

THERMAL PROPERTIES OF A NOVEL MEDIUM TEMPERATURE THERMAL ENERGY STORAGE COMPOSITE BASED ON SODIUM NITRATE AS PHASE CHANGE MATERIAL

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ABSTRACT

Thermal energy storage (TES) has been one of the main research topics during the last decades. The increase of energy costs and the growth of awareness of environmental concerns have promoted the development of new technologies and new materials for energy storage. Developing new materials with high storage density, thermal stability and low cost would reduce energy cost and improve the energy efficiency in well-known and established processes by recovering and storing heat. Moreover, it would solve the renewable intermittence.

The aim of this study is to formulate a $\text{NaNO}_3/\text{MgO}/\text{Cg}$ composite for intermediate temperature TES applications. Several compositions with different amounts of NaNO_3 as PCM, MgO as the ceramic matrix and graphite as thermal conductivity enhancer have been formulated. The main properties related to thermal energy storage applications have been characterized: melting point, latent heat, specific heat, thermal conductivity and thermal expansion coefficient. After being cycled the microstructure of the composite was characterized as well as their thermal properties in order to study the stability when they are charged and discharged at working conditions. The results show that the melting point of the PCM remains around the pure molten salt, the latent heat increases with the PCM content, as expected, as well as the energy density of the composite. Combining the effect of Cg addition and the insertion of the PCM in a ceramic matrix a novel TES material with enhanced thermal conductivity has been developed.

INTRODUCTION

Thermal energy storage can be classified in three major technologies sensible heat, latent heat and thermochemical heat storage. Among the three of them, latent heat thermal energy storage (LHTES) is most promising for heat storage due to the consistent temperature and large thermal capacity [1],[2]. Molten salts are among the most promising materials for thermal energy storage at medium and high temperature such as nitrates, carbonates and chlorides. These salts are thermodynamically stable, operate at low pressures and have relatively low costs. Although molten salt can be used both as

sensible heat storage medium and heat transfer fluid, their low thermal conductivity and low energy storage density are two key disadvantages, that leads to a limited power density and a large storage volume meaning a high cost. However, their applications as PCM's are often held up by chemical incompatibility (such as corrosion of containers) and low thermal conductivities. The low thermal conductivity of TES materials increases charge/discharge time and hence limits their applications [3]. In order to solve this drawback, several methods have been proposed for increasing the thermal conductivity of PCMs : adding conductive structures (extended surfaces like fins and annular substructures)[4], impregnating a porous matrix (impregnation) or dispersing a high conductivity particles within the PCM (mixing) [5]. Despite the insertion of thermal conductivity enhancers means the worsening of the energy density the TES material store [6] the reduction of the rate of heat storage and extraction during the melting and solidification cycles allows the use of this technologies in applications that require faster response time. Also the use of molten salts as phase change materials (PCM) at high temperature can induce the corrosion of the container during charge and discharge processes. Recently, in the study of composite materials has been included the encapsulation of the PCM in the matrix material structure therefore avoiding corrosion. At high temperatures this structure is a ceramic matrix that prevents the contact of the molten salt with materials that they react with. Combining and optimizing composites with both encapsulating the PCM and increasing the thermal conductivity would lead to an enhancement of the thermal performance and the lifespan of the TES material [7].

MATERIALS PREPARATION

Sodium nitrate has been purchased from Sigma Aldrich, with a purity higher than 99,5 %. The magnesium oxide based matrix was bought as hydromagnesite from LKAB Minerals Ltd. Finally, microsized graphite was purchased from Inoxia Ltd.

In order to encapsulate the PCM into the ceramic matrix, a high porous material is needed. The purchased ceramic matrix presents porous morphology as it can be seen in the secondary electron microscopy (SEM) image, Figure 1. According to the

materials data sheet, it is compound by hydromagnesite, and huntite ($Mg_3Ca(CO_3)_4$).

Table 1 Physicochemical properties of magnesium based material as bought

Physical properties	
Specific gravity	2.4 g/cm ³
Refractive index	1.56
Surface area	11 - 17 m ² /g
Hardness (Mohs ²)	2.5
Loose bulk density	0.4 kg/ltr
Chemical composition	
Magnesium as MgO	36-39%
Calcium as CaO	6-9%
Silicon as SiO	0.2-1%

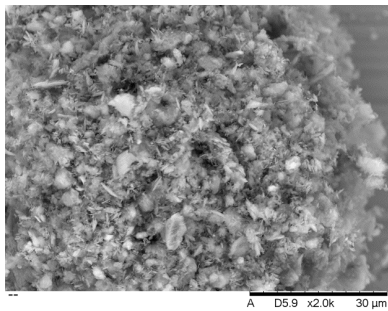


Figure 1 SEM image of the ceramic matrix as bought

The composite material's working temperature will be up to 500 °C as the PCM melts at 300°C so a pre-heat treatment has to be done to obtain a chemical stable ceramic matrix for this working temperatures, see Figure 2. The ceramic powder is placed inside a dense alumina crucible and then into a furnace. The materials is heated at 10 °Cmin⁻¹ to 350 for 30 min, and then heated at 10 °Cmin⁻¹ up to 500 °C for 30 min to decompose the hydromagnesite obtaining MgO. This process results on a weight loss of 54%.

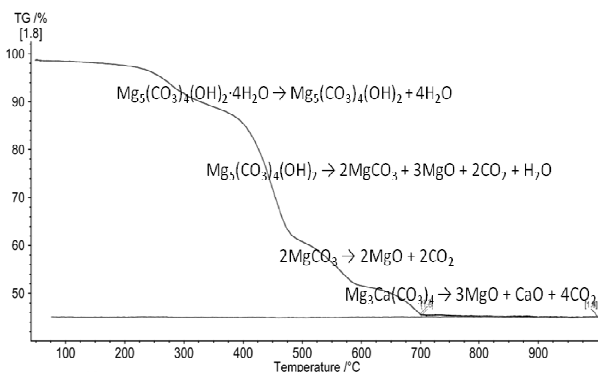


Figure 2 Thermal decomposition of magnesium based ceramic versus temperature.

The graphite particle size was tested in aqueous suspension using a dynamic light scattering (DLS) system (ZetaSizer nano ZS, Malvern Instruments, Ltd.). The samples were prepared by adding 3 mg of graphite into 5 ml of de-ionized water. After that the solution was dispersing by means of an ultrasonic bath during 5 minutes at room temperature. The result, see Figure 3 shows that the graphite powder presents a modal particle size distribution with a mean particle size of 500 μm.

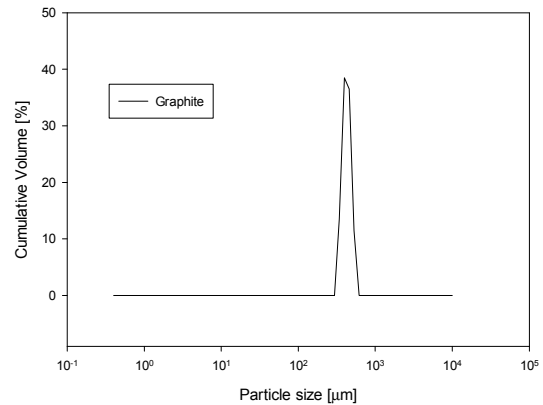


Figure 3 Particle size distribution test of graphite

Previous studies showed leakage when the amount of the ceramic matrix was reduced below 35%wt. However, with the addition of graphite the PCM that the matrix can encapsulate is up to 70% wt. Four concentrations of graphite (0, 0.5, 2 and 5%wt.) were used to analyze its effect in the composite properties. The salt was ground in a ball mill in order to reduce its particle size. After that the other components were added. To shape the mixture into tablets uniaxial compression was applied obtaining discs with 13 mm diameter, see Figure 4.



Figure 4 Three external boundary condition types

METHODS

In order to analyze the latent heat and the thermal stability of this new material for energy storage, the Simultaneous Thermal Analysis 449 Jupiter (Netzsch, Germany) was used. To perform the latent heat and thermogravimetric tests, a sample of around 25 mg was introduced in the STA pan. Both an empty pan as a reference and the sample pan were placed in the STA and the following thermal cycle was performed: isothermal of 5 min at 25°C, heating from 25°C to 350°C at 10°C/min,

isothermal of 5 min at 350°C, cooling from 350°C to 25°C at 10°C/min and finally isothermal of 5 min at 25°C. As it can be seen in Figure 5, the sample does not present any weight loss up to 350°C making the range from room temperature to 350°C suitable for this composite to work in-between.

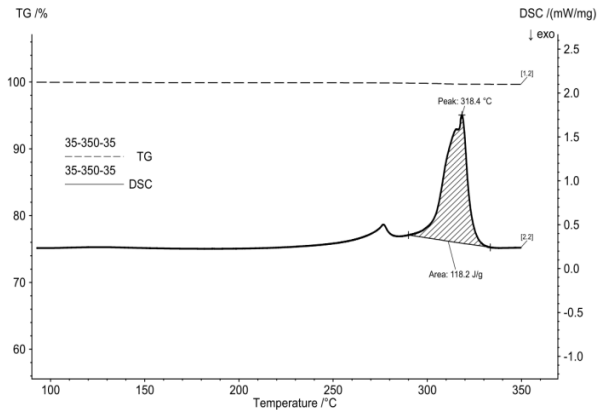


Figure 5 STA analysis of a composite with 70% NaNO₃ of PCM and 5% of Cg

Following the same steps before, a DSC analysis (DSC-2 Mettler Toledo) was performed in order to characterize the melting point, the latent heat and the specific heat of the composites. The measurements of each sample were performed three times in order to reduce the uncertainty and increase the accuracy. Sapphire calibration was also performed using the same temperature program. The latent heat was calculated as the area below the heat flow per gram of sample between 295 °C and 310°C. Both heating and cooling ramps were used for the determination of the latent heat. In Figure 6 are represented the latent heat of the composites versus the graphite fraction before and after 100 charging/discharging cycles.

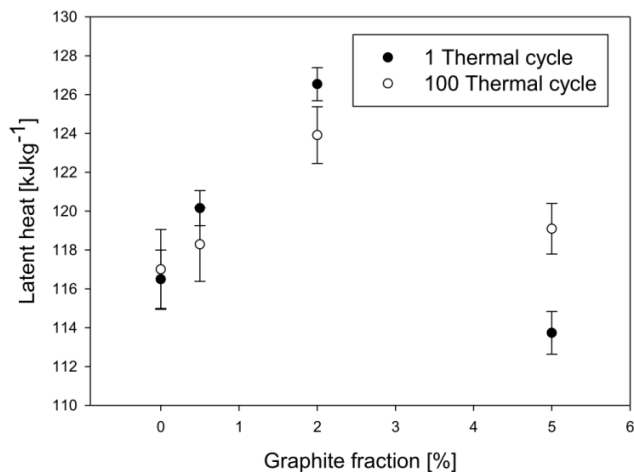


Figure 6 DSC results analysis

As it can be seen the addition of graphite slightly increases the latent heat when it is added 0.5% and 2% of Cg, whereas with 5% of graphite and after 100 cycles the composite present

a latent heat around the material without thermal conductivity enhancer.

Thermal conductivity tests were performed on Laser Flash Apparatus 427 (Netzsch, Germany). The samples were tested following the same temperature program than in the DSC. A 2mm thickness and 13mm diameter pellet was prepared. The surface of samples were flattened to obtain parallel surfaces and then coated with graphite in order to prevent direct transition of the laser beam and to help the energy transfer to the sample.

As mentioned before, one of the main drawbacks of the use of non metallic PCM's is their low thermal conductivity that make slow down the charge/discharge process. In order to improve the performance of the NaNO₃/MgO composite a thermal conductivity enhancer has been added, graphite. NaNO₃ is an inorganic salt that presents a thermal conductivity of 0.5 Wm⁻¹K⁻¹ [8] and graphite is a high thermal conductive material that according the literature its thermal conductivity is 209 Wm⁻¹K⁻¹ [9]. Figure 7 shows the thermal diffusivity measured by the LFA apparatus of different samples with different graphite content at different temperatures. As can be seen the addition of graphite increases the thermal diffusivity of the composite 15%.

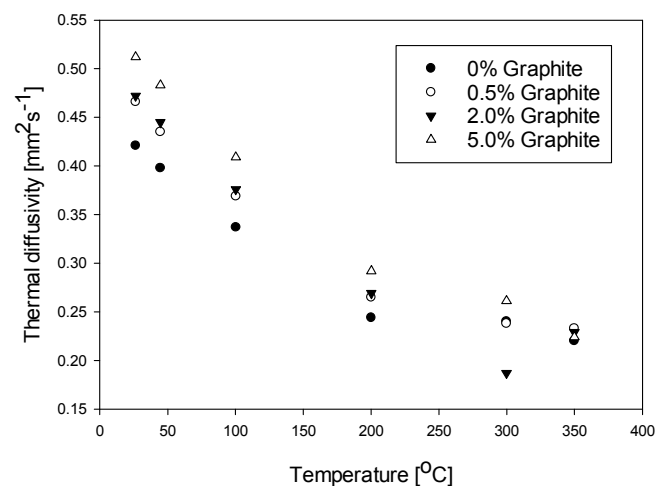


Figure 7 Thermal diffusivity results of composites with increasing content of Cg.

From the data obtained in the DSC measurements and the density, the thermal conductivity at different temperatures can be calculated (see Table 1) through Equation $\lambda = \alpha \cdot \rho \cdot C_p$.

$$\lambda = \alpha \cdot \rho \cdot C_p \text{ Equation 1}$$

where α is the thermal diffusivity measured by means of LFA, ρ is the density of the material determined by calculating the volume with a Calliper and weighting the sample tablets

pressed, and C_p is the specific heat values obtained by DSC measurements.

Table 2 Thermal conductivity of composite materials with different Cg content

T(°C)	$\lambda(\text{Wm}^{-1}\text{K}^{-1})$			
	0% Cg	0.5% Cg	2% Cg	5% Cg
350	0.48	0.50	0.49	0.55
300	0.52	0.51	0.40	0.67
200	0.53	0.57	0.58	0.70
100	0.73	0.80	0.81	0.95
50	0.86	0.94	0.96	1.09
25	0.91	1.01	1.02	1.17

In order to study the thermal properties versus charging/discharging cycles, the four compositions were tested up to 100 times. The charging step consisted on a heating ramp at $10\text{ }^\circ\text{Cmin}^{-1}$ up to $350\text{ }^\circ\text{C}$, then an isothermal step at that temperature during 5 minutes followed by a cooling at $10\text{ }^\circ\text{Cmin}^{-1}$ to room temperature. After cycled the samples 100 times they were analysed by means of XRD in order to characterize the phases presents in the composite. MgO based ceramic and Cg powder has been characterized by XRD in order to study their XRD patterns. In Figure 8 there are compared 5 XRD diffractograms, the red and blue profiles are the XRD results from the matrix and the thermal conductivity enhancer respectively and the other profiles represent the samples without being cycled(orange) and after being cycled with Cg (blue) and without (green). In the 3 composite XRD diffractogram it can be seen that the NaNO_3 , is the main compound in the composites. The main graphite pick it can be seen in the sample that presents 5% graphite at $2\theta=30.5$. Comparing the samples after being heated and cooled down 100 times it can be conclude that they are chemically stable in this process.

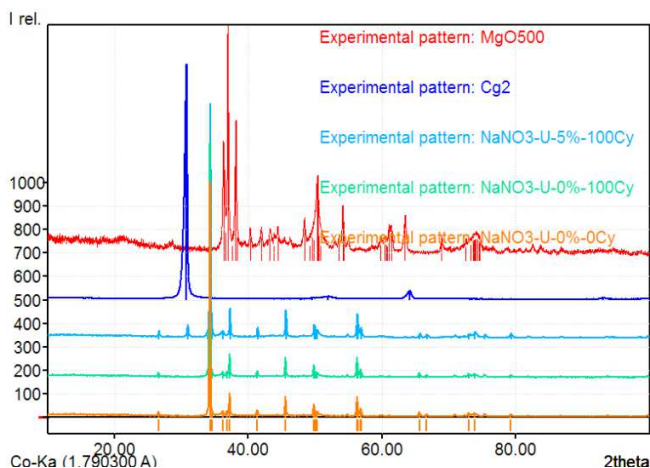


Figure 8 XRD comparison of the composites before and after being 100 times cycled

Hitachi TM-3030 has been used to study the microstructure of the composites once they have been cycled. In Figure 9 it can be seen a composite material with 0.5% and 2% of graphite. The surface of the pellet, once it is polished and prepared to be studied in the microscope shows an increment in the porosity when the graphite is added into the structure. The darker parts of the image are the graphite microsized particles distributed homogeneously in the composite. When the EDX analysis is performed, see Figure 10 it shows that the elements present in the composite are Na, Mg, Ca, N, O and C, as expected.

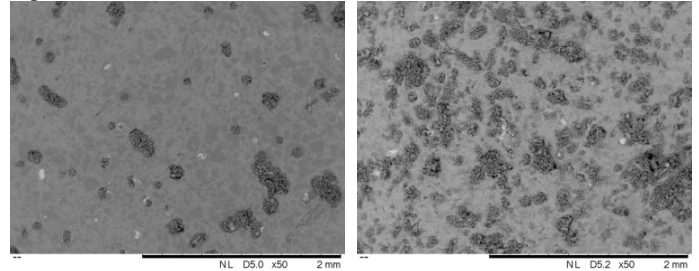


Figure 9 SEM image of the novel composite with 0.5 and 2% Cg respectively

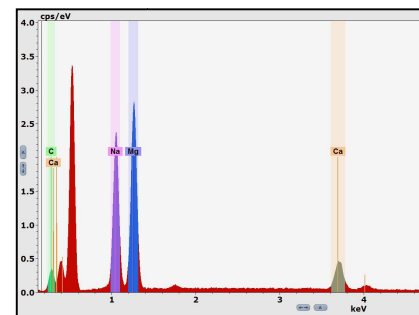


Figure 10 EDX analysis of the composite with 2% Cg

Mechanical characterization has been performed to study the compressive strength of the composites after being cycled. The mechanical properties of the composites were tested by a compressive strength machine LS100, (Lloyd Instrument) applying a constant load of 100Nmin^{-1} until the breakage. In Table 3 are summarized some characterized properties to study the composites with 2% of Cg once they have been cycled 100 times. It can be seen that the mechanical strength values slightly decrease, like the latent heat. Although thermal conductivity increases throughout the concentrations of graphite, other properties have to be taken into account such as latent heat and weight loss. Samples with 5% wt. of graphite show mass loss around 15% while samples with 2% of graphite present less than 5% of mass loss.

Table 3 Comparison of the results after 1 and 100 thermal cycles of the composite with 2%wt. graphite.

Cycles	Latent heat [kJ/kg]	Weight losses [%]	σ [MPa]
1	126.5	3.2	28
100	123.9	4.7	25

CONCLUSION

In the present study a novel composite for LHTES has been formulated. The objectives of the optimization of these formulations were to prevent the leakage of the PCM from the matrix to avoid corrosion and to study the enhancement of the thermal conductivity of the composite when graphite is added.

The results of this work show that the PCM presents higher melting point than the pure salt. However, it remains around 318°C when different contents of graphite are added. It has been proven the stability of this material with the TG experiments. These results show that the composite working temperature can be settled up to 350 °C.

One of the main improvements of the addition of graphite is the compaction structure that can be obtained. Adding graphite, the amount of PCM that can be contained into the ceramic matrix is higher at a maximum content of 70% of PCM. Adding graphite in the composite formulation was obtained an expected increase of the thermal conductivity.

After 100 cycles the main properties for TES remain almost stable showing no signs of chemical incompatibility between the materials present in the composite. The mechanical properties of the composites have not been affected after being cycled. It is possible to guarantee that the composite is able to accommodate the volume change due to the melting/solidification process of the PCM contained in the ceramic matrix.

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REFERENCES

- [1] A. de Gracia and L. F. Cabeza, "Phase change materials and thermal energy storage for buildings," *Energy Build.*, vol. 103, pp. 414–419, Jun. 2015.
- [2] D. N. Nkwetta and F. Haghghat, "Thermal energy

storage with phase change material—A state-of-the art review," *Sustain. Cities Soc.*, vol. 10, pp. 87–100, Feb. 2014.

- [3] F. Agyenim, N. Hewitt, P. Eames, and M. Smyth, "A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS)," *Renew. Sustain. Energy Rev.*, vol. 14, no. 2, pp. 615–628, Feb. 2010.
- [4] L. Fan and J. M. Khodadadi, "Thermal conductivity enhancement of phase change materials for thermal energy storage: A review," *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, pp. 24–46, Jan. 2011.
- [5] X. Py, R. Olives, and S. Mauran, "Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material," *Int. J. Heat Mass Transf.*, vol. 44, no. 14, pp. 2727–2737, Jul. 2001.
- [6] Y. Tomizawa, K. Sasaki, A. Kuroda, R. Takeda, and Y. Kaito, "Experimental and numerical study on phase change material (PCM) for thermal management of mobile devices," *Appl. Therm. Eng.*, vol. 98, pp. 320–329, Apr. 2016.
- [7] Z. Ge, F. Ye, H. Cao, G. Leng, Y. Qin, and Y. Ding, "Carbonate-salt-based composite materials for medium- and high-temperature thermal energy storage," *Particuology*, vol. 15, pp. 77–81, Aug. 2014.
- [8] D. L. T. Bauer and R. T. U. Kröner, "Sodium nitrate for high temperature latent heat storage," *The 11th International Conference on Thermal Energy Storage – Effstock 14-17 June 2009 in Stockholm, Sweden*.
- [9] J. Song, L. Ma, Y. He, H. Yan, Z. Wu, and W. Li, "Modified graphite filled natural rubber composites with good thermal conductivity," *Chinese J. Chem. Eng.*, vol. 23, no. 5, pp. 853–859, May 2015.