Zinc-rich eutectic alloys for high energy density latent heat storage applications

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ABSTRACT

The interest on latent heat storage (LHS) materials has experienced a remarkable increase during last years. The main advantage of PCM materials is their higher energy density compared to sensible materials one. In this article the synthesis process and structural and thermophysical characterization of $Zn_{84}Al_{8.7}Mg_{7.3}$, $Zn_{88.7}Al_{11.3}$ and $Zn_{92.2}Mg_{7.8}$ (at.%) eutectic metallic alloys have been performed in order to evaluate their potentiality as PCMs for LHS applications. Their correct synthesis process has been proved by the structural study and their melting/solidification temperatures, heat of fusion, specific heat and thermal conductivity have been investigated. The results show melting temperatures of 344 °C, 382 °C and 371 °C and heat of fusion of around 132 J g^{-1}, 118 J g^{-1} and 106 J g^{-1} for $Zn_{84}Al_{8.7}Mg_{7.3}$, $Zn_{88.7}Al_{11.3}$ and $Zn_{92.2}Mg_{7.8}$, respectively. The obtained energy densities for the investigated alloys are almost two times higher than the ones for similar metallic PCM reported in literature. On the other hand, the measured thermal conductivities are ranging in the solid state from 66 to 139 W m^{-1} K^{-1} and in the liquid state, from 33 to 58 W m^{-1} K^{-1}, which represent the main advantage of these PCM candidates when are compared to the most studied ones such as the inorganic salts. The proposed storage materials can be a highly suitable solution in TES applications when compact system, high power levels and very fast thermal responses are required.

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1. Introduction

In the last years, renewable energies have extensively grown in order to reduce the pollutant emissions, fight against climate change and to promote a sustainable development [1]. In this frame, the implementation and development of innovative technologies to optimize energy efficiencies in renewable energy generation systems are becoming fundamental keys to ensure a satisfactory and cost effective world energy supply [2,3].

In this line, thermal energy storage (TES) represents an interesting alternative which can maximize the overall efficiency of different extensively energy demanding processes. As an example, TES technologies can improve the energy efficiency, among others, in solar plants [4,5], industrial [6–8] or residential applications [9,10]. Among the different methods to store heat, the interest in latent heat storage (LHS) technology is increasing during the last years. Its main advantages are the quasi-isothermal operation

behaviour and large storage capacity associated to the use of latent heat. In the last years, different types of materials such as paraffins, fatty acids or inorganic salts have been widely investigated as phase change materials (PCM). However, despite their numerous advantages, these materials have a poor thermal conductivity, which is their biggest limitation. Numerous studies have been developed with the objective of enhancing the heat transport in storage materials by using simple heat exchange systems. These investigations cover a wide range of alternatives [11–15]; the use of extended surface or fins, high conductive shell encapsulation, impregnation of porous matrixes or the dispersion of high conductive particles. The results derived from these works have shown successful outcomes with thermal conductivity and heat transport enhancements. However, these values still present an important improvements gap.

As recently demonstrated by numerous researches, the use of metal alloys for TES is a very attractive alternative [16–30]. The metals and their alloys present high thermal conductivity values around 10 to 100 times larger than the conventional inorganic salts. The implementation of this class of materials in TES systems could provide fast thermal response and high operation power levels,

which might represent a breakthrough concept regarding current storage technologies. As an example, their implementation as storage media in concentrating solar power (CSP) technology could provide very suitable solutions to palliate thermal shocks, solar fluctuations, radiation transients or even to decrease the plant start-up time.

Different authors have suggested the use of metallic PCMs for energy storage where their main criteria to select a competitive metallic PCM were based on the high fusion entropy, availability and low cost of the metal components. Mainly two metallic systems have mainly attracted the attention of the scientific community [16–33]. On the one hand, for applications in the temperature range 580–1100 °C the Al-Si binary alloys were investigated where a decreasing in their specific heats and thermal conductivities with the increasing of Si content was observed [16–18]. On the other hand, for applications in the temperature range from 340 to 400 °C the Al-Mg-Zn binary and ternary alloys were identified as potential PCMs due to their suitable melting temperature, thermophysical properties and thermal stability [28–33]. In this case, the reported energy densities for the studied materials are quiet low (below 128 kWh m^3), which can limit their use in real application. Hence, a deep effort is still needed to identify new eutectic alloys with melting temperature below 400 °C and high energy density to obtain compact storage tank in order to decrease the cost of TES system.

Our approach in this work is to identify potential metallic PCMs with melting temperature below 400 °C and higher energy densities than the ones reported in literature. The main goal is to determine their relevant thermophysical properties in the field of thermal energy storage in order to demonstrate their suitability as storage media. In this work, Zn-rich eutectic metal alloys have been selected as potential LHS materials, in particular, $Zn_{84}Al_{8.7}Mg_{7.3}$, $Zn_{88.7}Al_{11.3}$ and $Zn_{92.2}Mg_{7.8}$ (at.%) eutectic alloys. Fig. 1 shows the calculated liquidus projection of Zn-Al-Mg ternary phase diagram [34], where the three investigated alloys are indicated (see Al-Zn and Mg-Zn binary phase diagrams in Refs. [35,36]). Once the correct eutectic compositions of the synthetized alloys are confirmed, the melting/solidification temperatures, phase transition latent heat, specific heat and thermal conductivity have been carried out.

2. Experimental method

2.1. Material synthesis

High purity ingots of Zn, Al and Mg metals have been used on the synthesis of the studied metal alloys. The ingots were supplied by Alealsa S.A with purity level higher than 99.99%. Small pieces of around 1–10 g were cut by diamond saw from the ingots to be later used in the preparation process. The stoichiometric amounts of the primary metals were obtained by a high precision digital balance (Cubis, Sartorius) with a precision limit of 0.1 mg. The pre-alloys, of approximately 60 g, were put inside alumina conical crucibles of volume of 19 ml supplied by Frialit-Degussit technical ceramics company and then, the systems were placed and hermetically closed inside of stainless steel reactors under Ar atmosphere in order to avoid any possible oxidation of the alloys. Then, the alloying process was carried out in an electrical chamber furnace with temperature stability of ±0.5 °C (Carbolite) at 450 °C during 4 h. After cooling down to room temperature, the solid samples were turned upside down and were melted again. This process was repeated three times in order to ensure a high homogeneity of the samples. The final cooling down of the samples was conducted at 10 K min^{-1} rate to ensure their correct crystallisation without the presence of any metastable phases.

2.2. Structural characterization

Once the alloys were synthetized, a structural characterization was carried out in order to validate the synthesis method and to check the obtained composition to be within the eutectic composition range. In this line, the identification of phases present in the alloys was performed by X-ray powder diffraction (XRPD) analysis (Bruker D8 Advance Diffractometer) in Bragg-Brentano geometry (θ-θ) using CuK$_{α1,2}$ radiation. A small amount of the powder was removed from the bulk sample using rotary tool (Dremel). The data were collected between 15° and 75° in 2θ with a step size of 0.02° and counting time of 8 s per step.

The microstructure and morphology investigations of the studied alloys were performed using a Quanta FEG 250 SEM operated in high vacuum mode at 30 kV and with a back scattered electron detector (BSED). The microscope is equipped with an Apollo 10 SSD energy-dispersive X-ray spectrometer (EDX) for elemental analysis. The error for quantitative standardless EDX analyses is around 5%. For these analyses, small pieces of alloy samples were cut by diamond saw and then, their surfaces were polished by using SiC papers and diamond pastes down to 1 μm grain size. Finally, the samples were cleaned by acetone ultrasonic bath.

To determine the density of the alloys a helium pycnometer AccuPyc II 1340 from Micromeritics was used. The estimated experimental error of the technique is less than ±0.002%. Small pieces of the samples of around 5 g of weight were cut by diamond saw and then, were used in the measurements. Before the samples density measurements, the instrument calibration was performed using standard steel balls. Then, the samples were placed inside of a 10 cm^3 size sample chamber and the densities were measured at room temperature.

2.3. Thermophysical characterization

The thermophysical properties were measured after verifying the correct composition of the alloys. Phase transition latent heats and melting/solidification temperatures, were determined by differential scanning calorimetry (DSC) (TA Q2000 calorimeter). For these measurements small pieces of samples were cut by diamond saw from bulk samples. The samples of around 50 mg inside open alumina crucibles were three times cycled between 200 and 450 °C under argon flow of 100 ml min^{-1}. In all the measurements heating and cooling rates of 10 K min^{-1} were applied. The estimated experimental errors of this technique for temperature and latent heat are ±0.01 °C and ±0.1%, respectively.

The specific heat was measured by modulated ramp DSC method, where a heating rate of 2 K min^{-1}, temperature amplitude of ±1 °C and a modulation period of 120 s were selected. Alloy samples of approximately 20 mg were cut by diamond saw from the bulk samples and were placed inside aluminium hermetic pans in a glove box under argon inert atmosphere. Then, the specific heat was measured, under argon flow of 100 ml min^{-1}, from room temperature to 300 °C with a step of 25 °C. Under these experimental conditions, the experimental error of these measurements is lower than ±3%.

The thermal conductivities were indirectly calculated from the experimental values of the thermal diffusivity, specific heat and density. For this propose, thermal diffusivities of the alloys were measured by a laser flash apparatus (Netsch LFA 457) in the solid and liquid phases. Disk shaped samples of 10 mm of diameter and 1.5 mm of thickness with graphite coating were measured. The samples were machined by a lathe to ensure parallel faces and smooth surfaces. These samples were introduced in a sapphire holder and the measurements were carried out under argon flow (50 ml min^{-1}). The thermal diffusivity was measured from 50 °C to 450 °C with a step of 50 °C in the solid phase and a step of 20 °C in