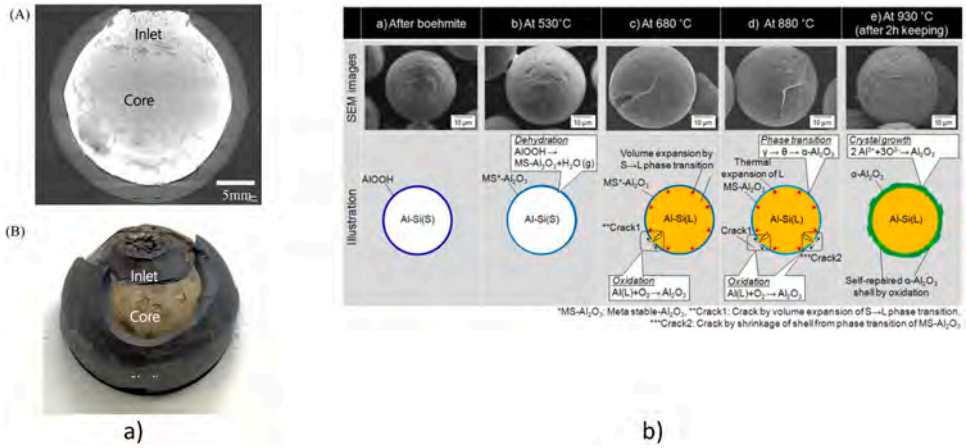

Fig. 8. Images of encapsulated C-PCMs in different size range: millimetric, with alumina encapsulating Cu-5.18 %Al PCM (reproduced from [131], under CC-BY-NC—ND-4.0 license) (a) and micrometric, considering alumina shell formation via bohemite treatment on Al-Si PCM (reproduced from [122], under Creative Commons Attribution 3.0 Unported Licence) (b).

nano-scale encapsulation. Nevertheless, Navarrete et al. [134] reported good results for nanocapsules of naturally grown Al oxides on Al80 %-Cu20 % alloy nanoparticles. These latter C-PCMs are intended to be dispersed within a mixture of solar salts with the aim of improving the storage potentiality.

2.2.2.3. Shape stabilization and form stability of metallic PCMs. Another valuable approach for the achievement of reliable and stable PCMs is thir shape stabilization, also referred as form-stability [36,108,135]. It consists in designing the material in order to autonomously recover its initial shape after the charge/discharge cycle. This approach offers to avoid the uncontrolled leakage of the PCM, when it is in its liquid form, which threatens PCM performances and applicability. Form stability has been mainly investigated and exploited for organic PCMs, where it relies on both chemical and physical principles. The former exploits covalent bonds [136], hydrogen bonds [137,138] or Van der Waals forces [125, 135]. Changing the chemistry indeed, and modifying functional groups, lead to the achievement of chemically stable composite PCMs. Physical form-stability on the other hand mainly relies on physical adsorption of the PCM [135], designing materials with supporting channels for the retainment of liquid PCM, as in the case of wood skeletons, impregnated with organic PCM [139,140], or metallic aerogels [141]. While physical form-stability could potentially be exploited also for metallic PCMs, to the authors' knowledge this has not yet been exploited and their geometrical stability during thermal cycles across the melting temperature is reached by means of containers or capsules.

An alternative proposed to produce form-stable PCMs proposed in literature is the use of composite PCMs based on the use of immiscible alloys, i.e., systems composed at least by two different elements which do not interact among themselves in both liquid and solid stage [142–144]. When an immiscible system is made up of phases with relatively temperature-independent composition, and the low-melting one has the minimal compositional changes during its solid/liquid transition, this latter can act as the PCM material in a C-PCM where the high-melting phase can act as a matrix. This strategy, employing immiscible metallic systems, avoids the reciprocal phase contamination due to the absence of interactions among the main elements of the system even when the system is thermally cycled. Moreover, if the PCM phase is properly dispersed inside the matrix, this latter may efficiently contain the volume changes associated to the phase transition of the PCM. Al-Sn and Fe-Cu are the first binary immiscible alloys suggested for the employment in the field of PCMs [145,146]. An example of the representative microstructure for immiscible systems, in particular Fe-Cu in this case, is provided in Fig. 9 [147]. In these cases, the low-melting Sn and Cu represent for each system the PCM phase. In addition to pure Al, the potential use of Al-alloys has been demonstrated [148,149] to be a valuable solution for the achievement of form-stability, tested with repeted heat cycles at the dilatometer.

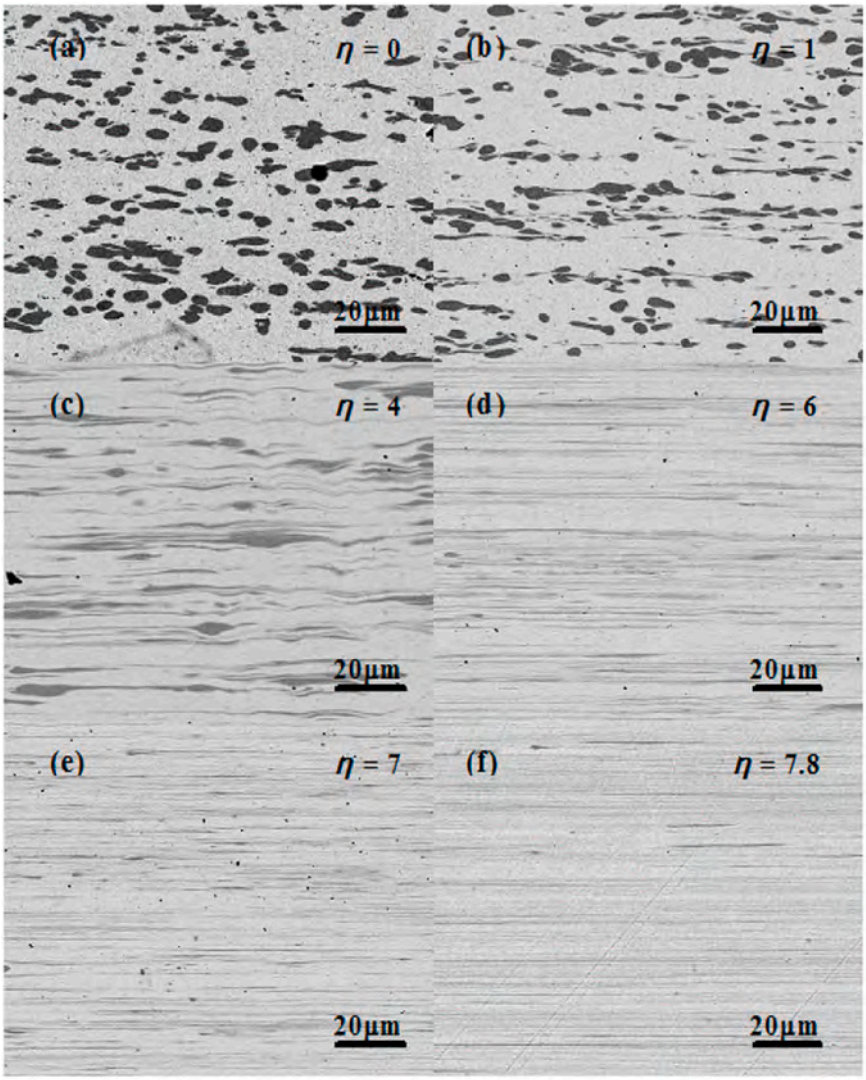

Fig. 9. SEM micrograph of Cu-14Fe alloy (Fe darker phase, Cu brighter one) at various strains, reproduced from [147], under CC-BY-NC—ND-4.0 license.

Another example of form-stable behaviour for fully-metallic immiscible systems, in this case, verified also within the first 100 thermal cycles, is given by Ag and Bi, as stated in the work of Liu et al. [150]. They produced via simple three step approach Bi nanoparticles dispersed in Ag matrix. Bi nanoparticles act as PCM. Their size control (in the paper ranging from 8.1 to 14.9 nm) offers the opportunity of tuning transition temperatures between 236–252 °C, lower than the melting temperature of bulk alloy, of about 270 °C. The employment of Ag matrix demonstrates to be useful also for effective thermal conductivity enhancement, which lays for the current systems between 100 and 150 W m^{-1} K^{-1}, depending on both the diameter and the volume fraction of the nanoparticles. PCM heat transfer enhancement with the introduction of metallic phases is treated in detail in the following chapter.

3. Metals as PCMs heat transfer enhancers

As stated before, although not being the only physical quantity governing heat transfer, thermal conductivity is usually considered as the reference parameter for the determination of PCM response fastness.

It is worth mentioning that, even though not considered in detail in this work, natural convection in liquid PCMs also plays a non-negligible role in its heating and solidification kinetics [151,152]. Moreover, it is worth mentioning that in C-PCMs, depending on the production technology, the natural convection may affect also the final morphology of the phases [153,154]. Within the C-PCM framework, natural convection can be either enhanced or weakened depending on the arrangement of the passive phase.

In general, Rayleigh's number is adopted for establishing whether the natural convection is triggered or not. Physically speaking, Rayleigh's number R_a is the ratio between the buoyancy forces, which favour the convective motion of the PCM, and the dissipative ones, which tend on the other hand to hinder this latter. R_a is defined as follows:

$$R_a = \frac{g\beta\Delta T L^3}{\upsilon\alpha} \tag{4}$$

g [m s^{-2}] represents the gravity acceleration, β [K^{-1}] the thermal expansion coefficient, ΔT [K] is the temperature difference between two different surfaces, L [m] is the characteristic length of the system, υ [m^2 s^{-1}] is the kinematic viscosity of the fluid and α [m^2 s^{-1}] the thermal diffusivity. When R_a reaches 1708, the natural convection is triggered. In the case of porous media, the characteristic length coincides with the diameter of the pores, whereas for channels, as in the case of lattice-based structure features, depending on the case, the gap distance or the hydraulic diameter can be considered. In general, the fluid motion within a porous medium can be described by the Darcy-Forchheimer model, which considers both laminar fluxes and eventual losses caused by the inertia of the fluid at medium/high velocities. In the latter case, on the other hand, the fluid, being constrained in a channel, can assume also Poiseuille velocity trend or even enter in a turbulence regime. In this view, the convection can be much more intense and channelized. Whether natural convection is triggered, heat transfer mechanism is enhanced within molten PCM, and heat power storage of composite materials can be increased as well. In the case of convection however, attention should be paid on the direction of heat flow which can locally affect the onset and the development of the convection motion [155].

In terms of porous structures, coherently with Eq. (4), natural convection can be triggered in composites for pores with higher diameters rather than small cavities [156]. While size effect and PPI (pore density) have been referred as a reference parameter for the natural convection, other literature work state the PPI as less relevant for other convection regimes (mixed, forced) [157].

Moreover, the authors also infer that also the regularity in the shape of the pores may have a negative impact on the natural convection. The use of staggered morphology, i.e., using semi-circles at the boundaries of the pores, rather than the adoption of a regular circular arrangement causes convection weakening within the composite, leading to slower melting rates. The impact of the pore dimensions on the natural convection, although characterized by particular topologies, is still highlighted elsewhere [158].

Porosities gradients introduced within the composite are studied as well [159]. In this case, the position of the different porosity features with respect to the heat source is crucial for positively impacting on the melting rate, exploiting lower porosities close to the heat source in order to favour heat conduction and larger pores far from the heat source in order to trigger convection.

Nevertheless, a discussion about molten PCM natural convection is out of the scope of the paper.

Depending on the peculiar applications, PCMs thermal conductivity should be properly tuned either for heat transfer applications (in this case, an enhancement is usually required) or thermal insulations (lower thermal conductivities are requested) [160]. Metals, as well as graphite-based materials, are principally added to low-thermally conductive PCMs for the first use, setting up composite materials as schematized in Fig. 10a. The size of the high-thermally conductive phases can determine different configurations of the C-PCM [161], ranging from the macroscopic to the nanoscopic scale [162,163] to avoid possible precipitations and segregations when the PCM is molten. Alternatively, C-PCM can be obtained combining the PCM to continuous, ordered or disordered networks within which PCM is percolated [109,164–167] [168], as schematically shown in Fig. 10b These latter, in particular, take advantage, beyond their intrinsic high thermal conductivity, from their porous nature. Porosity, indeed, can host the low thermally conductive PCM, granting high surface for heat exchange and low density [169–171]. Moreover, they serve also as supporting material for PCM, allowing to overcome potential leakage issues [172]. Lowering the scale instead, the high-thermally conductive phases are directly added to the PCM, which acts as a matrix, as underlined by Liu et al. [13]. In this latter case, the entity of transport properties enhancement mainly depends on the capability of the particles to set up continuous conductive path networks [160]. In addition, nanoparticles are attractive also for the promotion of alternative methods for the conversion of the energy, among which light absorption (see chapter 4). This feature will be explored more in detail in the following chapter.

The literature already offers a florid number of analytical models addressed toward the calculation of the effective thermal conductivity for composite materials. This approach is also known as effective medium approximation, where a single value of the thermal conductivity is calculated, considering the composite as a homogeneous medium. Effective medium approximation demonstrates to work well with systems having small heterogeneity fluctuations [173]. In general, the majority of them falls in the range determined by the theoretical upper and lower Wiener bounds, arrangement-independent models, which only relies on the volume fraction of the phases and the thermal conductivity of the single phases [174]. Within this interval, different models have been developed, first successfully considering the impact of non-interacting particles dispersed in a matrix. Maxwell, Bruggeman, Hashin and Shtrikman are some examples. On these bases, Lewis and Nielsen also modified the Halpin-Tsai equation in order to consider in the model the type of inclusion and their aspect-ratio. In some of them also the thermal resistance impact among the matrix and the inclusions, also known as Kapitza resistance, have been investigated. All these models demonstrate to give satisfactory agreement with experimental data when the loading of the particles is below the 30 % [175].

In this view, it is worth mentioning that the introduction of nano-sized fillers gives higher performances with respect to adding micro-fillers of the same nature in the same fraction. The use of nanoparticles indeed leads to larger density number of particle within a specific volume portion, and consequently shorter distances among

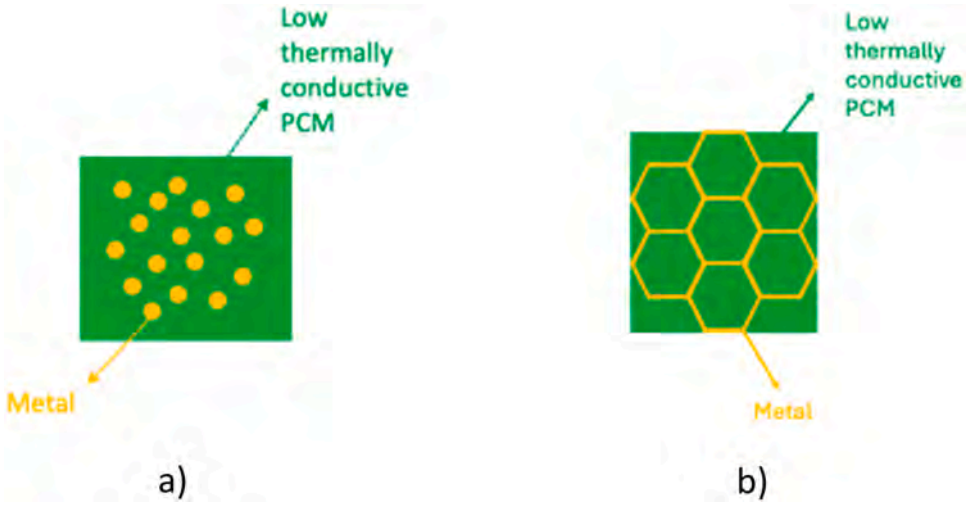

Fig. 10. Heat transfer enhancement techniques: introduction of high thermally conductive phases (a) and low thermally conductive PCM percolation in macroscopic metallic foam (b).

them. These statements, in addition to the larger surface area of nano-sized features, cause particle-particle correlation even at low volume fractions. Moreover, also the percolation threshold is achieved for limited nano-filler volume fractions [175].

The concept of percolation threshold lays in the so-called percolation theory [176]. The former refers to a critical volume fraction value above which continuous clusters are formed, resulting in the formation of interconnected networks, as in the case of porous macroscopic structures. Above the percolation threshold, thermal conductivity becomes independent from the both the geometry and the structure of the arrangement, simply dependent on the power law whose scaling exponent depends on the dimensionality of the considered network. Percolation theory demonstrates to work well also with homogeneous and highly disordered media.

In this sense, it is worth mentioning that the adoption of continuous porous matrix is claimed as the best method for enhancing thermal conductivity in PCMs, reaching values also above 220 per cent [169]. Some practical examples are provided in [177], where relationships derived for Cu foams and organic PCMs. As also stated by [175], the adoption of fillers leads to effective thermal conductivities closer to the lower theoretical bound, whereas the use of macroscopic porous structures leads to the achievement of approximately 75 % of the theoretical upper bound, even for extended volume fraction of the low-thermally conductive PCM [178], if combined with metallic skeletons.

As previously stated, metallic particles are used in combination with either molten salts or organic PCMs in order to increase their thermal conductivity [13]. However, careful attention should be payed to the selected material combination, since metals can suffer of corrosion in contact with molten salts. For this reason, metallic oxide particles can be also selected as thermal conductivity enhancers in the PCM matrix [179, 180]. Beside these latter, ceramic particles and carbon-derived materials [181], such as expanded graphite (EG), cover a promising role. Their network in the matrix determines the transport properties of the resulting composite, being arrangement-dependent properties [182]. It should be also mentioned that both oxides and carbon-based materials are introduced as well into metallic PCMs to further enhance their thermal conductivity.

For instance, Guo et al. [183] proposed liquid metal modified with polyethylene glycol and boron nitride, able to manage temperatures of Li-ion batteries via both efficient thermal conduction and photothermal effect. Liquid metal indeed, due to its soft and deformable nature is able to offer a conductive path among the fillers, ensuring 8.8 and 7.6 W m^{-1} K^{-1} out-of-plane and in-plane conductivity, respectively. Moreover, the use of liquid metal is useful for granting photothermal energy conversion, that will be discussed in Chapter 4. The multifunctional composite allows the Li-ion battery temperature to be lowered by 10 °C during charging and discharging rate with respect to the use of this latter without PCM.

As far as carbon-based materials are concerned, expanded graphite is applied to low-melting metallic PCMs, as in the case proposed by Huang et al. [184]. In the present work C-PCM was produced by mixing expanded graphite to Wood's alloy (Bi-25Pb-13Sn-12Cd) at 100 °C, i.e. above its melting at 73 °C. The time-dependence of PCM leakage within the C-PCMs produced with 70 to 90 mass % Wood's alloy can explained as the consequence of the pressure arising on the liquid metal by the low-expanding graphite.

3.1. *Metals as second phases in low-thermal conductivity PCM matrices*

The use of metallic phases with higher thermal conductivity as second phases in C-PCMs, dispersed in the low thermally conductive matrix, represents a common technique for the increment of heat transfer.

The size of the added particles is usually in the order of nanometers due to their intrinsic higher density with respect to the one of organic PCMs. The introduction of bigger particles indeed may cause their setting within the PCM matrix when is molten, severely limiting the homogeneity in their dispersion. Consequently, this statement leads to the inhibition of their starting beneficial effect throughout repeated cycles.

Moreover, it is worth mentioning that an experimental approach is usually preferred for derive the effective material properties of this kind of composite materials, also due to the lack of a precise control in the second phases dispersion. In this view, conventional experimental techniques for PCM characterization can be adopted for such composites, due to the negligible effect of the nanoparticles on the material volume, differently with what the authors will present in the following chapter.

The literature on the C-PCM experimental characterization suggests only Cu and Ag in the form of nanoparticles to be considered due to their intrinsically high thermal conductivity. The reduced size of the nanoparticles the possibility to not segregate when the PCM matrix undergoes solid-liquid transition.

3.1.1. *Copper nanoparticles*

Lin et al. [185] introduced PCMs plus Cu in the form of microcapsules inside wood via impregnation technique and deposited via chemical routes in the wood cells lumen. The resulting composite offers the solution to the PCM leakage problem and offers thermal conductivity

increments in both longitudinal and transversal directions (0.53 W m^{-1} K^{-1} and 0.37 W m^{-1} K^{-1}, which correspond to 362 and 211 % of increment with respect to the pure wood). This latter achievement mainly depends on the hierarchical structure of the wood, granting a continuous network for a more efficient path for the heat. From the thermal energy performances point of view, the resulting composite offers approximately 90 J/g thermal energy storage capacity with transition temperatures close to room ones.

Hu et al. [186] functionalized with reduced graphite oxide and Cu, melatonine foam impregnated with PEG with vacuum impregnation. The final product offers 148.3 J/g when PEG melts and 143.9 J/g in the crystallization stage. The resulting thermal conductivity of the whole composite reaches 0.4621 W m^{-1} K^{-1}, due to the high thermally conductive additions.

Zhao et al. [187] realized via solution combustion the synthesis of porous carbon matrix embedded with Cu nanoparticles, infiltrated with paraffin through vacuum impregnation. The resulting composite offers latent heat of 148.2 J/g and an increment of 145 % in the effective thermal conductivity.

Rezaie and Montazer [188] produced in one single step fatty acid, Cu nanoparticles and polyester fibres C-PCM. The process consisted in the direct synthesis of Cu nanoparticles and the direct impegnation of the fibres with fatty acids. In particular, two different eutectic mixtures myristic/lauric and myristic/stearic acid with two different transition temperature ranges and enthalpies (29.4–34.2 °C and 35.7–52.7 °C, and 40.3–53.9 J/g and 41.9–55 J/g). Cu nanoparticles cause an increment of 77.5 % in thermal conductivity.

3.1.2. Silver nanoparticles

Ma et al. [189] produced porous carbon supports from Cyperus Alternifolius, to be filled with PCM. In this case polyethylene glycol was chosen. The authors also dispersed in this matrix silver nanoparticles for increasing thermal conductivity in the whole body, reaching 0.676 W m^{-1} K^{-1}. Moreover, the resulting composite showed appealing melting enthalpy of 137.7 J/g and anti-leakage behaviour.

Wen et al. [190] prepared Lauric Acid PCM supported by expanded graphite, in turn modified with Ag nanoparticles. Thermal cycles, performed alongside with TGA tests demonstrate the reliability of the composite, which grants 129.5 J/g of storable latent heat. The additions of the second phases to the bare lauric acid offers thermal conductivity enhancement up to 2.85 W m^{-1} K^{-1}.

Zhang et al. [191] exploited Polyethilene glycol as PCM with the introduction of graphene nanosheets functionalized with Ag nanoparticles. The layered structure grants the shape-stability of the composite. This latter offers 166.1 J/g of latent heat storage. The addition of the Ag nanoparticles increases the thermal conductivity up to almost 95 %.

As in the case of stochastic foams, also numerical analyses are performed in order to evaluate the performances of this type of composites.

3.2. C-PCMs with metallic networks

Metallic structures have been used several times to enhance the heat transfer potential of PCMs, specifically of the organic ones. Beside the aforementioned nanoparticles, fibre configuration is considered. An example is provided by Ren et al. [192]. They numerically studied the morphology and the orientation of stainless-steel fibres dispersed inside paraffin matrix. The authors stated that curved fibres are more effective in enhancing thermal transport in the paraffin at 0.95 porosity with respect to straight ones, whereas these latter are better with lower level of porosity, i.e., 0.9. Moreover, they establish the effectiveness of thermal conductivity as the main heat transfer mechanism with respect to the natural convection, which contributes at least to 71.8 % to the whole storage amount.

Other examples are ‘conventional‘ finned structures, one of the most representative solution due to their exchange surface increment, coupled with their ease of fabrication. Saha et al. [193], in this view, investigated for instance the optimum Al fin arrangement used as thermal enehancer for organic PCMs.

Additionally, metallic phase continuous network, with conductivity several times higher than the low-thermal conductivity PCM they are combined with, can be considered. The metallic networks are often open-pore foams or lattices. These latter are characterized by high porosity volumes, and are thus suitable to produce C-PCM with high storable heat (given by the high volume of PCM filling porosity) and high thermal conductivity offered by the metallic phases with respect to that of the classical organic PCM (see Chapter 2). With respect to the addition of highly conductive nanoparticles approach, metallic networks can offer higher thermal conductivity enhancement due to the interconnected network of highly metallic phases and the higher aspect ratio of the structure [176]. In general, porous media are already studied and adopted for applications involving exchange processes such as heat exchangers, catalytic converters, fuel cells or batteries [194–196]. They are also appreciated for their energy absorption properties [197]. However, due to the size of the metallic networks, the effective C-PCM material properties related to their use in TES/TEM system (specific heat capacity, thermal conductivity) cannot be characterized by conventional techniques for homogeneous PCMs, as discussed by Li et al. [198]. Rather specific testing rigs are needed (see as example the work by Yazdani et al. [199]). The possibility to consider the composites based on metallic networks (often macroscopic scale) as composite mades by two phases with bulk material properties, with no thermal resistence at their interface, allowed several numerical modelling on the termal response of the structure, which were in several cases experimentally validated (see for example [50]).

The effective thermal properties of porous media are often numerically evaluated. While this is quite easy for density and specific heat, the calculation of effective thermal conductivity, as previously discussed, requires information not only on each phase amount and properties, but also on the phase arrangement. This is often done not only for lattices, which are based on a 3D repetition of a unit cell of known grometry (at least nominally), but also for foams, whose geometry is often approximated to that of unit cells with the same phase content and properties, but with an idealized arrangement. In these cases the closeness between theoretical to experimental effective thermal conductivity should be validated before using effective thermal conductivity for calculation of the performances of C-PCMs based on porous skeletons (see for example [50,200].

3.2.1. Porous media – foams

A porous media is a kind of material that contains a solid matrix with interconnected or disconnected pores [13]. Porous media can be either stochastic disordered foams or lattices, characterized by regular geometrical features. These porous structures can be saturated by PCMs to realize heat storage thus forming a C-PCM, in which the porous structure remains as a ‘solid’ skeleton, as the PCM is in the molten state.

When a high conductivity, high heat transfer surface porous structure is filled by low-thermal conductivity PCM, the resulting C-PCM has a greater thermal conductivity with respect to that of homogeneous PCM. Further, if the pores are at the micro or nano scale, the porous media may also offer form-stability for the PCM, which can maintain its original shape without any leakage, on the bases of the physical adsorption described in the previous chapter. Metals are often adopted as porous matrices for these C-PCMs even if carbon-based materials are explored as well. Nada and Alshaer [201] for instance, presented the possibility of simultaneously enhance thermal conductivity percolating paraffins in carbon foams and adding multi-walled carbon nanotubes directly into the paraffin itself. Analytical models for the composite effective thermal conductivity as a function of the temperature and the percentage of multi-walled carbon nanotubes are derived from experimental tests. In particular, the authors state that the overall conductivity of the system can be improved adding increasing amount of nanotubes

directly into the paraffin. In similar C-PCMs, expanded graphite or ceramic matrices are adopted for introducing shape-stabilization multifunctionality [167].

As far as the disordered structures are concerned, stochastic foams are the most adopted tool for the achievement of heat transfer enhancement within low thermally conductive PCMs. Metallic foams with high thermal conductivity, i.e., Cu and Al among the others, are the most studied ones both from the numerical and experimental point of view, due to their high thermal conductivity among widely commercially available pure metals, 400 and 235 W m^{-1} K^{-1}. The lower density of Al, about 2.7 kg/dm^3, with respect to the 8.93 of Cu, advantages the former where conductivity enhancement is combined to lightweight requests. Besides, notwithstanding the lower thermal conductivity (about 90 W m^{-1} K^{-1}), and bulk density of commercially pure Ni close to that of Cu (8.9kg/dm^3), Ni foams have been sometimes proposed as porous media due to their strength and structural/chemical stability, in addition to their commercial availability. Significant examples of C-PCM produced by filling Cu, Al or Ni foams are illustrated and commented below.

3.2.1.1. Cu foams. Focusing the attention on copper foams, they have been proposed in combination to paraffins, among others, by Zhang et al. [202], who investigated the role played by pore size on heat transfer. The authors also investigated the role of this latter, as well as metallic volume fraction, on the on the possible onset of natural convection within the molten PCMs. As previously presented natural convection can occur in homogeneous PCMs under specific conditions, with the consequent modification of heat transport with respect to the case of thermal conduction only. In a similar C-PCM based on porous Cu skeleton filled by organic PCM, Lafdi et al. [155] investigated the conditions leading to natural convection and effect of heat flow rirection.

Several studies on the use of Cu-based foams to produce C-PCM when filled by organic PCMs are addressed toward PCM heat transfer enhancement in systems containing Li-ion batteries. The aim is to adequately manage the heat generated by power electronics, which can reduce performances of the battery itself, threatening its reliability and shortening its lifetime. Zhang et al. numerically studied the impact of the organic PCMs, embedded in a porous Cu-based matrix, [203]. In this sense heat absorption offered by the PCM may buffer the temperature of the battery, which takes gain in terms of life span.

In this sense, the introduction of Cu foams has a beneficial impact in reducing PCM transients.

Sutradhar et al. [190] developed a one-dimensional analytical model for predicting melting and solidification behaviour of paraffin under different thermal loads. The presence of voids, changing its volume, and Cu metal foam, directly coupled with paraffin, are implemented in the model as well. The introduction of the Cu foam reduces both melting and solidification time of the paraffin, by 28.15 % and 272 %, respectively. Consequently, melting and solidification rate increases of 31.25 % and 107.5 %. The developed model demonstrates to be in good agreement with experimental data.

3.2.1.2. Al and Ni foams. The peculiar combination of high thermal conductivity and low density makes Al foams appealing for TES/TEM purposes. Foams in generala indeed, are characterized by high surface-to-volume ratio due to the offered large surface area of heat exchange [14,20]. Moreover, their employment is already suggested for multifunctional purposes [71].

For example, Wan et al. [204] suggested the use of Al-based foams as useful tools for multifunctional purposes, among which heat dissipation, due to their peculiar properties. Indeed, Al foams can rely on their very low density, high transport properties (both electrical and thermal) and satisfying mechanical behaviour, which can be tuned working on the porosity amount of the foams, as well as its arrangement in the composite. A temperature span of 10 °C allows the storage of 350 mV and 1.3 mW.

On the other hand, as far as the thermal peformances are concerned, a summary of experimentally derived effective thermal conductivity of C-PCMs based on Al foams filled with paraffines has been given in the introduction of the paper by Martinelli et al. [205], which clearly highlights, among others, the main effect of porosity volume fraction.

Abid et al. [206], adopted the Ni foams, known to have good compatibility with graphene, to obtain a 0.5 % mass graphene-coated Ni foam via Chemical Vapour Deposition. A paraffin was then poured in this skeleton, consisting of 90 % volume porosity and 12.7 PPI (pores per inch). The resulting C-PCM, designed to be coupled with Li-ion batteries for the electric vehicles, had a thermal conductivity 23 times higher than that of the homogeneous organic PCM. The effectiveness of the composite is achieved with a reduction of the 17 % in the maximum temperature rise of the battery.

Huang et al. [207] evaluated the influence of impregnating either Ni or Cu foams with Myristyl Acid (a fatty acid) PCM via vacuum impregnation. In particular, the pore size variation, in relatively fine porous foams (40, 70 and 90 PPI), is taken into account for evaluating and processing C-PCM thermal performances. Ni foams are favoured in terms of MA impregnation. Due to the fine metallic structures, some conventional characterization techniques has been adopted by the authors to evaluate the C-PCM behaviour, such as DSC, TGA (which demonstrated the stability and reliability of the composite) in addition to thermal conductivity meter. In general, the latter tests experimentally demonstrate that both foams increase their in thermal conductivity as the pore size is reduced, i.e. as surface to volume ratio increases. At 40 PPI, the use of Ni and Cu foam results in PCM thermal conductivity increment of 1.8 and 7.51 times with respect to the one of the pure PCM.

A comparison between the performances offered by C-PCMs alternatively containing Ni- or Cu foams, as porous media characterized by far different thermal conductivity, has been investigated also numerically. Zhang et al. [208] numerically investigated (modelling foams as lattices) foams the advantages offered by the percolation of paraffin, employed for TEM aims in the cooling of electronics, in either Ni or Cu foams. The first one offer a resulting thermal conductivity higher 3.5 times than the one of pure paraffin, whereas Cu exhibits a further increment in the thermal conductivity, 12.485 times than the one of Ni.

3.2.1.3. Additional improvements in thermal efficiency of porous C-PCMs. Literature suggests also the adoption of mixed approaches, combining metallic skeleton to high thermally conductive second phases or coatings addressed toward thermal conductivity improvement. An example of foam surface functionalization, in view of improvement of the thermal conductivity of the porous structure, is proposed by Hang et al. [209]. The authors realized the percolation of organic PCMs inside Cu foam, whose surface was functionalized with either graphene oxide or reduced graphene oxide. In this case paraffin and PEG1000 were chosen as PCMs, both granting 111.5 J/g latent heat. Also in this case, the use of copper and carbon-derived materials as second phases results in a thermal conductivity increment of 300 %.

As far as the combined use of second phase enhancer and porous structure is concerned, it is worth mentioning the example proposed by Chen et al. [210], in which the complex design of the C-PCM also meet the target of a reduced leakage of the molten PCM phase, moving toward the C-PCM form stability. The authors created form-stable hybrid composite impregnating paraffins into triblock co-polymer network SEBS (Styrene-b-(Ethylene-co-Butylene)-b-Styrene) and depositing the resulting mixture onto High Density Poly-Ethylene substrate. Melting temperature and related storage potential of the resulting composite were determined to be 50.56 °C and 151.6 J/g. With this solution, the hybrid C-PCM (SEBS/paraffin/HDPE) exhibited a low and constant leakage rate of about 0.016 mass %/h at 80 °C, leading after 150 h to only 2.36 mass % leakage. The C-PCM performances are further enhanced by the percolation of the hybrid composite in Cu foam with

porosity 0.98 and pore density 20 PPI which increases approximately 8 times the thermal conductivity with respect to that of the SEBS/paraffin/HDPE C-PCM (from 0.27 W to 2.142 W m^{-1} K^{-1}).

The use of metallic foams to produce C-PCM is not only restricted to the use of organic PCM. An interesting application of metallic skeletons filled by metallic material in reported by Tianrui et al. [211]. In addition to monitoring the benefits offered by percolating n-tricosane into Cu-foam, 47 alloy, a combination of Bi, Cd, Sn, Pb and In (in the mass percentages of 44.7 %, 6.3 %, 8.3 %, 22.6 % and 19.1 %, respectively) is used in combination with the Cu foam. The impact of the foam porosity is numerically evaluated between the two different combinations. The results established that only a 5 % of Cu-foam addition is sufficient for the achievement of a beneficial effect on both thermal management and homogenization in the temperature within the PCM domain.

Open porous structures can be produced by less conventional techniques and with unconventional pore geometries. For example, Chang et al. [212] produced a 3D C-PCM structure by assembling bidimensional graphite-coated copper grid, and filled the structure by organic PCM.

Powder metallurgy was also explored as a viable approach for the construction organic PCM-filled heat exchangers and metallic hollow spheres PCM containers, as depicted by Andersen et al. [213]. The authors suggested powder sintering method in order to build up porous metallic fibres and hollow metallic spheres to be filled with organic, low-thermally conductive PCMs. The results demonstrated the technology to be capable of producing simple, fast and compact PCM accumulators with charging/discharging power density in the order of one kilowatt per liter. The successful results of the work come from the strong knowledge on the production technology, adapted from pharmaceutical industry, packing industry and metal injection moulding [214].

3.2.2. *Porous media – lattices*

Most investigated in recent years are in any case lattices, whose complex geometrical features can be produced by additive manufacturing techniques, with optimized lattice unit cell type (see some examples provided in Fig. 11), volume fraction and size. Aluminium alloy is often employed as the main material due to its relatively ease of production with these techniques. Several features of these C-PCMs have been investigated experimentally or numetically. Moon et al. [215] highlighted the necessity of embedding the low-thermally conductive paraffins in high-melting matrices in order to enhance the heat transfer and consequently, the power density. In order to demonstate this statement, the authors built ad-hoc AlSi10Mg metallic structures via Additive Manufacturing (AM) techniques in order to show the potentiality of the materials combination in view of heat exchangers purposes.

Similarly, various geometrical features, made of the same alloy and filled with two organic PCMs, were produced and investigated by Yazdani et al. [199]. The authors demonstrated the faster charging time of the experimental TES unit in the presence of lattice structure with respect to one made by some fins.

AM techniques led also to the production of optimized skeleton structures (Fig. 11a), generated by Topology Optimization (TO), which represents an added value for heat transfer enhancement within PCMs [216]. The authors, i.e., Iradukunda et al. [217], were indeed, able to build, hybrid heat sinks which combine conductive and convective cooling able to lower peak temperatures in a more efficient way with respect to conventional topologies.

A good examples of the C-PCM which can be produced by combining various lattices to a filled organic PCM is offered by Piacquadio et al. [218]. The authors designed and built by AM techniques structures based on connecting points of cubic cells (rod f2ccz, bcc, bccz and f2bcc, represented in Fig. 11b) structures with the same cell width (5 mm) and porosity ranging from 70.7 to 82.4, made of AlSi10Ng alloy. They were then filed with n-Octadecane paraffin. Their main goal is the experimental study of the transient heat transfer within the proposed composites. The results suggested f2ccz to be most suitable candidate for the achievement of the most efficient performances among the proposed configurations.

Other lattice types have been recently been investigated due to their processability enabled by via AM. Triply Periodic Minimal Surface (TPMS) structures demonstrate great potential for heat transfer enhancement. Indeed, they offer high surface-to-volume ratios, which make them appealing for mass/energy transport applications [219]. Zhang et al. [220] experimentally demonstrated the advantages in adopting TPMS-based composites in order to lower paraffin melting time of 10 % with respect to the situation without metallic skeleton. The choice of the lattice architecture, as well as the relative density allow to tune composite thermal conductivity. Qureshi et al. [221–224] numerically investigated the thermal behaviour of Al-Si10Mg Triply Periodic Minimal Surface (TPMS) based PCMs, highlighting the advantages offered by these latter with respect to conventional foams in pure heat conduction regime under different configurations.

Zhou et al. [225] choose the AlSi10Mg alloy to produce a PCM-based lightweight structure for thermal control in space applications based on

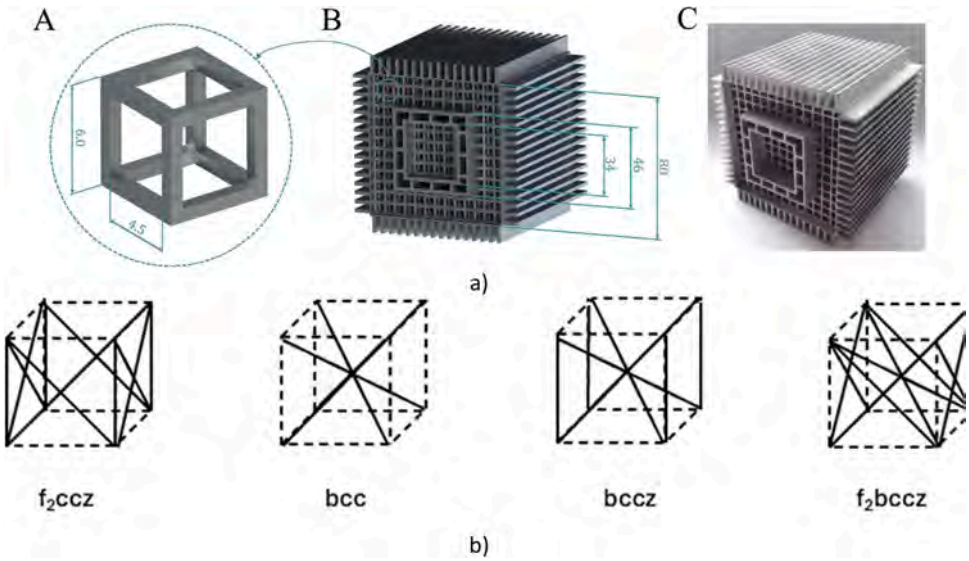

Fig. 11. Scheme of the selected lattice structures adopted for: the study of Morciano [216](a, under CC BY 4.0 license) and the study of Piacquadio et al. [218] (b).

Pyramid-type lattice produced by Selected Laser Melting (an AM process). The structure containing this metallic skeleton had mass less than one-half that of conventional structure. At the same time, when filled with higher volume fraction of organic PCM (n-Tetradecane), the produced C-PCM structure is able to double the thermal capacity of the system with respect to the alternative, more conventional systems.

Adopting similar geometries, made of several rod-shaped supporting columns, Guo et al. [226] produced a lattice-structure plate in AlSi10Mg alloy via SLM, then embedding it with N-tetradecane PCM. Thermal performances of the resulting C-PCM are tested both experimentally and numerically. Even if the volume fraction of the Al-alloy structure was low, its addition to the bare PCM causes an increment in the thermal conductivity of 13 times with respect to the one of this latter.

The contemporary numerical and experimental analyses were performed also by Zhang et al. [227]. The authors proposed to analyze thermal performances of metallic truss-based structure filled with PCMs quantifying the impact of the volume fraction of porosity (and thus of PCM) of the structure, heating orientation and heat flux.

Liu et al. [228] investigated via numerical modeling the impact of both porosity and pore density on the thermal performances of metal foams impregnated by PCMs under different gravity conditions, i.e., 5, 0 and −5 g. In the first two gravity conditions, the reduction of the porosity has a beneficial effect in improving the thermal performances in the C-PCM, while has a limited impact in the remaining case. Pore density, on the other hand, does not affect the performances at high gravity, while its decrement increases PCM natural convection.

3.2.3. *Porous skeletons – C-PCMs with anisotropic features*

Alternative solutions to the use of foam and lattice structures described above are also possible, specifically when anisotropy in thermal conductivity of the final C-PCM is requested by specific applications. The use of second phases to which the production process induces specific orientations is an example [229].

Anisotropic or orthotropic porous materials can be filled by PCMs obtaining C-PCMs with anisotropic or orthotropic characteristics. One interesting example is given by Fink et al. [230], in which production methods to achieve strongly orthotropic material with Lotus-riot-type structures characterized by elongated interconnected pores were revised: from unidirectional solidification of Cu melt containing high amount of dissolved gas to compacted metal fibers, to sintered expanded metal sheet, to expanded multi-layer (in this case a technique also used to obtain honeycomb structures). Examples of combinations of these structures, hosting organic PCMs and forming composites for TES/TEM structures with orthotropic thermal conductivity, are presented.

In view of designing TES systems with honeycomb Al-alloy structures, which often are produced with hexagonal sides alternatively of single or double thickness, Li et al. [231] provided models to estimate directional dependence of effective thermal conductivity of honeycomb-based C-PCMs.

At the same time, the effective thermal conductivity and anisotropy relationships with porosity for fluid-saturated frame and prismatic cellular honeycomb metallic structures were numerically investigated by Bai and Nakayama [232] and compared to composite structures obtained by filling lattices (cubic, octet-truss, tetrakaidekahedron rod-cells).

Gopalan et al. [233] numerically compared the charging/discharging behaviour of homogeneous PCMs with that or honeycomb-based C-PCMs or Lattice Frame Materials (LFMs). Suitably oriented honeycomb structures are effective in improving the performances of the resulting heat sinks by improving their thermal conductivity along heat direction, which is stated to be the most dominant parameter during charging/discharging of PCMs.

The effective thermal properties and, especially, the thermal response of honeycombe based C-PCM are often numerically investigated, even if in many cases validated by experimental tests [234,235].

Engineering materials for the achievement of anisotropic thermal conductivity already finds various applications in common-life fields, such as textiles [236], addressed toward the achievement of a comfort temperature, building sector [237,238], for the control of inner temperature, but also heated seats [239]. Thermal conductivity anisotropy is appreciated also for other engineering applications among which electronics [240], heat sink [241], space cube satellites [242], heat ignition pipe [239], especially thought for favoring heat dissipation along a specific direction, without damaging the surroundings, and preserving the correct functioning of the devices, as in the case of Li-ion batteries [243].

4. Metals adding functionalities to PCMs

In this chapter the possibility to add extra metallic phases as second phases or porous structures to organic PCMs, in view to add specific functionalities to the obtained C-PCMs beyond the thermal energy storage and management purposes considered up to now.

Specifically, several energy conversion mechanisms are exploited to promote faster heating transients, shape stabilization (already mentioned in some of the previously introduced C-PCMs) and mechanical strength, EMI shielding and other functionalities.

4.1. *Energy conversion mechanisms*

In the view of the multifunctionality, the design of composite PCMs is also addressed toward the introduction of other phases or supports [244] which can promote alternative energy conversion mechanisms, able to stimulate PCM phase transition and lead to more efficient thermal energy storage. The most relevant examples involve solar-thermal, solar-thermal-electric, electro-thermal and magnetic-thermal energy conversion mechanisms [160,245,246]. All the listed mechanisms improve the sustainability of the energy utilization process at the base of the PCM technology [246,247].

4.1.1. *Solar-thermal energy conversion*

Solar-thermal energy conversion mechanism involves the introduction in the PCM of second phases, able to properly absorb the solar radiation in specific wavelength ranges. Indeed, pure PCM capability absorption is usually limited by poor capability absorption or high reflectivity [160]. The physical mechanism of interest is the photothermal heat generation. Solar energy absorption may trigger different mechanisms at the atomic scale, depending on the nature of the material, which can promote an increment in the temperature of the PCM (Fig. 12).

Three different mechanisms are involved in the photothermal heat generation: localized plasmonic heating of noble materials, nonradiative relaxation of semi-metals and thermal vibration of molecular materials.

The first effect, typical of metallic materials, involves as a first step the interband excitation of conduction electrons from a lower energy to a higher energy state with the absorption of an electromagnetic radiation. In particular, it is based on local surface plasmon resonance (LSPR) effect, triggered by the absorption of the electromagnetic radiation. When irradiating light frequency matches metal-based particles resonant frequency, a collective excitation of the free electrons inside the metal is triggered due to the so-called localized surface plasmon resonance. Thermal energy is generated by electron agitation. In more detail, the decay of the electron can occur either through radiative emission or

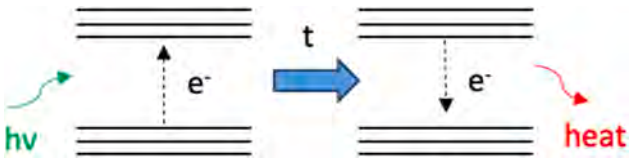

Fig. 12. Schematic representation of the solar-thermal energy conversion.

electron-electron coupling. The latter type of decay causes the redistribution of the electron energy, which leads to plasmonic particles temperature rise. Electron-phonon and phonon-phonon coupling leads to heat dissipation to the surrounding medium. This mechanism is typical of the conductive materials [160,248].

Nonradiative relaxation of semi-metals mechanism on the other hand, is the dominant mechanism in the photothermal effect for semiconductor materials. Also in this case, the first step involves the interband absorption of electrons. In this case, transition electrons are involved. The excitation has to be able to promote these latter from lower to higher energy states across the bandgap, peculiar of semiconductor materials. Excited electrons may come back to the lower state, releasing energy in the forms of either photons or phonons. If the process involves the latter, heat is generated.

The last effect, typical of very low conductive materials, is the thermal vibration in molecular materials. In this case, electrons are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) via photoirradiation at a certain frequency. Electron-phonon coupling related to electron relaxation causes the heat generation [160].

The efficiency of process conversion is described by Eq. (5) in the work of Liu et al. [245].

$$\eta_{solar-thermal} = \frac{\int_{T_i}^{T_m} mC_{p,s}dT + m\Delta H_m + \int_{T_m}^{T_f} mC_{p,l}dT}{E_d St} \quad (5)$$

The terms at the numerator are the same ones of Eq. (1), whereas the ones at the denominator are: E_d [W m^{-2}], the irradiation intensity of the solar input; S [m^2], the area of the sample and t [s] the irradiation time.

Liu et al. [246] propose another relationship (Eq. (6)) for the evaluation of the photo-thermal conversion efficiency:

$$\eta_{solar-thermal} = \frac{m\Delta H_m}{E_d St} \quad (6)$$

Similarities can be easily found comparing Eq. (5) and 6, where the latter exhibits only the latent heat contribution.

Solar-thermal-based PCMs find applications in the field of photothermal collection, desalination, industrial waste thermal recovery and electronic thermal management [246].

In some cases, the photo-thermal behaviour can be offered by PCM containment tool itself. Peng et al. [249] employed photo-deposition and electrostatic adsorption method for the preparation of two types Au/TiO_2 shells, microencapsulating PCMs. The aim of the work is addressed toward the achievement of photocatalytic hydrogen production and thermal energy storage. The focus was on the performance evaluation of employing TiO_2 in the form of rods rather than flakes. The results highlighted in particular the advantages of using rod instead of flakes in terms of conversion efficiency.

However, in the majority of the cases, photo-thermal agent is not covering the role of the container in the composite but offers this feature in the form of nanoparticle. Beyond Au ones, Ag and Cu are widely employed for this purpose. As explained in the previous chapter, these latter also offer thermal conductivity enhancement.

Zeng et al. [250] realized mesoporous poly-dopamine nanoparticles, which can be activated with the IR-light (Infrared light) for promoting wound repair. The poly-dopamine nanoparticle, which covers the role of the amin carrier, is functionalized with PCM, Cu ions and tetracycline. The combination of these latter offers the possibility to heal infections.

Other examples related to the use of Cu nanoparticles come from the previously mentioned works of Zheng et al. [251] and Zhao et al. [187]. The former achieved 97 % light-to-thermal conversion efficiency, employing percolated paraffin into Cu foam loaded with graphene aerogel in order to build up a compact solar heating systems, whereas the latter obtained satisfying photo-to-thermal effect adopting porous carbon matrix embedded with Cu nanoparticles, infiltrated with paraffin through vacuum impregnation.

As previosuly declared, also Ag nanoparticles give the possibility to achieve photo-to-thermal conversion.

Ma et al. [189] obtained 82.7 % of photo-thermal conversion efficiency, producing porous carbon supports filled by polyethylene glycol as PCM, where silver nanoparticles are dispersed. Lauric Acid supported by Ag nanoparticles-modified expanded graphite leaded to 81.2 % solar-to-thermal conversion efficiency in the work of Wen et al. [190]. Solar-thermal conversion efficiency up to 92 % was instead achieved by Zhang et al. [191], who exploited Polyethylene glycol as PCM with the introduction of graphene nanosheets functionalized with Ag nanoparticles.

Zheng et al. [251] percolated paraffin into Cu foam loaded with graphene aerogel in order to build up a compact solar heating systems. This combined use of high thermally conductive materials, raise up by 9 times the thermal conductivity of pure paraffine. The introduction of graphene aerogel also allowed the achievement of form-stability and 97 % light-to-thermal conversion efficiency in case of use of the material for solar to thermal energy storage (see Chapter 4).

4.1.2. Solar-thermal-electric energy conversion

Based on similar principles, also the solar-thermal-electric conversion is exploited with PCM [245]. In this case, PCMs are coupled with either thermoelectric generators or coolers [252]. The first involves the production of electrical energy from temperature gradients, accordingly to the Seebeck effect (Fig. 13a). In particular, a linear relationship exists between the temperature gradient applied at the extremes of a thermoelectric generator device and the produced voltage. Temperature source can be the solar light for instance [245]. In this sense, PCM, if applied at one of the opposite ends of the generator, is useful in keeping constant the temperature where is located. This statement is experimentally demonstrated by Wang et al. [253].

The efficiency of the energy conversion in this case is quantified as follows (Eq. (7)):

$$\eta_{solar-thermal-electric} = \frac{UI}{E_d S} \quad (7)$$

where U and I represent the output voltages [V] and current [A], respectively. As in Eq. (7), E_d and S stand for the irradiation intensity and the surface area of exposure.

Numerical evidence in the potential advantages of adopting such a type of composite materials is depicted by Motiei et al. [254], who introduced PCM as heat sink in a photovoltaic-thermoelectric generator and simulated the whole behaviour of the system exploiting environmental boundary conditions. Huo et al. [255] determined the compatibility between PCMs and flexible thermoelectric devices. In ambient conditions, the devices exhibited cooling effects exceeding 10 °C. Thermoelectric generators, with the introduction of PCMs, can generate 7.3 μW/cm^2 at approximately 22 °C, supplying enough power for the realization of self-powered sensors. Cui et al. [253] experimentally demonstrated the feasibility of integrating PCMs and thermoelectric generators with concentrated photovoltaic systems, addressed toward maintaining the system at the correct operating temperature. Muthu et al. [256] applied PCM to solar parabolic dish and thermoelectric generator, studying the influence of operating parameters for the generation of electricity. Liao et al. [257] proposed a double PCM in the working operating range of 0–40 °C for the use of thermoelectric generators with an increment of 35.8 % of the performances with respect to employ only single one PCM. Jaworski et al. [258] studied the impact of the PCM as cooler modules for thermoelectric generators. The entity of the output in terms of voltage and current under different working conditions is evaluated. PCMs coupled with thermoelectric generators demonstrated to be effective also if considered for space cooling applications, as stated by Zhao and Tan [259] where the implementation of the PCM leaded to electric energy saving of 35.3 %. The same authors worked on numerical evidence of the effectiveness of the proposed

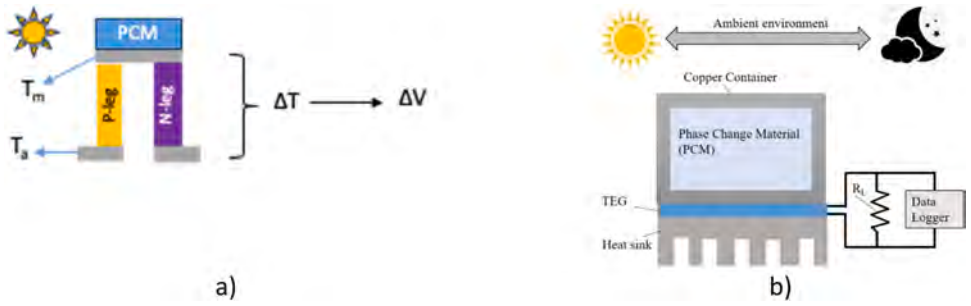

Fig. 13. Schematic representation of the solar-thermal-electric energy conversion mechanism (a) and model scheme of Tuoi et al. [261] (b, under CC-BY.NC—ND 4.0 license).

system [260].

Also in the case of PCM-thermoelectric generator coupling, metallic structures can be added to organic PCMs in order to further enhance heat transfer toward the heat storage unit as in the case of Li et al. [262] which increase both thermal control and thermoelectric efficiency due to the higher composite thermal conductivity. Borhani et al. [263] investigated the impact of introducing metallic foams at either one or both sides of thermoelectric generators in terms of porosity and pore density. In this sense, the scientific literature offers other approaches, such as the one of Huang et al. [264] which adopt the introduction of expanded graphite than metallic foams, in order to promote thermal anisotropy in the composite (2.62–6.11 W m^{-1} K^{-1} for the axial direction and 2.93–12.99 W m^{-1} K^{-1} for the radial one). Tuoi et al. [261] developed an analytical model, supported by experimental activity for the calculation of power density derived from the employment of thermoelectric generator coupled with organic PCM, contained in a copper container (Fig. 13b). The resulting device offers a power density of 37.5 μW/cm^2 in the temperature span of 5 and 35 °C, whereas grants 11.9 μW/cm^2 in a real environment, where the temperature oscillates between 12 and 24 °C.

Thermoelectric materials rely also on the Peltier effect. In this case, the thermoelectric material acts no more as a generator, but as a cooler. Indeed, the application of an electric current causes a temperature gradient within the thermoelectric device. Also in this case, PCM is applied at one of the two ends of the device, maintaining its temperature constant.

PCMs are also used in combination with thermoelectric coolers (TEC), which rely on the other hand on Peltier effect. Manikandan et al. [265] showed the advantages in adopting this approach. The benefits in the implementation of TEC, in combination with PCMs embedded in Cu foam, for battery module TEM are explored by Jiang et al. [266]. The use of TE materials and PCMs also finds application in the biomedical world for improving the quality of the life of Multiple Sclerosis patients, in order to reduce their skin temperature and keep it at a comfortable level [267].

On example of multifunctionalization of C-PCM composites is offered by Cottrill et al. [268]. The authors coated Cu and Ni foams to further improve the skeleton thermal conductivity by graphene via chemical vapour deposition, before impregnating it with octadecane (a paraffin) as PCM in order to harvest electrical energy from daily temperature fluctuations.

4.1.3. *Electro-thermal energy conversion*

The application of an electric current to a composite PCM may also enable the exploitation of the Joule effect to increase its temperature. This occurs through electron friction within the electrically conductive components of the composite, potentially driving the PCM toward its phase transition temperature [245]. Moving electrons indeed, cause heat generation and dissipation colliding with other molecules when they are driven under an electric field (Fig. 14). PCMs then absorb resistive heat [247]. In this case, the efficiency of the process is

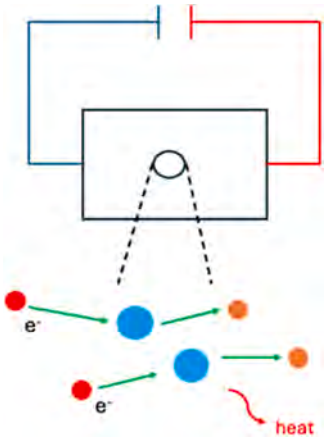

Fig. 14. Schematic representation of the electro-thermal energy conversion mechanism.

described by the following relationship (Eq. (8)):

$$\eta_{electro-thermal} = \frac{\int_{T_i}^{T_m} mC_{p,s}dT + m\Delta H_m + \int_{T_m}^{T_f} mC_{p,l}dT}{UIt} \quad (8)$$

n this case, the numerator is the same of Eqs. (1) and 5, whereas the denominator presents the multiplication of the input voltage U [V], the input current I [A] and the working time t [s].

Hu et al. [186] functionalized with reduced graphite oxide and Cu, melatonine foam impregnated with PEG with vacuum impregnation. The final product offers 148.3 J/g when PEG melts and 143.9 J/g in the crystallization stage. The resulting thermal conductivity of the whole composite reaches 0.4621 W m^{-1} K^{-1}, due to the high thermally conductive additions. These latter allow the achievement of light-to-thermal and electric-to-thermal transitions. Tabassum et al. [269] employed expanded graphite, nano-organophilic montmorillonite and ammonium phosphate as flame retardants, to be added to methyl stearate PCM. The authors demonstrate the synergic effect of the additives for thermal stability achievement, as well as their effectiveness in promoting electro-to-thermal conversion. The efficiency of the mechanism is 72 % and small voltages, i.e., 1.4 V, can be applied in order to trigger the effect. The addition of the other materials to the PCM causes also an increment in the thermal conductivity of the whole composite, which reaches 3.6 W m^{-1} K^{-1}.

4.1.4. *Magneto-thermal energy conversion*

Last but not least, the magnetic-thermal energy conversion mechanism can be achieved in composite PCMs properly introducing magnetic phases inside the composite. These latter can generate large amount of heat due to the electronic friction related to the alternation of the magnetic field, which, consequently, causes periodic alternate electron

motion. Superparamagnetic materials experience current flowing in the electrons, due to Neel or Brownian relaxation [245,247] (Fig. 15). In general, magnetic nanoparticles, characterized by a single magnetic domain, exhibit magnetic anisotropy. In other words, their magnetic moment tends to get aligned along preferential directions, depending on the ones of the magnetic field itself. The average time between two consequent alignments is the relaxation time. This latter is related to two distinct physical phenomena: Neel and Brownian relaxation [270].

The first one involves only the internal magnetic moment alignment of the nanoparticle, without the rotation of the whole nanoparticle itself.

Every change in the magnetic moment direction is not completely reversible at all due to magnetic inertia phenomena. This leads to energy dissipation into heat.

The temperature dependance of Neel relaxation type is described by an Arrenhius-type function, and simple thermal fluctuations can affect the magnetic moment rotation response and energy dissipation [270].

On the other hand, when Brownian relaxation is involved, the magnetic moment and its relaxation are related to the rotation of the whole nanoparticle. The relaxation time in this case depends on interaction between the nanoparticle and the medium in which it is dispersed. As a matter of fact, the friction related to the nanoparticle alignment itself causes the heat dissipation. As a result, the relaxation time depends on the hydrodynamic volume of the nanoparticle and the temperature-dependent viscosity of the medium [270].

The impact of the boundary conditions in terms of external magnetic field could be relevant as well in the literature for both dissipation mechanisms [271,272].

Eq. (9) describes the efficiency of the process:

$$\eta_{magnetic-thermal} = \left(\int_{T_i}^{T_m} mC_{p,s}dT + m\Delta H_m + \int_{T_m}^{T_f} mC_{p,l}dT \right) \Big/ \left(\frac{1}{2} * L * I^2 \right) \tag{9}$$

The term in the parenthesis is the one related to the heat absorption, L [H] is the self-inductance of the coil and I [A] the input current.

An example in the literature involved the coupling of the organic PCM with magnetic materials, such as Ni. Fang et al. [273] build up a super-versatile PCM-based composite. Paraffin wax was selected for the TES/TEM role. This latter was percolated via vacuum impregnation inside Ni foam, which imparts magnetic behavior to the composite. The PCM-foam composite is then embedded in multi-walled MXene foils via vacuum filtration process and then the whole structure is encapsulated in Polydimethylsiloxane. The composite demonstrates photo-thermal and magneto-thermal behaviour, combined with heat storage of 170 J/g. Moreover, EMI shielding behaviour is achieved with 88.2 dB, employing 25 μm thickness. Hussain et al. [206] presented the realization of Ni-foam, coated via Chemical Vapour Deposition with graphene and percolated with paraffin as PCM, addressed toward their use in view of Li-ion batteries TEM. Although the introduction of the paraffin in the composite causes a shift in its transition temperatures and a reduction in both latent and specific heat of almost 30 %, the resulting thermal conductivity of the composite is 23 times higher. Moreover, a reduction of 17 % in the maximum temperature rise achievable by the Li-ion battery is reached.

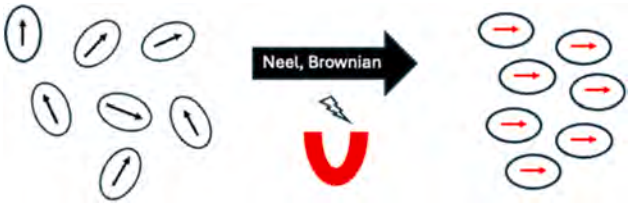

Fig. 15. Scheme of the magneto-thermal energy conversion.

4.1.5. Efficiency and losses

The fully comprehension of the abovementioned multi-physics processes involving composite materials made up by more than one phase is not an easy task to be tackled. Eqs. (5)–9 offer, in a first approximation, a rough estimation of the efficiency of the system. However, they do not take into account any losses that may affect both the numerator, not all the heat produced will be exploited by the PCM, and the denominator, not all the available energy source can be used. The introduction of various physical effects indeed involves the addition of energy losses which threaten the performances of the composite, not at the moment taken into account in Eqs. (5)–9. However, for a correct and detailed estimation of the system efficiency a case-by-case description of the system should be developed. Involving much more than one only physics, a decoupling approach on the descriptive relationships can simplify the problem for the derivation of more straightforward solutions.

In general, the most trivial are the heat leakages. The addition of photo-sensible nanoparticles within the organic PCM matrix for instance can affect the viscosity of the system, consequently, modifying and weakening the convection [274]. Moreover, nanoparticles either related to solar-to-thermal or magnetic/electro-to-thermal are dispersed in a low conductive matrix. In this view, the heat tends to be locally confined, especially if nanoparticles are highly dispersed within the matrix, being the conductive thermal resistance of this latter not negligible. The heat produced moreover, can flow out of the composite if this latter is in contact with a conductive medium via heat conduction mechanism.

In addition, if the composite achieves a temperature higher than the surrounding environment, convection heat transfer is triggered as well, being a cause of further heat leakage. Radiative losses, eventually depends on the atmospheric condition.

As far as the external sources are concerned, the abovementioned Equations do not take into account for instance the absorption and the reflection capabilities of the nanoparticles in the case of the photo-thermal effect. Indeed, these physical properties determine the capability of the system to exploit the solar irradiation, and in which amount and depends on the surface preparation/exposure. On the other hand, magnetic and electric losses, leading to changes through the working cycles, can cause the alteration of the system responses.

In this view, also the long-term performances of such C-PCMs with the related efficiency calculations have to be carefully taken into account, in order to establish also their reliability.

4.2. Metals as supports for shape stabilization

In this chapter metallic phases exploited for supporting composite form-stability are reviewed. A first successful approach is achieved with the employment of small elements. Chen et al. [275] proposed to produce form-stable PCMs with the employment of metallic ions, in order to set up metallorganic frameworks with different morphologies depending on the different metallic ion. Lv et al. [276] presented nano-silica particles, whose pores ranges among 30 and 100 nm, able to adsorb on their surface liquid paraffin in order to set up shape-stable composites to be coupled with battery modules for TEM purposes. The introduction of this technology, with respect to the use of the bare PCM, allows the achievement of almost 6 °C temperature reduction. Rezaie and Montazer [188] achieved shape stabilization producing in one single step fatty acid, Cu nanoparticles and polyester fibres C-PCM.

Moreover, as previously stated for the adoption of capsules, also the introduction PCM-foams composites offer new perspectives for form-stability purposes [125]. Zhang et al. [209] obtained form-stability functionalizing Cu foams with graphene oxide in order to give stable sites to the PCM. The previously presented works of Ma et al. [189] relies for instance on this principle, combining PEG, porous carbon supports and Cu nanoparticles. The same material combination is adopted by Zhao et al. [187] and Zheng et al. [251], who adopted instead the

aerogel strategy. Zhang et al. [191] and Chen et al. [210] adopted instead Ag nanoparticles in place of Cu ones.

In addition to the examples provided, the concept of shape-stabilization also transfers to fully metallic structures. Indeed, in the view of form-stability, Sharar et al. [277] exploited Ni-Ti-based Shape Memory Alloys (SMAs) for PCM purposes. The authors demonstrated effective repeated temperature management offered by the austenitic-martensitic solid-solid transition, typical of SMAs. Moreover, they also underlined the possibility of tuning their thermophysical properties via slight changes of the composition of the alloy.

The same authors also compared the performances of Ni-Ti-based alloys with other classes of PCMs highlighting the advantages offered by SMAs: high volumetric latent heat (183 MJ m^{-3}) and high thermal conductivity (12.92 W m^{-1} K^{-1}), combined with the possibility of avoiding the design of any container, due to the repeatable solid-solid transformation [278], granting form-stable behaviour.

Another example is provided by Chen et al. [279], who prepared Bi-Sn-In alloy for low-temperature TEM, to be added with Ag particles (1–4 wt. %) and percolated in the Cu foam. Shape stability tests were performed in order to investigate the proper foam porosity to avoid possible PCM leakages. The increment of Ag particles in the composite causes a shift in the melting point toward higher temperatures and slight decrement in the storage potential. However, its synergistic effect with the Cu foam, able to set up highly thermally conductive networks within the composite causes a sensible increment in the thermal conductivity. Its value switches from 16.4 W m^{-1} K^{-1} of the pure Bi-Sn-In to 22.4 W m^{-1} K^{-1} with the addition of 4 wt. % Ag nanoparticles and 42.7 W m^{-1} K^{-1} with the further addition of Cu foam.

4.3. *EMI-shielding and other PCM functionalities improved in metallic C-PCMs*

Relevant examples are offered by the perspective of add load bearing capability to the PCM or other features, such as sound absorption or electromagnetic interference shielding (EMI shielding), that will be treated more in detail in the next chapter.

This section collects the reported other functionalities for metal-based C-PCMs. The most reported application involves the use of macroscopic metallic structure for imparting mechanical properties to PCMs. In general, the scientific literature mainly presents studies on organic-based C-PCMs mechanical properties characterization beyond the mere thermophysical ones. These latter are principally addressed toward batteries [280] and concrete [281–283] C-PCMs integration, specifically thought for structural applications, or capsules for PCMs [284], thought for the stability estimation of the composite, subjected to repeated thermal cycles of dissimilar materials.

On the other hand, the reported works on C-PCMs consisting of at least one metallic phase are much more scarce. Aggogeri et al. [285–287] realized and evaluate the effectiveness of sandwich panels with metal foam core impregnated with organic PCMs to be coupled with Ultra High Precision (UHP) machining tool. Their performances indeed can be affected by temperature, that the prototype demonstrate to effectively stabilize in the 20–50 °C range. Moreover, the addition of the metallic foam provides to the multi-functional composite high damping properties as well as high stiffness to weight ratio. In this sense, also Kennedy [288] highlighted the potential added value of the Al foams for the concurrent improvement of thermal and mechanical organic PCMs performances.

Indeed, where Composite Phase Change Materials are designed in order to fulfill thermal and mechanical demands at the same time, Wirtz et al. [289] proposed the employment of Al-based composite laminates with rectangular channels for PCM hosting. The work relies on both numerical and experimental bases. The results state an excellent performance-to-weight ratio.

Also Additive Manufacturing (AM) techniques are employed. Atinafu et al. [290], as well as Haydn and Wadley [291], highlighted the potentiality of porous structures addressed toward the production of organic PCM shortcomings, building up composite materials. In this sense, the advent of the Additive Manufacturing (AM) techniques also enables the production of regular periodic structures [292]. Their potential in the thermal field, is described by [293].

PCMs find wide applications also in the biomedical field. Their capability of maintaining the temperature [294] enhances the effectiveness of various biomedical applications, in addition to other features among which being non-electric, avoiding risks of electric shock, easy to handle, easy to recharge thermally, having long life and being widely available. In this view, Zhang et al. [295] designed multi-functional silver-silica-based microcapsules for n-eicosane PCM. The capsules were realized via interfacial poly-condensation, followed by silver reduction. The final silver outer layer not only does not excessively penalize PCM thermal response but also gives to the whole composite 130 Ω*m in view of electrical conductivity and grants sterilization rate of 95 % at the contact time of 4 h for Staphylococcus Aureus and Bacillus Subtilis. Feng et al. [296] used PCM as carriers for medical applications, encapsulating copper sulfide loaded Fe-doped tantalum oxide and the photosensitizer zinc phthalocyanine, which work as melting enhancer for PCM and anti-cancer agent, respectively, similar to the case presented by Chen et al. [297].

Another application can be found in the optical field. Kang et al. [298], Raeis-Hosseini and Rho [299] also present the integration of Phase Change Materials role in the world of rewritable data storage and optoelectronic devices [299]. In this sense, PCMs have attracted the attention of the researchers due to their effective refractive index change in addition to reversible phase transition, high endurance, switching speed and data retention [300]. Luo et al. [301] proposes a layered Metal-Dielectric-Metal (MIM) structure with the introduction of $Ge_2Sb_2Te_5$ PCM in order to achieve tunable infrared detection, radiation cooling and Infrared (IR) laser camouflage.

As previously said, Feng et al. [273] proposed multifunctional composite PCMs for EMI shielding. Shielding effectiveness of a material refers to the ratio of the received power of an incident electromagnetic wave with and without the presence of this latter material [302]. It relies on three different mechanisms: reflection, absorption and multiple rebounds (Fig. 16). The first one mainly depends on the mobile carriers of the material itself which interact with the incident electromagnetic wave. It is one of the most dominant contributions in electrically conductive materials [303].

Absorption instead depends on the presence of interacting dipoles with the wave and is related to the thickness of the material. Shielding effectiveness also depends on the possibility of having multiple reflections within the material itself, mainly related to the presence of defects and interfaces.

5. Conclusions

The present review collects examples related to the use of metallic materials, classified in the broader context of inorganics, in the PCM field. This review work, within every section, presents the current state of the art on their employment, highlighting their pros and contras, in addition to identify possible literature gaps, addressed toward the

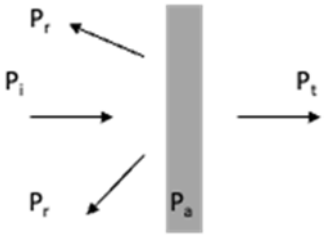

Fig. 16. Scheme of the Electromagnetic interference shielding.

achievement of a broader understanding of their behaviour in PCM field.

In general, although this class of PCMs is the least explored one with respect to the ones presented, metals offer the possibility to be combined in alloys as well, covering a wide span of application temperatures (range from −40 °C beyond 1000 °C), which coincide with PCM transition temperature. Moreover, they exhibit clear advantages in terms of energy density, i.e., latent heat per unit volume, and thermal conductivity, strictly connected with PCM response fastness. In this view, for a fully comprehension of the PCM transient behaviour, the authors claimed thermal diffusivity as an another fundamental thermophysical property, which is usually not taken into account within the cited PCM studies. Its quantification, considering also its temperature dependency, may deepen the understanding on the PCM thermal response. Also, the development of standardized methods which allows the possibility to switch from alfa to k can be valuable tool also for further compare the different PCM.

Despite the aforementioned advantages, several factors have to be taken into account for the practical application of metallic PCM, among which their reactivity with whatever surrounds them. Chemical segregations, corrosion issues and their high reactivity with the environment in their molten state, indeed, may change irreversibly their chemical composition and, consequently, their PCM performances. At the moment, the studies related to this topic mainly focus on the bare compatibility between the PCM liquid metal and its containment unit, lacking on the study of potential degradation of heat transfer performances. It is worth mentioning, indeed, that the production of corrosion phenomena may alter the conductive thermal resistances involved, modifying thermal conductivities of the materials as well as their geometrical features.

In this sense, some general aspects are presented in the review but, being the involved corrosion phenomena a quite complex matter, depending on both the specific material combinations and the system boundary conditions, the task should be considered case by case with the development of proper physical descriptions.

As presented in this work, the adoption of chemically stable suitable containers, capsules or shape-stabilization approaches successfully preserve the integrity of the PCM.

Moreover, due to their outstanding properties, metals are also used in combination with PCM of other nature, i.e., organics and inorganic salts, in order to build up composites able to improve the efficiency of the bare PCMs, which present deficiencies especially in the heat transfer. In this sense, a florid literature is related to the adoption of continuous macroscopic high thermally conductive metallic network, either disordered as foams, or ordered, as repetitive lattices. Metals are also dispersed in form of nanoparticles in low thermally conductive matrices in order to raise their thermal transport properties.

The latest trend involves the use of metals addressed toward the design of composite with multiple functionalities beyond the classical ones. In this view, the current literature still lacks at the moment of properly descriptive multi-physical coupled models, able to physically describe, the multifunctional features of the composite. However, modelling multi-functional behaviour of these PCMs is not straightforward as well as the proper definition of the system efficiency. In this sense, a decoupling approach in the physics can represent a reliable tool for a much more straightforward understanding of the problem. Moreover, another point that should be taken into account is the reliability and the integrity of such systems within repeated cycles, more precisely mimicking PCM simulated behaviour. This analysis will certainly state the long-term effectiveness of such multifunctional C-PCMs.

The current review proposed to shed a light on the potentialities of metals to be implemented in multifunctional systems, offering a broader vision beyond PCM features, which mainly rely on their thermophysical properties. At the moment, the literature is scarce on that topic. This perspective, however, aligns with future trends aimed at developing increasingly complete systems and more effective machining tools or electronic devices.

CRediT authorship contribution statement

Matteo Molteni: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Elisabetta Gariboldi:** Writing – review & editing, Visualization, Validation, Supervision, Funding acquisition, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Elisabetta Gariboldi reports financial support was provided by European Union. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

The authors do not have permission to share data.

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