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Considerations for the use of metal alloys as phase change materials for high temperature applications

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ABSTRACT

The use of paraffin, salts and salt hydrates as phase change materials (PCMs) have been researched extensively and used in a number of commercial applications. However, metals and metal alloys, which possess a high storage density on a volume basis as well as a substantially higher thermal conductivity, has received much less attention. This paper discusses the considerations for the use of metal and metal alloys as phase change materials for high temperature thermal storage applications, as well as summarises the literature on the limited research in this area. Although some pure metals and metal alloys present interesting thermal properties to be used as PCMs in thermal storage systems, there is a lack of understanding on the implications of the metallurgical aspects related to the melting and solidification of these materials under thermal cycling at high temperatures. The main issues to be considered include vapour pressure, undercooling, corrosion, segregation, changes in composition and microstructure, changes in thermal properties and undesired reactions. Further research is needed before these materials can be used as PCMs in thermal energy storage systems in industry.

1. Introduction

Climate change mitigation is one of the key issues to address for researchers and energy makers [1,2]. It is stated that there is an urgent need to develop a new energy supply system as sustainable as possible, that take into account our economic system and our social environment, with the aim of maintaining our resources for future generations. The widespread use of renewable energy has some handicaps, the most important being the intermittence of the resource. The mismatch between supply and demand can be overcome by storing the energy in the form of electricity, heat or mechanically.

Thermal energy storage (TES) is nowadays playing an important role as a complementary technology for renewable energy [3], enabling this energy resource to be utilised throughout the day and night [4].

TES can use three methods to store heat: sensible heat (SHTES), latent heat (LHTES) and thermochemical storage (TCS) [5]. However, SHTES and LHTES using phase change materials (PCMs) have been more fully-developed and are more widespread in the market [6].

PCMs for high temperature TES systems are actually based on molten salts or eutectic salts compounds [7]. However, metals can be a very important alternative, which researchers have started to explore [8].

In general, the required properties for a PCM to be used for heat storage can be summarized into three sets of requirements [9]: technical, economic and environmental *Physical and technical requirements* determine the size and suitability of the thermal storage for a certain application. Low density variation and small volume change, high energy density, small or non-subcooling, non-phase segregation, low vapour temperature, chemical and physical stability, and compatibility with other materials are the most important properties to be considered when choosing a material within this group.

Thermophysical requirements are important for heat storage because the best thermal properties will support the greatest energy efficient system performance. A reproducible phase change at a temperature tailored to the application, with large phase change enthalpy (ΔH) and specific heat (Cp), as well as high thermal conductivity, and thermal and cycling stability, are the most relevant.

In addition, *economical requirements* are extremely significant, as a low price is a key issue to consider for a material for PCM implementation at large scale.

Last but not least, *environmental* concerns include the ability of the PCM to be recycled or reused, and other environmental factors such as the CO_2 footprint, which needs to be minimised, a low embodied

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energy, which is directly related to energy savings at the end of its life-cycle, or a low toxicity.

Although all of these requirements have their own importance for the development of TES technology using PCM, the improvement of thermophysical properties can provide new challenges as some of them are incompatible thus forcing to find a compromise between the most important ones.

The main objective of this paper is to assess the use of metal and metal alloys for TES, and to highlight which are the challenges of applying these types of materials from the materials science point of view.

2. State of the art on use of metal and metal alloys as TES materials media

Gasanaliev and Gamataeva [10] analyse the thermophysical properties of various thermal cycles and have also specified the perspectives of using metal alloys for heat accumulation. A technical and economic analysis showed that accumulators with high-temperature phase-transition (melting point > 500 °C) as heat-carriers, particularly eutectic compositions of salt and metal multi-component systems, are most suitable for non-traditional energy sources [11].

Of all the PCMs used for thermal energy storage, eutectic metal alloys have the greatest thermal conductivities and best stabilities. The analysis of published data on thermodynamic parameters of metal-based multi-component systems [12,13] has made it possible to single out the most promising ones to be used as working materials in heat accumulators (Table 1).

Sharma et al. [14], Liu et al. [7] and Rathod and Banerjee [15] considered some metals and metal eutectics with low melting temperatures as high temperature PCM. The authors claim that these metals have not yet been seriously considered for PCM technology because of weight penalties. However, when volume is taken into account, they become good candidates due to their high heat of fusion per unit volume. Metals and metal alloys also have high thermal conductivities, so fillers normally added in PCM (with added weight penalties) are not required.

A list of some selected metals and alloys is presented in Table 1. Some of the features of these materials are common to all: (i) low heat of fusion per unit weight, (ii) high heat of fusion per unit volume, (iii) high thermal conductivity, (iv) low specific heat, and (v) relatively low vapour pressure.

Birchenall and Telkes [16], and later Kenisarin [17], were the first authors who analysed the possibility of storing thermal energy by using the heat of fusion of metals. Starting from that work, Birchenall and Riechman [18] have studied some metal eutectic alloys. Thermal properties of alloys were determined by a differential-scanning calorimeter (DSC) and differential-thermal analysis (DTA). The compositions of the selected alloys were taken from the literature. Initial metals were alloyed in a graphite crucible. The eutectic composition was proved by optical metallography. Experimental facilities were preliminary calibrated by means of pure metals. The measurement error of DTA was 4% for heat of fusion, and 3 K for melting temperature. For DSC, the measurement error was 2% and 1 K, respectively. Five years later, Farkas and Birchenall [19] published new results of the determination of thermophysical properties of some new alloys.

Wang et al. [20] developed and investigated two compositions based on aluminium and silicon. The first alloy, $AlSi_{12}$, contained 12 wt % silicon, and the second alloy, $AlSi_{20}$, 20 wt% silicon. $AlSi_{12}$ had a melting temperature of 576 °C and a heat of fusion of 560 J/g, and $AlSi_{20}$ 585 °C and 460 J/g, respectively. Owing to the best properties, alloy $AlSi_{12}$ was chosen for further studies (its thermophysical properties are given in Table 1). This alloy was used to develop and test a high-temperature isothermal electric heater intended as thermal energy storage at night, when the tariff for the electric power is essentially lower.

Sun et al. [21] investigated one of the ternary eutectic alloys based on aluminium, listed by Farkas and Birchenall 16, Al (60 wt %)–34Mg–6Zn. In this study, the compatibility of the specified alloy with materials such as stainless steel SS304L and carbon steel C20 was investigated. The variation in thermal properties of the alloy in regards to the number of melting and solidification thermal cycles was also studied.

The metal samples investigated were immersed in a capsule, which were placed in a stainless steel crucible. The crucible with samples underwent 1000 thermal cycles between 442 and 455 °C. The duration of one melting and solidification cycle was 34 min. The measurement of thermal properties was conducted using a DSC. The change of melting temperature of the alloy is presented in Table 2. Note that controlling the cooling rates may improve the phase formation stability. Thereby, a considerable change in melting temperature of the alloy was not observed. On the other hand, the heat of fusion tends to decrease as the number of cycles increase: −0.13% after 50 cycles −7.46% after 500 cycles and −10.98%. The reason of this decrease has not been established, but it could be explained as a microstructure change as stated by Feng Li et al. [29].

Khare et al. (2012) [26] used a materials selection procedure and found that metals such as Al, Mg, Si and Zn, and their eutectics 88Al–12Si and 60Al–34Mg–6Zn were highly suitable as a PCM for the duty considered in their research (steam generation from 400 to 750 °C). Their properties, heat of fusion, thermal conductivity, etc. have advantages in the application considered over traditional molten salts, with 88Al–12Si showing the best environmental performance as well. The heat transfer effectiveness of this alloy was also evaluated by the e-NTU method [26] and favourably compared to the HiTech nitrate based molten salt using heat exchanger geometry. The authors used materials selection software based on a multi-objective optimisation methodology, by considering environmental conditions and eco-properties.

Sun et al. [4,21] determined the thermal stability and corrosion characteristics of Al-34%Mg-6%Zn alloy when used as latent heat energy storage material. The melting temperature and latent heat of fusion for this alloy were 454 °C and 314.4 J/g, respectively. Thermal stability was checked for 1000 thermal cycles, but the microstructure potential changes were not taken into account. The container materials considered in the corrosion tests carried out in this study were stainless steel (SS304L) and carbon steel (SteelC20). The DSC results indicated that the change of the melting temperature of the alloy was in the range of 3.06–5.3 °C, and that the latent heat of fusion decreased 10.98% after 1000 thermal cycles. The results showed that the Al-34%Mg-6%Zn alloy under study had reasonably good thermal reliability as a latent heat energy storage material. Table 1 shows the details of the above-mentioned material.

Cárdenas and León [23] listed the metals and metal alloys with melting temperatures above 300 °C proposed and studied by various other researchers as possible high temperature PCM. As previous authors, they claimed that the use of metal alloys as a PCM had been underestimated by researchers even though they have desirable properties such as high thermal conductivity, high corrosion resistance, and small volume change associated with phase change, and no subcooling. Therefore, for certain applications, metal and metal alloys present higher thermophysical properties and they are able to compete with salts, especially when weight is not a decisive factor. Nieto-Maestre et al. [35] focused in the particular temperature range between 285 °C and 330 °C for direct steam generation DSG, using Thermo-Calc software and SSOL4 thermodynamic database for different ternary and quaternary metallic systems combining Mg and Zn, with Cu and Ni for the ternary systems and Mg-Zn-Al-Cu, Mg-Zn-Al-Sn, Mg-Zn-Cu-Sn, for the quaternaries, though the most promising eutectics in terms of T_m and ΔH_f were the ternary combinations.

In addition, some authors propose that the use of eutectic metals as TES medium is feasible for industrial processes [18], that metals and metal alloys can be used as waste heat storage media [36], and that $AlSi_{12}$ [20] and $AlMg_{34}An_6$ [21] are also suitable to be used as PCM.