Research papers

A comprehensive study of the phase segregation of a urea-based phase change material tested under thermal cycling conditions

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A B S T R A C T

Eutectic mixtures are used as PCMs due to the possibility to tailor the melting temperatures and mainly because the phase transition occurs at a unique temperature. Eutectic mixtures are assumed to be congruent melting and solidification materials. Compositional segregation has rarely been reported, when have been researched for its use as PCM. However, the previous premise does not always match the observed facts. The presented work aims to deepen the knowledge regarding the use of eutectic mixtures as PCMs and to determine the influence of operation parameters in the eutectic PCMs potential phase segregation.

The eutectic mixture formed by urea and sodium nitrate can be an interesting candidate for use as a phase change material for thermal energy storage in space heating and domestic hot water applications. Nevertheless, the eutectic mixture showed an unforeseen segregation phenomenon when it was exposed to repeated melting-solidification cycles using volumes in the scale of grams. As a result, the phenomenon was studied to determine the potential causes. An experimental campaign was performed to study the urea and sodium nitrate eutectic mixture under different conditions: consisting of thermal cycling using representative masses, and subsequently, the segregated materials and obtained samples were analyzed by different techniques (including XRD, HTXRD, and DSC); and the production of samples under different cooling conditions that were analyzed using microscopy (PLM and SEM). The results established a relationship between the operation conditions, with the resulting crystal structures, which explain the phase segregation in the eutectic mixture. A mitigation measure was determined consisting of mechanical stirring.

Acronyms

TES	Thermal energy storage
LHTES	Latent heat thermal energy storage
PCM	Phase change materials
DHW	Domestic hot water
U-SN	Urea and sodium nitrate
DSC	Differential scanning calorimetry
XRD	X-ray diffraction
HTXRD	Hot temperature x-ray diffraction
PLM	Polarizing light microscopy
SEM	Scanning electron microscopy
EDX	Energy dispersive x-ray spectroscopy

1. Introduction

In recent years, thermal energy storage (TES) has become increasingly important in different engineering applications. TES allows solving the problems arising from the time lag between generation and demand for heat. One interesting TES type is the use of the latent heat involved in the solid-liquid phase transformations as the thermal storage medium. The materials employed for latent-heat thermal energy storage (LHTES) purposes are known as Phase Change Materials (PCMs).

Currently, many researchers work on the development of PCMs for different applications in buildings and some PCMs are already commercially available. However, the use of LHTES for building heating and domestic hot water systems has been investigated to a limited extent, partly because of the reduced availability of materials suitable

for the required temperature range (about 65–90 °C). PCMs should meet a long list of physical, chemical, thermodynamic, kinetic and technical parameters, which greatly reduce the feasibility of a material to become a suitable PCM. One of these requirements to be met by the PCM is congruent melting. When the liquid and the solid material have the same composition along the melting/solidification process the transformation is called congruent and the segregation does not pose any problem for the use of the material as a PCM. This is the case when pure compounds are used. However, incongruent melting happens when the PCM consists of a mixture that suffers either a transient or a persistent compositional change on the phases involved in the transformation upon the melting/solidification cycle.

Most mixtures present a semisolid melting interval instead of a unique melting temperature. In these cases, due to the segregation, the originally homogeneous PCM composition changes to form a solid with stratified composition which will not melt/solidify anymore as the original monolithic homogeneous material because it will be formed with zones of different composition, and thus different melting temperatures. To retrieve the latent heat stored in the initial material in a reproducible way, the correct composition of the mixture constituents is required throughout the whole sample [1]. Thus, the phase segregation can severely reduce the storage density because the latent heat on solidification cannot be released completely, sometimes only to a small fraction. To prevent this situation, PCM eutectic mixtures have been sought for [2–7]. They present a single melting temperature. When the molten eutectic mixture is cooled down and reaches the eutectic temperature the two solid phases form from the liquid, presumably at the same time, precipitating together and thus resembling the solidification behavior of pure compounds. In this context and due to favourable thermal, economic and environmental characteristics, the authors of the present article have been working on the development and characterization of the urea and sodium nitrate eutectic mixture to be used as a PCM for domestic hot water (DHW) and space heating application. The eutectic mixture is formed by 71.25 wt% urea and 28.75 wt% sodium nitrate, has a melting point of 85 °C, a melting enthalpy of 172 J/g, a price below 1 euro/kg and is formed by two biodegradable materials, usually employed together for soil fertilizer. Besides, this mixture poses a high volumetric energy density of 245 MJ/m^3, with a material specific weight of 1.48 g/cm^3 at 25 °C (solid) and 1.423 g/cm^3 at 89 °C (liquid). Thus, this mixture is a good PCM candidate for latent heat thermal energy storage (LHTES) for domestic hot water and other building applications.

The phase diagram of the urea-sodium nitrate system and the main thermal properties of the eutectic composition have been previously researched and reported [8,9]. During this research, phase segregation was observed when the material endures several melting-solidification cycles [10]. The phase segregation did not take place when small samples were submitted to quick thermal cycles in the DSC, nor when a large volume of material remained molten for a long time in a closed container, without thermal cycling.

Compositional segregation has rarely been reported, or even mentioned, when eutectic mixtures have been researched for their use as PCM. Congruent melting and solidification has generally been assumed in those cases [3,5,11]. However, Rathod and Banerjee [4] indicated that the stability of the eutectics had not been sufficiently researched to ensure their long-term performance.

The assumption that the eutectic mixtures solidify by producing both solid phases together does not always match with the observed facts. In addition to being an uncommon phenomenon, the reasons why few articles studying PCM eutectic mixtures report phase segregation may include the fact that the published research has generally been carried out in small containers, most of them consisting in DSC crucibles. The sample volume is important when it comes to phase segregation [12]. The typical DSC crucible height might be too small to produce any segregation. When larger containers are used, effective phase segregation can occur, preventing the segregated components of having a good

contact with each other during the thermal cycling process. Therefore, using the same mixture the phase segregation was observed in a T-history experiment while not in a DSC measurement, as it is the case of the semicongruent melting of CaCl$_2$·6H$_2$O [13].

Presently, the scientific literature discusses two main hypothesis to explain the macro-segregation phenomenon of eutectic mixtures: the natural convection during solidification [14–16] and, more recently, the material supercooling [17,18]. However, crystallization related aspects (mainly the eutectic formation and macrostructure) could provide an additional explanation, which has been insufficiently researched. In order to get a deeper understanding of the phase segregation phenomena in PCMs, the following paragraphs gather the most outstanding findings regarding these aspects.

i) Convection in metallic alloys can cause long-range transport of individual species, leading to macro-segregation (Boettinger and Banerjee [16]). Khadivinassab et al. [14] point out that macro-segregation occurs when the alloying elements are transported over lengths larger than the grain size, causing depletion or enrichment of the solute levels within the sample. Flemings [15] and Heinrich [19] report that, under natural convection, the cause of segregation can be related to the interdendritic flow phenomenon (flow of enriched melt exuded near the dendrite arms solidification-surface).

ii) The supercooling phenomenon provides a different explanation to understand the segregation phenomenon in eutectic mixtures. Authors point out that the instability introduced by supercooling causes a change in the eutectic composition. Lane [20] indicated that when one of the components in an eutectic mixture presents supercooling while the other one solidifies on the melting temperature, segregation might occur although it does not usually happen. Gunasekara et al. [21] added that eutectic mixtures do not pose compositional segregation if supercooling is absent. Upon supercooling, the phase separation is understood using the lever rule on the supercooled phases in the phase diagram.

iii) The crystallization behavior of eutectic mixtures has been widely studied in metallurgy. The kinetic aspects of the eutectic formation is a complex process involving many different parameters, and as a result leading to different microstructures. Several eutectic typologies have been defined according to different aspects, like the crystal growth mechanism or the microstructure morphology. Also, the mechanisms that drive the eutectics to segregate and to report macro-segregation have been analyzed in metallurgical alloys [14,22,23]. The literature reports that there is a strong relationship between the crystallization conditions (specially the cooling rate), the obtained eutectic typology, the supercooling, and the macro-segregation [24,25].

Summarizing, several parameters may have a synergic responsibility on the phase segregation occurring in eutectic mixtures. The present study aims to analyze the phase segregation phenomenon observed in the urea and sodium nitrate eutectic mixture after several melting and solidification cycles took place. The research analyzes the phase segregation phenomenon occurred in the mixture under various cooling rates and different container configurations. The objective is to understand the mechanisms that cause it (supercooling, convection or crystallization related parameters) and their interrelation.

The produced eutectic microstructures have been analyzed to determine whether there could be a relationship between the phase segregation and the attained eutectic microstructure. Potential prevention methods or ways to regenerate the material and to evaluate its suitability as a PCM have also been studied.

Taking into account that phase segregation may affect many eutectic PCMs, the study of the urea and sodium nitrate eutectic mixture also aims to contribute to get knowledge regarding on the behavior of eutectic mixtures under real operation conditions and representative

masses. No studies regarding in-depth study of the variables that influence the phase segregation on eutectic mixtures were found in the literature.

2. Experimental

The experimental work was set up to determine the influence of different parameters on the phase segregation observed in the urea and sodium nitrate eutectic mixture (onwards referred to as U-SN eutectic) from the macro, micro, physical and thermal point of view. Several studies were performed: thermal cycling, crystallization under isothermal and dynamic conditions to determine the resulting crystal structure, morphological analysis and phase determination.

Thermal cycling tests at macro scale were carried out to determine the influence of the cooling rate, supercooling and volumetric configuration in the quantity of the phase segregation. The sample temperatures were monitored during the tests. Microscopy was used to evaluate the influence of the cooling rate in the structures formed. Additionally, X-Ray diffraction was used to determine the phases formed and Differential Scanning Calorimetry to determine their thermal behavior.

Fig. 1 schematically shows the experimental study carried out for determining the underlying mechanisms of the phase segregation of the U-SN eutectic. Table 1 gathers the identification of the equipment employed to carry out this study. Each experimental campaign is described with more detail in the following subsections.

2.1. Sample preparation

A sample batch containing 50 g of the U-SN eutectic mixture, composed of 71.25 wt% of urea and 28.75 wt% of sodium nitrate, was prepared by using pure urea and pure sodium nitrate (both 99.9 % purity) supplied by Sigma-Aldrich. After weighted, the materials were introduced into a glass flask, closed with a rubber plug. They were subsequently immersed into a glycerine bath at 95 °C until fully molten and continuously stirred to promote a good temperature homogeneity. The molten material was distributed into the corresponding testing tubes (or glass sample holders, see Section 2.3.1), filling in with 4–5 g of the molten mixture in each tube. The tubes were placed into a desiccator with phosphorus pentoxide as desiccating agent until complete solidification occurred, in order to prevent any water absorption. Afterwards, the tubes were hermetically sealed with threaded plugs and gaskets, and kept in a cabinet until use.

Table 1
Analytical techniques used for the evaluation of the tested samples.

Analytical technique	Brand	Model
Differential Scanning Calorimetry (DSC)	Mettler Toledo	DSC1
X-Ray Diffraction (XRD)	Philips	X'pert Pro
High-Temperature X-Ray Diffraction (HTXRD)	Bruker	D8 Advance-HTK2000 camera
Powder Diffraction File (PDF) database	–	–
XRD data treatment software	PANalytical	X'pert HighScore
Photography	Panasonic	DMC-FZ100
Polarizing Light Microscopy (PLM)	Leica	DMLP
Scanning Electron Microscopy (SEM)	Jeol	JSM-7000-F
EDX spectrometer	Oxford Instruments	INCA Energy 350
Weight scale (0.1 mg accuracy)	Ohaus	Discovery 114C
Thermostatic bath with Bluesil 47 V20 silicone thermal oil	Lauda	RP845

2.2. Thermal cycling tests

The objective of this experimental campaign is to evaluate the influence of the cooling rate, the supercooling and the volumetric configuration on the phase segregation of the samples submitted to thermal cycles. Test tubes filled in with the PCM were immersed into a programmable thermostatic oil-bath where the material was thermally cycled under different thermal process conditions.

Tests were carried out using two different container configurations in order to evaluate the influence of the volumetric configuration on the phase segregation and to assess whether convection had an important role in macroscopic segregation. The containers consist of test tubes with similar dimensions (see Fig. 2), one vertically immersed into the silicone oil bath while the other one is immersed in a horizontal arrangement. Natural convection within the liquid should predictably be more significant in the vertical arrangement than in the horizontal one. The vertically immersed tubes were filled up to 80 % of the full available volume (up to 80 mm height). The horizontally immersed tubes had equivalent dimensions to the vertical tubes, but with different feeding configuration as shown in Fig. 2. When immersed into the oil, they formed an inverted "T" and accordingly, the PCM height was 4 mm.

To evaluate the influence of the cooling rate on the phase segregation, tests were carried out under two cooling rates: 2 °C/min (deemed as "fast") and 0.3 °C/min (deemed as "slow"). The cycling was carried out in the following temperature range: 25–95 °C. The horizontal and vertical samples were tested together, both of them simultaneously immersed in the same bath. A T-type thermocouple (accuracy ±0.5 °C) was placed inside the PCM in one sample per testing batch to monitor
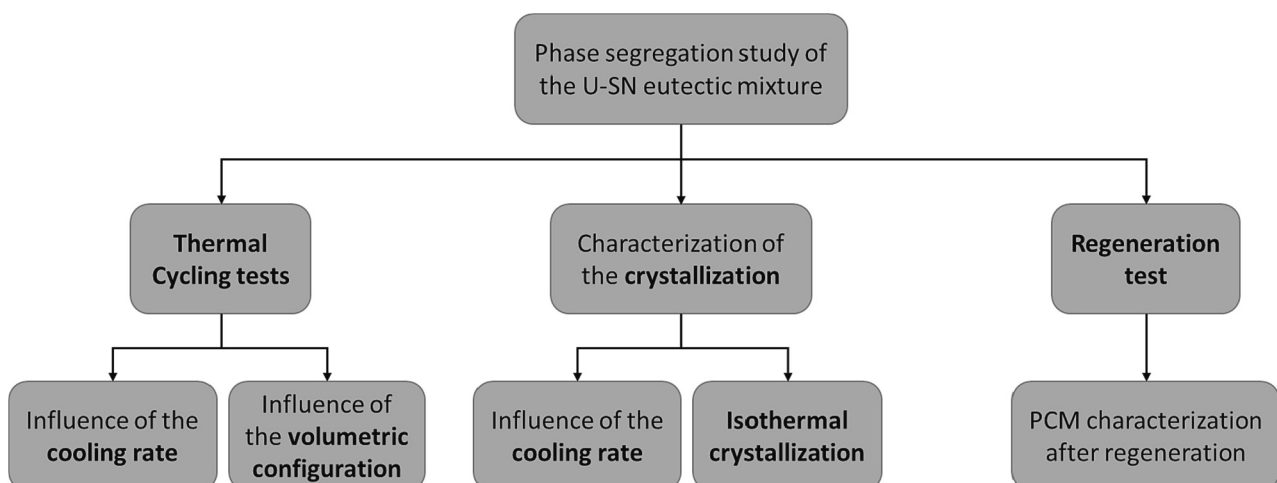

Fig. 1. Schematic representation of the phase segregation study of the U-SN eutectic mixture.
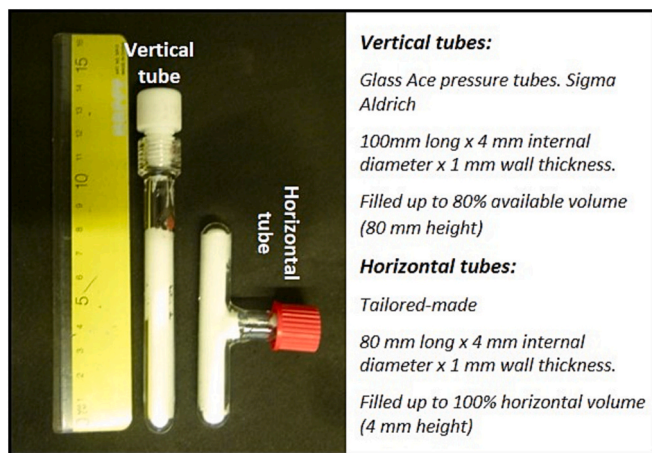
Fig. 2. Tubes used for tests (thermal cycling and nucleation and crystal growth assessment) on vertical and horizontal arrangement, containing the same sample mass (4–5 g).

the temperature and to determine the melting and crystallization temperatures in each case. Table 2 gathers the testing conditions employed in this experimental campaign.

After the thermal cycling tests finished, the samples were analyzed by means of visual inspection and XRD of the segregated zones. Visual observation, aided with photography, was used as the main assessment method to determine if solid phase segregation took place during the solidification process along the thermal cycles. This is a qualitative method but, due to the volume size of the samples, differences of the segregated volume in different samples were both, significant and clearly distinguishable.

X-ray diffraction (XRD) of the raw materials (pure urea and pure sodium nitrate), the fresh (non-cycled) eutectic mixture and the segregated materials from thermally cycled samples, were carried out (the specific XRD procedure is described in Section 2.5). The segregated materials were extracted from the segregated zones of a specimen submitted to 33 cycles at 0.3 °C/min, one sample from the bottom, one from the top and one from the middle.

2.3. Characterization of the crystallization under different cooling conditions

To provide a meaningful understanding of the relationship between the cooling conditions, the phase segregation after thermal cycling and the morphological features of the solidified product, several aspects related to the crystallization of the U-SN eutectic mixture were observed and analyzed.

Table 2
Experimental conditions of the thermal cycling tests in the temperature range of 95 to 25 °C. Samples contain 4–5 g of U-SN eutectic mixture.

Number of cycles	Cooling rate	Configuration	Number of samples	Observations
90	2 °C/min	Vertical	4	One sample with thermocouple immersed into PCM
33	0.3 °C/min	Vertical	4	One sample with thermocouple immersed into PCM
16	0.3 °C/min	Vertical	1	No temperature monitoring
		Horizontal	1	No temperature monitoring

2.3.1. Influence of the cooling rate - analysis of microstructures produced under different cooling conditions

Due to the low melting point of the U-SN eutectic, it is not possible to prepare traditional metallographic samples. As a result, samples were produced by pouring the molten U-SN mixture on top of glass sample holders to form a thin flat layer of the material. Four samples were prepared following two different cooling conditions. Samples 1 and 3 were produced by pouring liquid U-SN eutectic at 95 °C onto a glass holder at room temperature, thus solidifying by quenching, and placing a glass coverslip onto it to produce a very thin layer. Samples 2 and 4 were produced by pouring liquid U-SN eutectic at 95 °C onto a glass holder at 80 °C, inside a heating cabinet, thus solidifying under near-equilibrium conditions.

The samples were analyzed by optical and electronic microscopy and the phase evolution with the temperature was studied by means of HTXRD and DSC. The procedures are described in Section 2.5.

2.3.2. Determination of the crystallization under isothermal conditions

Samples prepared following the methodology described in Section 2.1, one in a horizontal tube and one in a vertical tube, were molten at 95 °C in the thermostatic bath and then cooled down to the eutectic mixture melting point, 85 °C. Subsequently, the thermostatic bath temperature was reduced in 1 °C and held at that temperature for 1 h to determine (by means of visual recognition) whether crystallization occurred during that time. This procedure was repeated by decreasing the set-temperature in 1 °C each time, to 84 °C, 83 °C and 82 °C, until crystal formation was visualized during the soaking period. The experiment was performed twice. In the second experiment, the first crystals formed in the liquid were extracted by a pair of tweezers and stored in a glass vial inside a desiccator until they were finally grounded and analyzed by means of XRD.

2.4. Regeneration of the material after segregation

In order to evaluate the reversibility of the phase segregation, the following test was performed. After the thermal cycling tests were carried out, two samples that had been tested for 33 thermal cycles at 0.3 °C/min, clearly exhibiting three segregated zones, were gently stirred by hand with the result of complete sample melting. The resulting liquid (after stirring and complete dissolution) was left to solidify into a desiccator and the obtained solid was ground and analyzed by XRD and DSC. These techniques were used to determine whether the composition and/or the thermal properties were different from those of the original eutectic mixture and if any irreversible damage could have occurred.

2.5. Analytical and microstructural characterization

The analysis of the materials was carried out aided with several different techniques, detailed next. The identification of the equipment used can be found in Table 1.

2.5.1. X-ray diffraction XRD

The specific methodology employed for the XRD measurements has been described with detail in [6]. All the samples analyzed by XRD were manually ground in an agate mortar and stored in a desiccator until the XRD took place.

2.5.2. Polarized light microscopy PLM

The microstructure was observed by transmitted polarized light microscopy PLM. The samples produced onto glass holders, were observed without any further manipulation or preparation.

2.5.3. Scanning electron microscopy and energy dispersive x-ray spectroscopy EDX analysis

Observation and microanalysis in the SEM was carried out under 10 kV using a beam current of the order of 0.1 nA. Secondary electrons and

backscattered electrons imaging were employed, as well as EDX chemical identification. The samples were coated with a Carbon layer of about 20 nm produced by evaporation under vacuum using a Quorum Technologies Q150T ES coater.

2.5.4. High-temperature x-ray diffraction HTXRD

Used to determine the evolution of the crystalline phases with the temperature from 30 °C to 94 °C. One measurement was carried out every 2 °C. The XRD scan time was 19 min for each time step. The samples diffraction area was 50 mm². Samples were diffracted as produced, without any grinding or other type of processing. A desiccant agent was introduced into the X-Ray diffraction cabin to avoid water uptake and any subsequent modification of the U-SN eutectic phases due to a third component in the system.

2.5.5. Differential scanning calorimetry DSC

The DSC measurement procedure used for the thermally cycled samples is fully described in [6]. The temperature program consisted on two heating ramps and one cooling ramp, all at 1 °C/min rate. Isothermal segments of 10 min took place on either side of the dynamic segments. The first heating segment serves to settle the sample on the bottom of the crucible to achieve a good contact. The thermal properties were determined from the first heating ramps for experiments described in Section 2.3.1, and from the cooling and the second heating ramps for experiments described in Section 2.4.

3. Results

The results of the experimental tests: *thermal cycling, characterization of the crystallization under different cooling conditions and regeneration of the material after segregation* are shown in the following sections.

3.1. Thermal cycling tests: Phase segregation assessment

During the thermal cycling, phase segregation was observed: solid particles gradually appeared on the top and the bottom of the samples that did not fully melt along the subsequent thermal cycles. Consequently, above the original melting temperature, the samples exhibited three zones: solid particles at the top (translucent crystals), solid particles at the bottom (tiny white crystals), and liquid in the middle zone. In all cases, the segregated volume increased with increasing the number of cycles. However, the segregated volume also depended on the cooling rate.

3.1.1. Influence of the cooling rate

Segregation took place under both cooling rates employed in the study. Fig. 3 shows the evolution of the segregation obtained during the melting/solidification cycles, for a cooling rate of 0.3 °C/min and 2 °C/min.

The segregation per cycle was higher in the samples exposed to 0.3 °C/min. After only 8 cycles, the segregated solid in these samples was visually 3–4 times larger than the solid segregated in the samples tested under 2 °C/min. The difference was easily appreciated at plain sight, as it can be seen in Fig. 3. The segregates obtained in the samples after 33 cycles under slow cooling rate show a significantly larger segregated amount than the samples submitted to 35 cycles under high cooling rate.

The thermocouple immersed into the PCM provided the determination of the crystallization temperature in every cycle. The thermal cycling tests showed that the U-SN eutectic presents supercooling when submitted to both, high and low cooling rates. The supercooling was larger with larger cooling rate. Fig. 4 shows the supercooling of the samples tested under both cooling rates for 33 cycles. It can be noticed that the tests carried out at 2 °C/min cooling rate present random crystallization temperature in the first cycles. This is due to the stochastic nature of supercooling and the fast cooling rate. After some
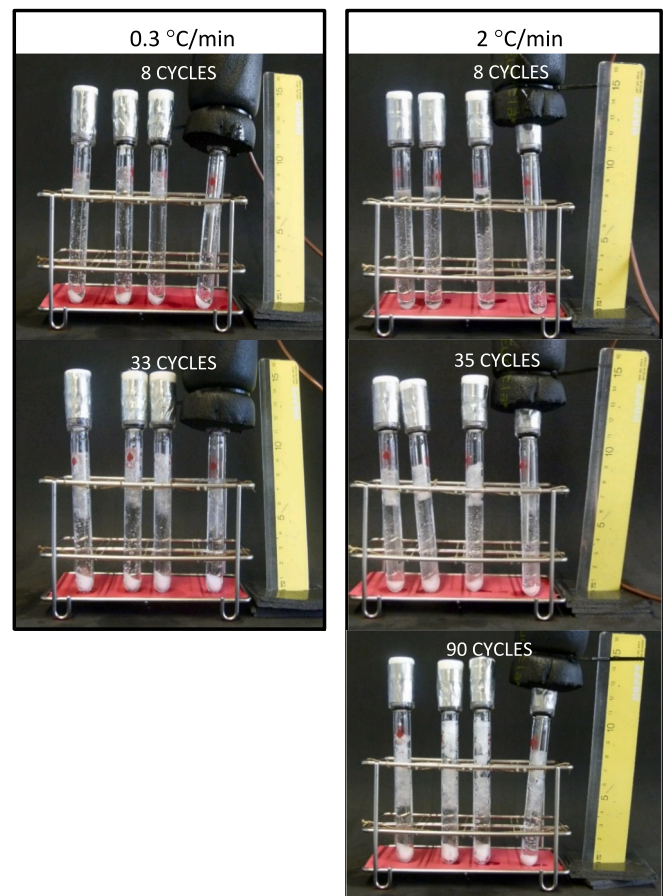

Fig. 3. U-SN eutectic samples presenting phase segregation after a selected number of thermal cycles at cooling rates of 0.3 °C/min and 2 °C/min. Photographs of the samples taken at 95 °C.
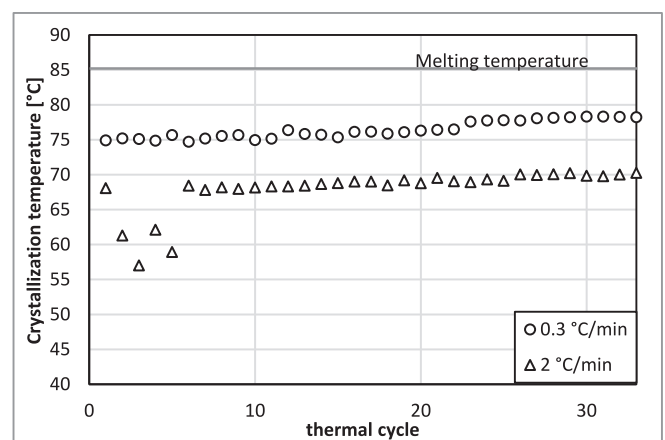

Fig. 4. Crystallization temperature of monitored samples during thermal cycling (25 °C-95 °C) under cooling rates of 0.3 °C/min and 2 °C/min.

thermal cycles, phase segregation became visually evident and the measured crystallization temperature stabilizes around a value of 68–70 °C, corresponding to a supercooling of 15–17 °C. In the case of the tests carried out at 0.3 °C/min cooling rate, the measured crystallization temperature ranges from 75 to 78 °C, corresponding to a supercooling of 7–10 °C. Under both cooling rates, the supercooling degree subtly diminishes with the number of cycles, which is deemed to the pre-existence of crystals (due to the phase segregation), which promote

the crystallization according the heterogeneous crystallization theory [26,27].

The results raise some questions since the largest supercooling registered correspond to a sample tested under 2 °C/min cooling rate, which showed smaller phase segregation than the others when the thermal cycling experiments concluded. Then, if the supercooling could be the cause of the phase segregation, as one of the hypothesis in the literature considers [18,28,29], taking into consideration our results there cannot be a direct link between the supercooling degree and the proportion of segregates. There must be other mechanisms and/or parameters influencing the macrosegregation behavior.

3.1.2. X-ray diffraction XRD of the segregated material

Fig. 5 shows the XRD diffraction patterns of the solids segregated on the top, middle and bottom of the tubes after 33 thermal cycles, using a cooling rate of 2 °C/min, as well as those of the pure urea, pure sodium nitrate and the fresh eutectic mixture.

The peaks-position showed that no new phase formed in any of the studied cases. Only urea and sodium nitrate were present in the cycled samples. As a result, it can be concluded that the mixture did not decompose or degrade to a significant amount. The peaks relative intensity and their position serve to evaluate the compositional changes in a qualitative manner, taking the diffraction pattern of the original U-SN eutectic mixture as a reference. Specifically, the relative intensity of the peaks corresponding to urea, placed at the 2Theta position of 22.5°, and sodium nitrate, placed at the 2Theta position of 29.6°, can be used to determine the differences of the segregated materials. At a first glance, the patterns corresponding to the segregated top and bottom zones are different from each other. The pattern of the upper portion show both urea and sodium nitrate peaks. Their relative intensity indicates a larger proportion of urea than the reference material: it has a urea content larger than the eutectic composition. On the other hand, the diffraction patterns of the specimens from the bottom portion of the tubes show almost no urea, only sodium nitrate peaks are appreciated. Thus, the solids on the bottom of the tube are sodium nitrate crystals. It must be remarked that the specimens were extracted after full solidification took place, carefully cutting them out from the selected zones in the sample.

3.1.3. Influence of the volumetric configuration: vertical and horizontal arrangements

The samples show the phase segregation, both when horizontal and vertical geometrical dispositions are used. Fig. 6 shows the segregation in the horizontal and vertical samples after 16 cycles. It can be noticed that segregation occurs in both tubes, and the horizontal tube has similar
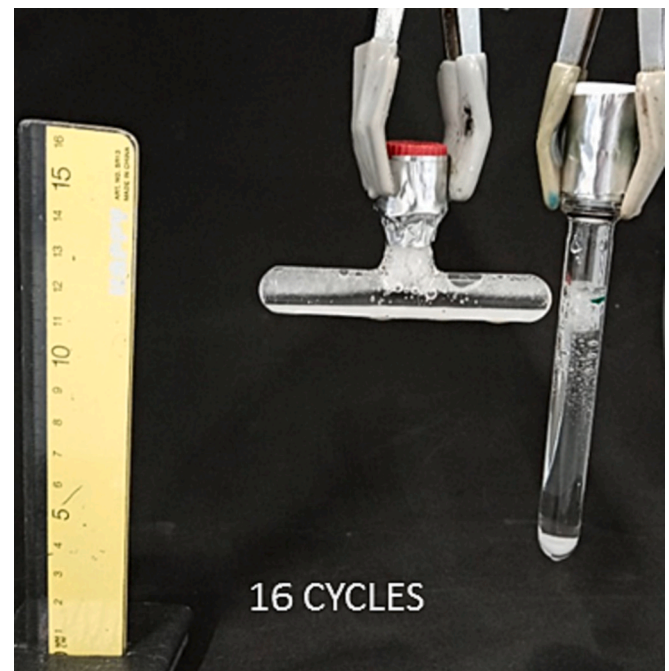

Fig. 6. Tests carried out with the U-SN eutectic PCM for 16 melting/solidification cycles.
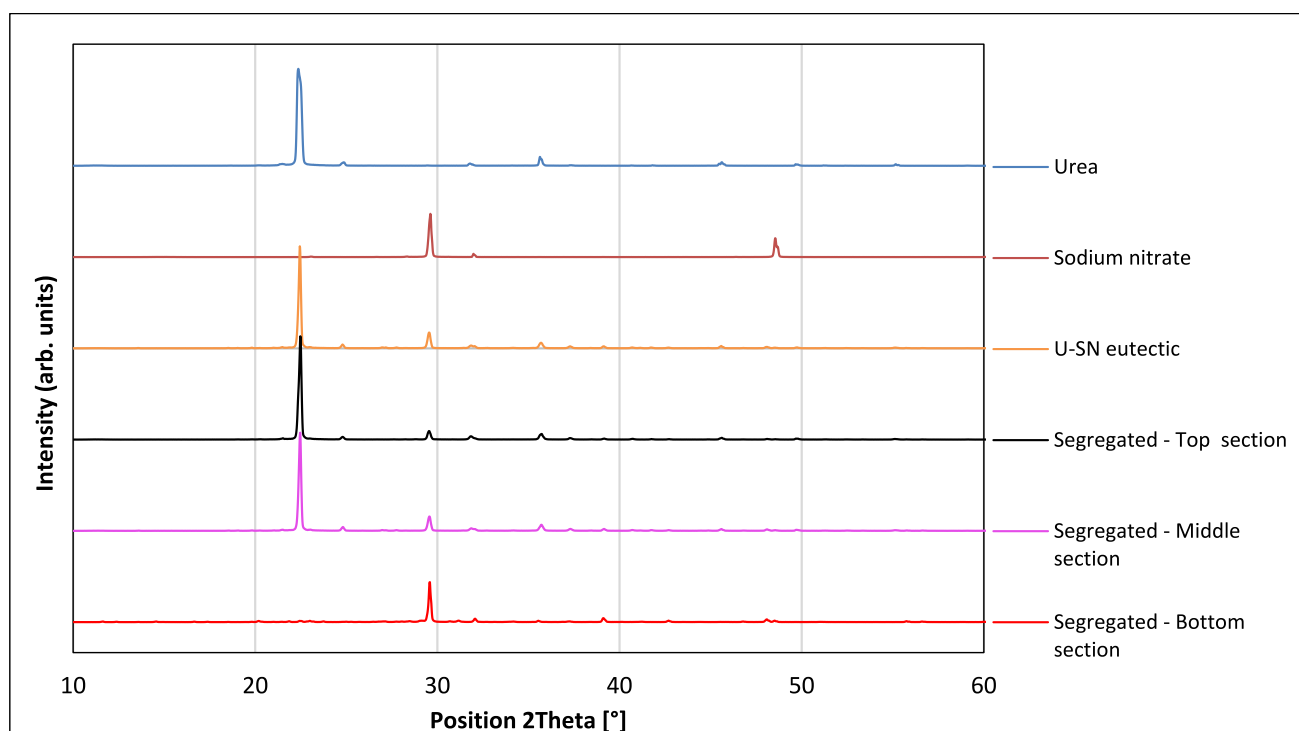

Fig. 5. X-ray diffraction patterns of pure urea, pure sodium nitrate, original eutectic mixture, and the top, middle and bottom sections of a segregated sample.

or slightly greater segregated volume (note that the tube curvature might distort the image of its content, hindering a clear comparison between the tubes). This suggests that convection did not play an important role in the phase segregation. If that would have been the case, the vertical tube should have shown a considerably larger volume of segregated solids than the horizontal tube, due to the higher natural convection of the vertical configuration. Nevertheless, the herein observed results are suitable only when small volume samples are employed and, the influence of the convection on the phase segregation could be significant if considerably larger volumes are used.

As shown along this section, the tested samples exhibited a greater segregation proportion when low cooling rates are used. The reasons for this behavior are not clear, but a plausible explanation is the formation of different microstructures depending on the cooling conditions; thus, the next section is devoted to the characterization of the crystallization under different cooling conditions.

3.2. Characterization of the crystallization under different cooling conditions

The objective of this section is to study the type of eutectic microstructure of the U-SN mixture obtained in different working conditions and its potential influence on the phase segregation. The eutectic morphology and the phase segregation are related to each other, specifically to the type/size of the eutectic microstructure. Irregular eutectics are heterogeneous and therefore the eutectic spacing varies widely in different zones. As a result, in those zones where the eutectic spacing is large, they are prone to phase segregation [22].

3.2.1. Influence of the cooling rate

3.2.1.1. U-SN eutectic microstructural and morphological analysis – Microscopy. The microstructure of samples solidified under different cooling conditions was observed and analyzed by visual inspection (macro photography), PLM and SEM, the latter including compositional analysis. Specific samples were prepared for this study, described in Section 2.3.1. The different cooling conditions produced different morphological features, distinguishable from each other under visual inspection, without the need of a microscope. Fig. 7 gathers some representative macrographs and micrographs (PLM) of samples 1 and 2. Sample 1 solidified by quenching from the liquid to room temperature. Sample 2 crystallized in conditions close to the equilibrium, at 80 °C.

From the images in Fig. 7 a and d, it can be inferred that high cooling rates lead to the formation of different morphological microconstituents. High cooling rate (Fig. 7 a) produced spherulites and rhombohedral crystals (Fig. 7 b) and some small morphological elements (Fig. 7 c), poorly distinguished by the employed microscopy technique.

Low cooling rate (Fig. 7 d) produced large spherulites. No other

morphological feature could be identified by means of the polarized light microscopy technique (Fig. 7 e and f).

The samples were subsequently observed and analyzed in the SEM. Backscattered electrons were used to observe the microstructure. Backscattered electrons serve to distinguish microstructural features with different composition because the microconstituents that contain heavier elements in their chemical composition produce higher intensity signals than those with light elements in the composition. Microconstituents containing heavier elements are seen as bright light-grey or white colored features. The microconstituents composed of low atomic weight elements render darker features, dark grey to black. In any case, the composition of the different microstructural features was analyzed by EDX of selected crystals.

Fig. 8 shows a micrograph of sample 2 together with the EDX spectrum of the different crystal formations observed in it. The EDX peaks corresponding to the darker crystals indicate the presence of Carbon, Oxygen and Nitrogen, which match with the urea ($CO(NH_2)_2$) elemental constituents. The EDX spectrum of the lighter crystals indicates Sodium, Carbon, Oxygen and Nitrogen peaks, which corresponds to sodium nitrate ($NaNO_3$). The presence of Carbon in the analysis corresponds to the Carbon coating required onto the samples to make them electrically conductive for SEM observation.

Fig. 9 shows SEM images of samples 1 and 2 at increasing magnifications. The observation and microanalysis of the microstructure was greatly limited due to the low melting point of the U-SN eutectic mixture. When large magnification is required (or during the microanalysis on small areas), the electron beam focuses on a tiny area and heats up the material. Since the melting temperature of the material is low, the electron beam intensity is high enough to promote diffusion and the decomposition of the phases present in the samples and in some spots local melting occurred. Indeed, it was possible to observe in front of our eyes the morphological evolution taking place in sample 1 while focusing at high magnification onto some grey fibers and particles. Areas which initially were homogeneous, featureless zones, evolved to become a dark grey zone with small light-grey particles embedded into it. The light grey precipitates are sodium nitrate, precipitating onto the dark-grey urea matrix from the decomposition of a phase, which could be a supersaturated solid solution or a different metastable phase.

In all the cooling conditions used in this study, the mixture crystallizes forming "irregular type" eutectic structures, which according to the literature are prone to show phase segregation [14,22,23] (regular structures would be the case of eutectic lamellar or rod-like features [30]). Several different microstructural features can be distinguished, ranging from large columns, to prismatic crystals, fibrous crystal clusters and small precipitates. The lower the cooling rate the larger the size of these crystals.

Columnar crystals are stout long prisms with a column-like appearance. Dark-grey large columnar grains of different sizes were observed
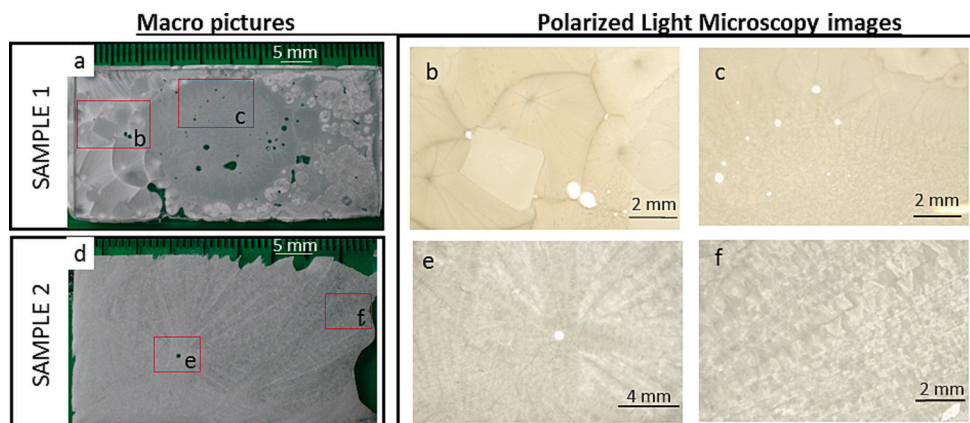

Fig. 7. Microstructure of samples obtained under different cooling conditions: Sample 1 quenched from melting to room temperature. Sample 2 solidified in conditions close to equilibrium. The red rectangles on the macrographs (left) correspond to the zones shown in the micrographs depicted on the right. The images were obtained by macrophotography and Polarized Light Microscopy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
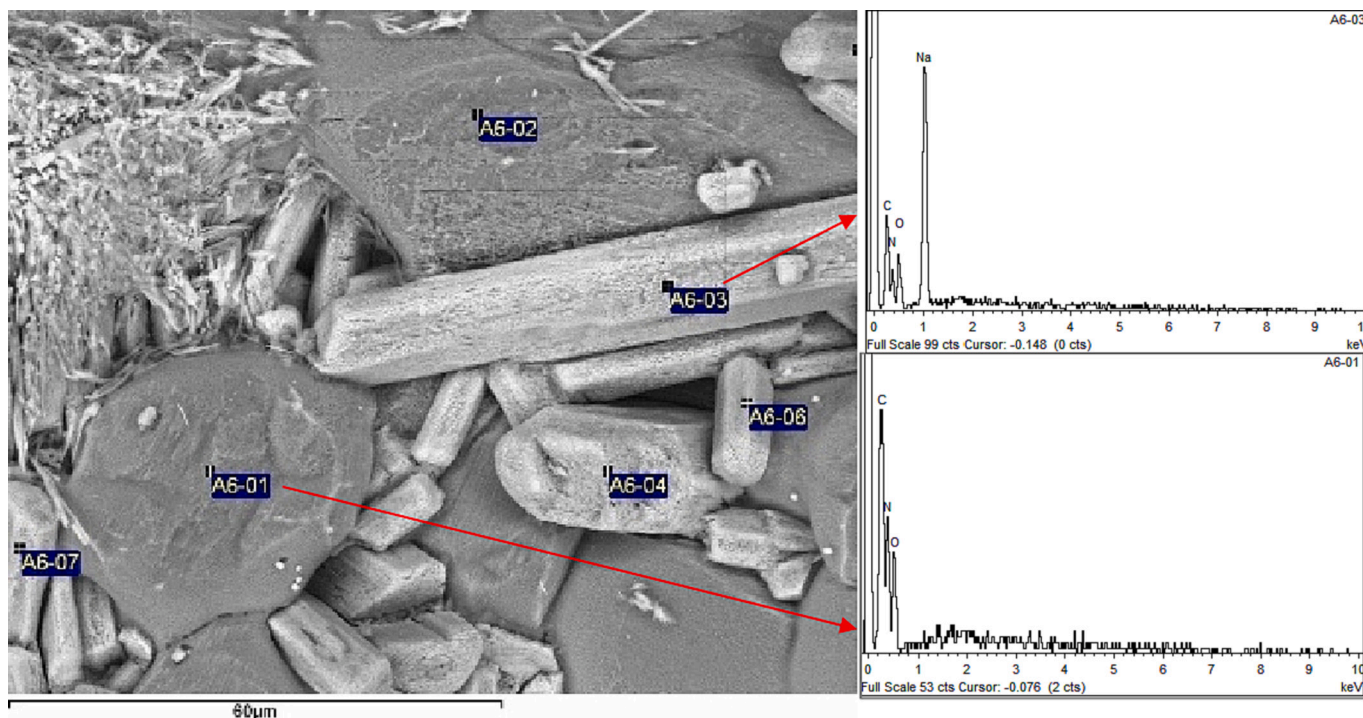
Fig. 8. SEM Micrograph of the U-SN eutectic mixture solidified under very low cooling rate (sample 2). Backscattered electron image, including EDX analysis of the grains indicated on the image. Lighter zones correspond to sodium nitrate, and darker zones correspond to urea.
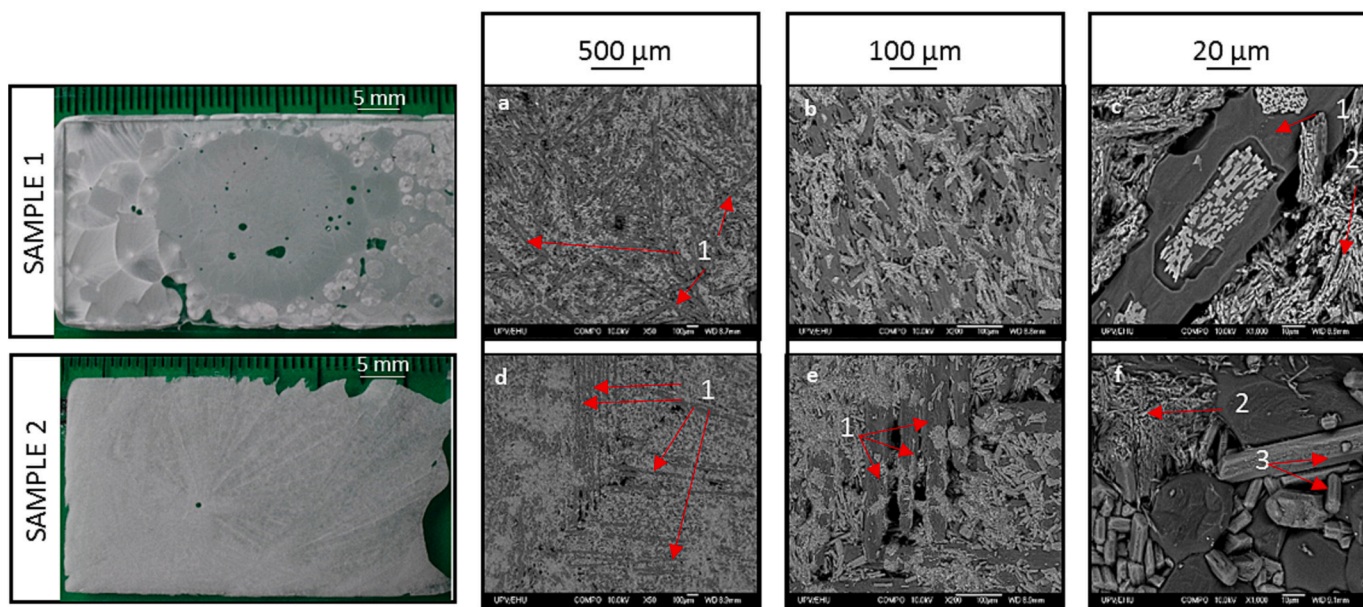

Fig. 9. Macro pictures and SEM backscattered electrons images of U-SN samples produced under different cooling conditions. The arrows included in the images point out the different type of microstructural features visualized on the images (1:columnar, 2: fibrous, and 3: prismatic crystals).

in all the samples as shown in Fig. 9 (corresponding to features identified with number 1 on all the pictures gathered in that figure). They are composed of urea and can be considered the main crystallization habit of this compound. These columnar grains have a length up to 0.4 to 0.8 mm in the case of samples 1, and as long as 20 to 30 mm in sample 2. The fact that the samples were purposefully produced as a thin layer led to horizontally grown long columns and small prismatic crystals perpendicular to the sample holder direction (which are vertically grown up

columns). The long columns on sample 1 (quick cooling) were composed of supersaturated metastable urea. When the electron beam focused on small areas of these columns, sodium nitrate precipitates formed. Fig. 10 (b and c) shows the sodium nitrate precipitated into some urea crystals.

Well-developed prismatic elongated grains, with opposite faces parallel to one another, often striated along their length or across their width were present only in sample 2 (very slow cooling). These prisms, present in different sizes, can be observed in Fig. 9 f labelled with
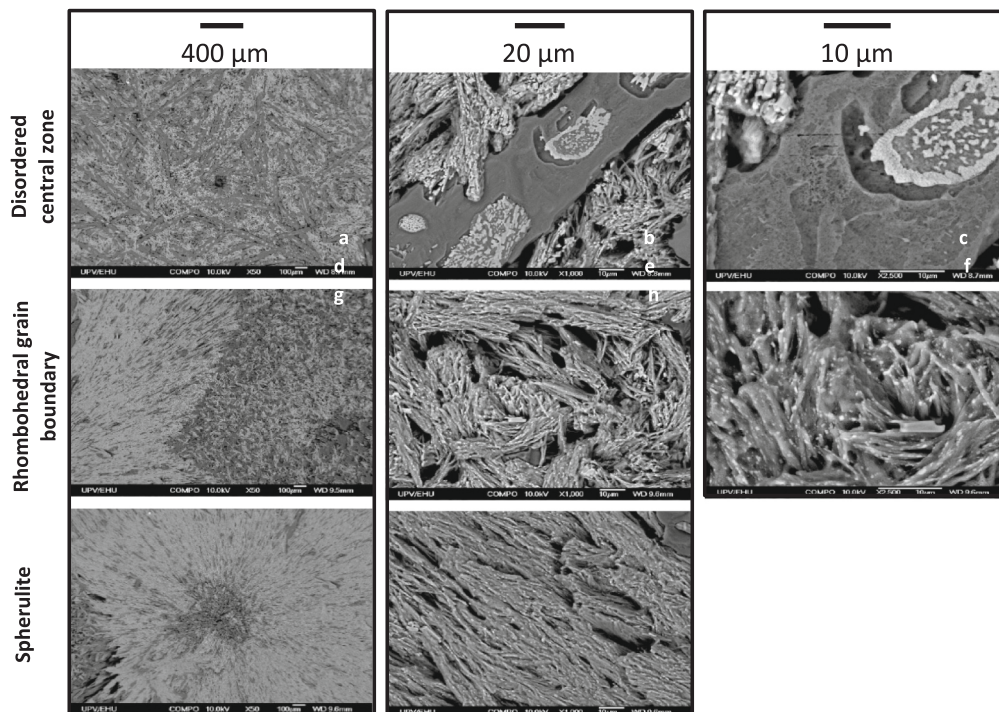
Fig. 10. Rapidly cooled U-SN eutectic PCM (sample 1). SEM images of different zones: (a) disordered central zone; (b) and (c) show a urea column (supersaturated with sodium nitrate) surrounded by eutectic-morphology areas, observed in the central zone of sample 1; (d) rhombohedral grain boundary; (e), (f) and (h) fibrous clusters of the metastable phase that evolves to form the eutectic precipitates into the rhombohedral and spherulite grains; (g) spherulite.

number 3. EDX analysis confirmed that they correspond to sodium nitrate. Most features observed in sample 2 present very large size because of the extremely slow solidification rate employed. However, some few small zones of bundles of minute fibrous crystals were observed in this sample. They are clusters of submicron diameter fibers indicated as number 2 in Fig. 9 f. It was not possible to analyze them due to their small size and the low melting point of the material.

Sample 1 also have fibrous fibers, labelled with the number 2 in Fig. 9, aggregating with each other to make up bundles of fibers or to form a large arrangement of parallel or radial fibers in between the urea columns. Fig. 10 b, e and f shows some conglomerates where there is not a preferential alignment of the fibers, while in other cases they form spherulites (Fig. 10 g and h). The center of all the spherulites in this sample is rich in urea, while the radially grown fibers, as said before could not be determined. Nevertheless, they display a lighter colour than urea pointing towards being sodium nitrate or a solution containing Sodium in their composition. When a closer magnification is used, these fibers in all the formations (Fig. 10 b, c, e, f and h) become heterogeneous and display light dots, resembling a eutectic formation where the precipitates form when the electron beam focuses on supersaturated urea. Taking into account that these features appear in a great proportion in the quenched sample, they may indicate that the fibers correspond to a metastable phase that forms and remain stable until certain stimuli promotes its decomposition.

The results of our work indicate that supercooling increases as the cooling rate increases, therefore reinforcing the possibility of formation of metastable phases. The formation of the metastable phase in the U-SN eutectic mixture is in agreement with the XRD results obtained in a previous study, published in [8,10,31] indicating the existence of one or more metastable phases that decompose into the stable phases when an annealing thermal treatment is supplied to the material. Samples 3 and 4, prepared using the same procedure as samples 1 and 2, were analyzed by means of HTXRD.

3.2.1.2. Determination of the phases formed. Samples 3 and 4 (similar to

samples 1 and 2, respectively) were analyzed by means of HTXRD. The obtained diffraction patterns evolution is shown in Fig. 11. Both samples exhibit peaks in positions corresponding to urea and sodium nitrate, as indicated in Fig. 11, where the red triangles show 2Theta positions corresponding to urea and black triangles show the positions corresponding to sodium nitrate. Peaks in other positions correspond to unidentified metastable phases. Sample 4 was composed only by urea and sodium nitrate, while sample 3 additionally showed several peaks that do not correspond to any known phase. Consequently, an unidentified metastable phase formed in the samples produced under high cooling rates. This is in agreement with the work published by Galenko et al. [32], who determined that rapid solidification of eutectic systems can suppress the eutectic formation and instead produce a homogeneous metastable phase with the initial chemical composition (the composition of the liquid phase). Besides, Bevan Ott et al. [33] reported that metastable phases form in eutectic systems when the material supercools.

The diffraction patterns of both samples show no changes from 30 °C to 84 °C. At 86 °C most of the peak signals disappear due to the material melting (U-SN eutectic point is ≈ 85 °C), but some peaks remain until significantly higher temperatures. It is not clear whether this is due to regional phase segregation, or to the specific test conditions such as the lack of stirring in the sample holder and the arrangement of the samples in very thin layers.

The equilibrium eutectic mixture and the metastable phase formed at high cooling rate display a similar phase-change temperature. Sample 3 and fresh U-SN eutectic samples were measured by DSC after having different treatments in order to get more knowledge regarding both stable and metastable phases. Fig. 12 shows the DSC thermograms of the following samples, evaluated in the first heating segment:

- Sample 3 – as produced (not ground)
- Sample 3 after 1 h at 80 °C
- Sample 3 after 5 h at 80 °C
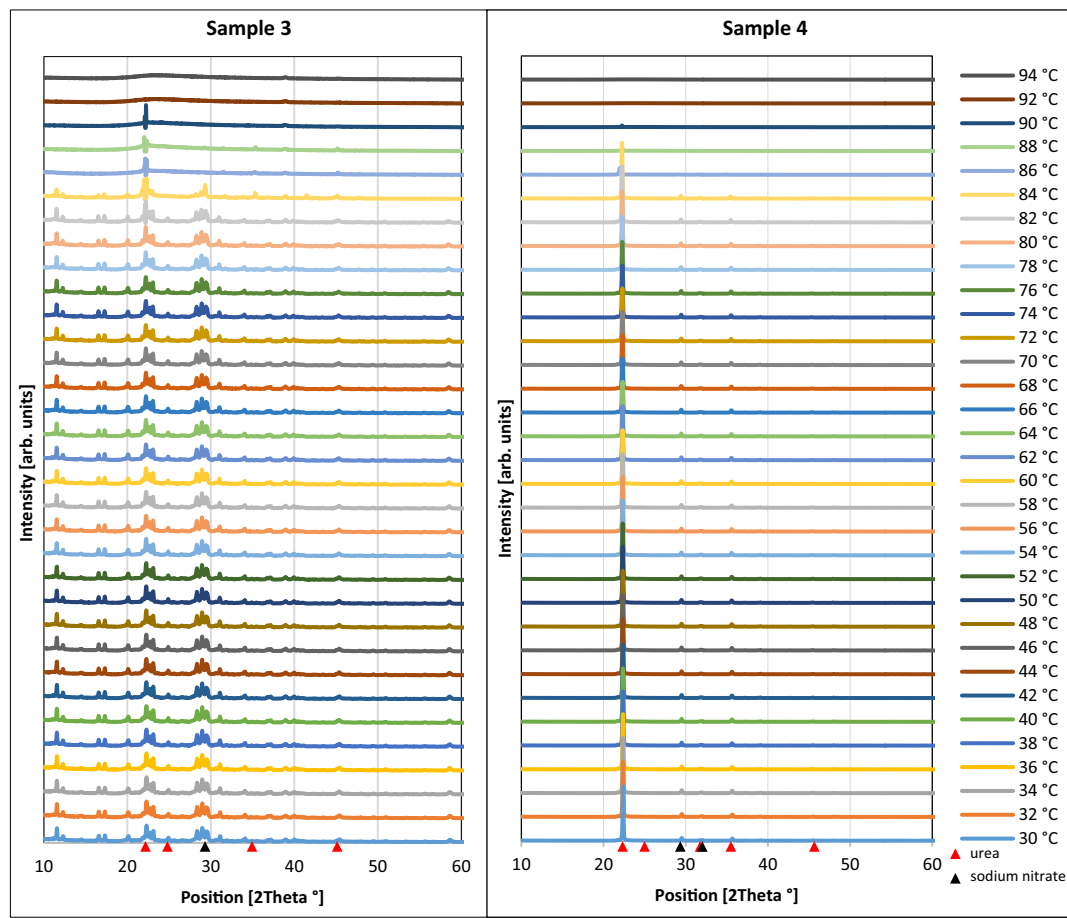- Fresh U-SN sample prepared under the regular procedure

Fig. 11. Evolution of the Diffraction patterns of samples 3 and 4 with temperature from 30 to 94 °C.
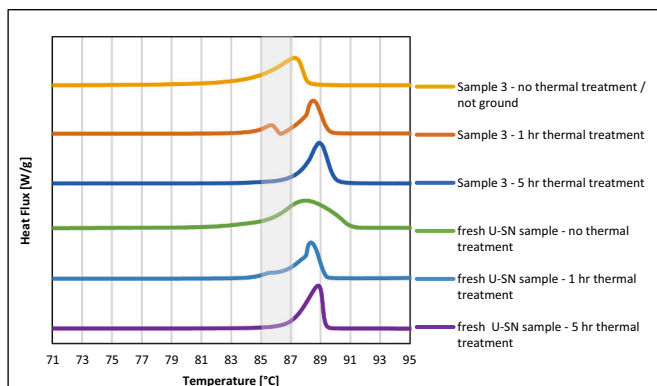

Fig. 12. DSC thermograms of sample 3 with no thermal treatment and not ground (yellow); sample 3 after 1 h at 80 °C (orange), sample 3 after 5 h at 80 °C (dark blue) fresh U-SN sample prepared under the regular procedure with no thermal treatment (green); and fresh U-SN sample prepared under the regular procedure after 1 h at 80 °C (light blue) and a fresh U-SN sample prepared under the regular procedure after 5 h at 80 °C (purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- Fresh U-SN sample after 1 h at 80 °C
- Fresh U-SN sample after 5 h at 80 °C

The analysis showed that sample 3, which was determined to be composed by a phase different from pure urea and/or sodium nitrate, shows one wide peak when it was not thermally treated ($T_{onset} = 85$ °C).

However, after 1 h thermal treatment at 80 °C, sample 3 showed two well-defined peaks indicating that there are two phase changes. The thermal treatment induced a partial transformation allowing the separation of the peaks that otherwise would be overlapped. Finally, sample 3 show one single sharp peak after 5 h thermal treatment ($T_{onset} = 87.6$ °C). The onset temperature of the sample before° and after 5 h thermal treatment varied more than 2 °C.

The fresh U-SN eutectic samples showed a wider peak when no treatment is performed and a peak with a shoulder after 1 h thermal treatment. After 5 h thermal treatment the U-SN fresh sample showed a unique sharp peak, similarly to sample 3. The onset temperature of the non-treated and heat-treated samples were 85.2 °C and 87 °C respectively.

These findings show that, due to the close proximity of the two phase-change temperatures, during the thermal cycling tests there is only one melting temperature plateau. They also explain why DSC analysis did not identify the presence of two different phases in previous DSC measurements. Previous works by the authors [8,9,31] foreseen the presence of both, stable and metastable, phases when the regular sample preparation procedure is carried out, due to the need of heat-treating fresh samples for XRD analysis. However, it could not be confirmed or elucidated until now.

3.2.2. Isothermal crystallization

To experimentally observe the crystallization process in near to equilibrium conditions, the molten U-SN eutectic mixture was isothermally soaked for 1 h at 85 °C (melting temperature). No crystallization was observed. The temperature was reduced 1 °C and the sample soaked for 1 h, repeating this procedure until crystals were observed. The first crystals were observed after 4 min at 82 °C. They consist in the long

needle-like crystals shown in Fig. 13 a and b, which initiated in several nucleation points. Fig. 13 e and f show the crystallization of the first crystals in the horizontal tubes. Due to the shape of horizontal tubes and the perspective from which the pictures were taken, the image is distorted and the straight crystals seem to be curvy. The samples required more than 30 min at 82 °C for complete solidification (Fig. 13 c). These crystals grew long for a significant time, to form radial structures and finally filling in the remaining gaps. The formation of phases with a different morphology could not be visually distinguished.

The first crystals formed were extracted out from a subsequent experiment, repeated for this purpose, and analyzed by means of XRD. The resulting diffraction pattern shows intensity-proportionality changes between the urea and the sodium nitrate peaks referring to the original U-SN eutectic mixture.

Fig. 14 shows the diffraction signals of in the 2Theta positions from 20 to 60°, where two major peaks are shown, one at 2Theta positions 22.4° (corresponding to urea) and 29.6° (corresponding to sodium nitrate). The qualitative analysis of the set of peaks of urea and sodium nitrate points towards a smaller proportion of sodium nitrate than the content of that compound in the eutectic sample.

Taking into account the XRD results and the EDX performed in the columnar grains (similar shape to these first forming needles) points towards urea being the material that crystallizes in the first place. The presence of sodium nitrate in a lower proportion is assumed to be caused by the impossibility to isolate the needle-like crystals by the used means. The growth of one material crystals without inducing the simultaneous crystallization of its eutectic couple from a eutectic mixture liquid is called non-reciprocal nucleation. The nonreciprocal nucleation of the eutectic mixture and the fact that a urea containing phase nucleates first, explain why urea crystals were found as nucleation point of the

spherulites when the experiments were carried out under high cooling rate. The visual observation of the crystals obtained in these experiments agrees with the microstructures observed in the microstructural analysis. Long urea containing crystals grow first, and then eutectic like microstructures formed by urea and sodium nitrate grow in between the long crystals.

The solidification of the two phases forming grains which are not in intimate contact results in phase segregation, which is macroscopically observable when the material volume is sufficiently large. This behavior resembles the solidification of proeutectic compositions and is a reported cause of semi-congruent melting, i.e. phase segregation [17,18,34].

3.3. Regeneration of the material after segregation

The thermal cycling tests led to phase segregation. Some samples exhibited the presence of bubbles and the decrease of the crystallization temperature after several cycles (Fig. 3), which in addition to phase segregation could be an evidence of thermal degradation, thus reducing the percentage of urea while forming degradation products, some of them gaseous. Additionally, degradation could also be a potential cause for the segregation. In order to ascertain if this was the case, the tests defined in Section 2.4 were carried out, consisting of stirring a sample which had been thermally cycled for the maximum number of cycles (33) until complete dissolution of the solids was attained. Subsequently, the material was evaluated. The visual inspection showed that full dissolution of the segregated solids occurred by simple and gentle stirring in a very short time.

The XRD analysis carried out indicated that the regenerated sample presented the same diffraction pattern than the original fresh U-SN
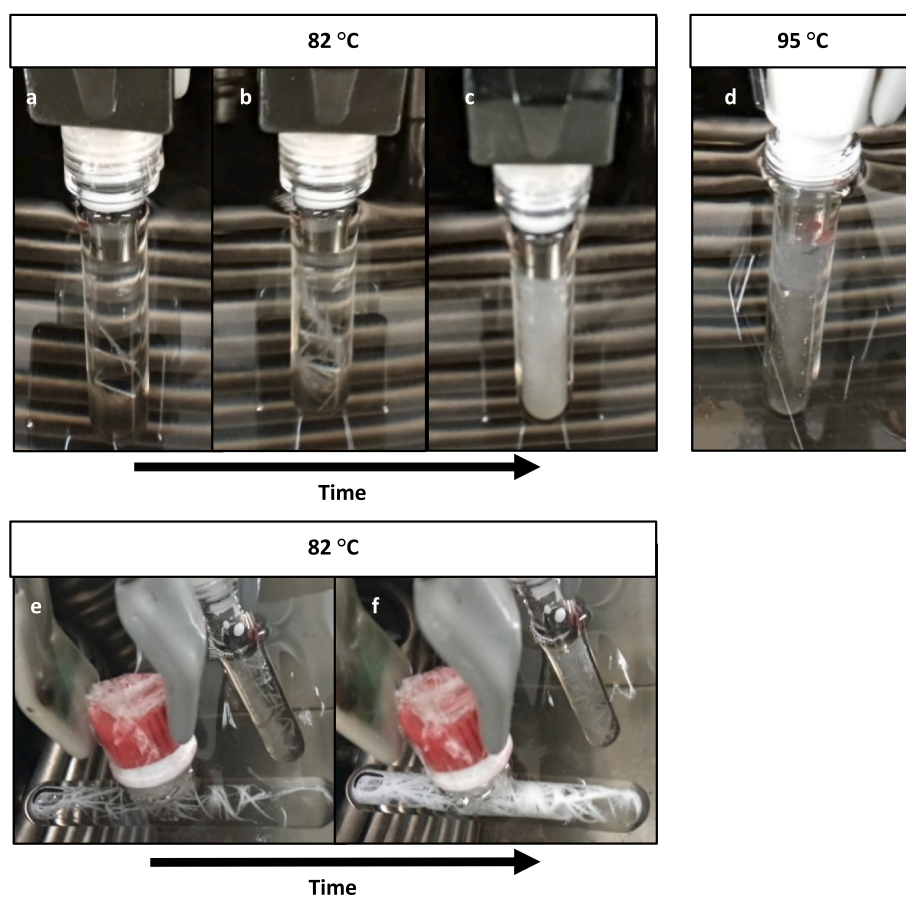

Fig. 13. Evolution of the primary crystal growth at 82 °C. Above, crystal growth in the vertical tubes (a, b, and c). The sample at 95 °C during the melting process (d). Below, the evolution of the primary crystal growth at 82 °C in the horizontal and vertical tubes (e and f).
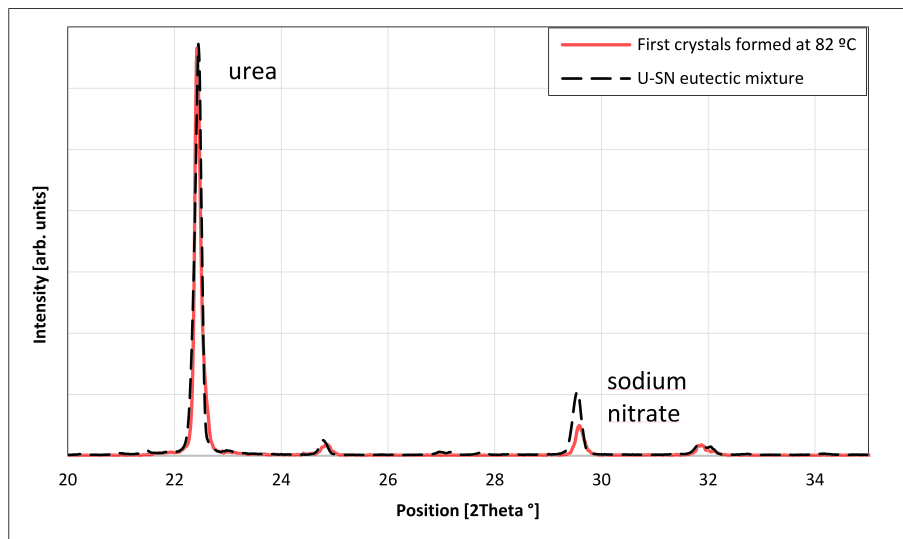
Fig. 14. XRD signals in the 2Theta positions 20° to 35° of two samples: the first crystals produced under isothermal conditions (82 °C) and a U-SN eutectic freshly produced and ground sample. Two major peaks are shown, one at 2Theta positions 22.4° (corresponding to urea) and 29.6° (corresponding to sodium nitrate).

eutectic PCM. The same diffractions of the eutectic mixture, i.e. the pure urea and sodium nitrate peaks, in similar proportions are found in both cases. This diffraction pattern is also similar to the pattern of the middle portion of a specimen thermally cycled for 33 cycles. These three patterns can be seen together in Fig. 15. Accordingly, phase segregation does not lead to irreversible compositional modification that could be considered significant.

The DSC thermographs of the regenerated sample and those of a fresh, non-thermally cycled sample, are displayed on Fig. 16 (cooling ramp and second heating ramp of the DSC thermal program), while the main results obtained are gathered in Table 3. The results confirm that the regenerated mixture poses similar thermal properties to the non-cycled U-SN eutectic on melting, specifically similar melting temperature and similar enthalpy of fusion. The stochastic nature of supercooling in the small DSC samples explains the large differences encountered on the onset crystallization temperature.

The results indicate that it is possible to reverse the phase segregation by means of mechanical stirring at a temperature above the melting temperature, 95 °C. This fact evidences two things, on one hand, the degradation was negligible under the employed testing conditions and by no means responsible for phase segregation, and on the other hand, the segregation can be easily reversed to regenerate the original
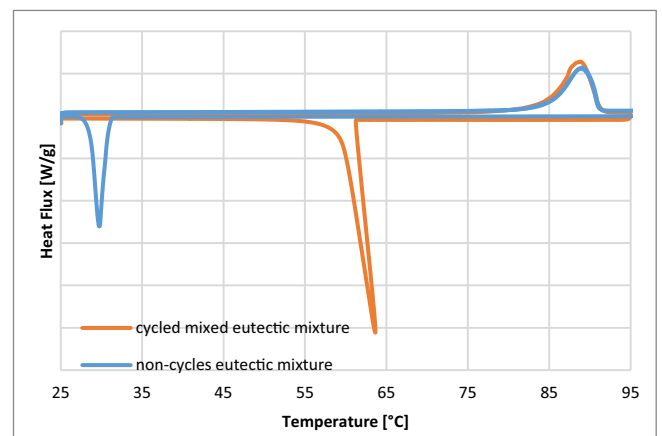

Fig. 16. Thermogram of a sample that has been regenerated by mechanical stirring after phase segregation and a fresh non-cycled U-SN eutectic sample. Thermal behavior on heating and cooling.
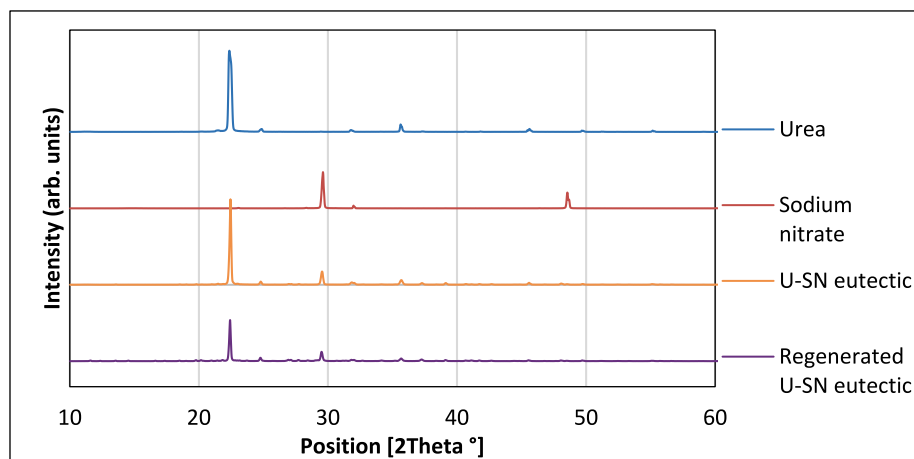

Fig. 15. XRD diffraction patterns of the pure urea, pure sodium nitrate and, and a sample that was stirred to mix-up the segregated and liquid zones until regeneration.

Table 3
Onset temperature and latent enthalpy of the U-SN eutectic regenerated sample measured by DSC.

Specimen	Onset temp. on melting	Latent enthalpy on melting	Onset temp. on crystallization	Latent enthalpy on crystallization
Regenerated sample	84 °C	174.2 J/g	61.4 °C	160.3 J/g
Fresh U-SN eutectic mixture	84.4 °C	168.8 J/g	28.6 °C	153.4 J/g

material.

4. Discussion

This section approaches a holistic discussion of the attained results to evaluate the phase segregation of the U-SN eutectic mixture. In the introduction three hypothesis were mentioned as possible causes for eutectic macro phase segregation: convection, supercooling and crystallization related parameters.

According to the afore-reported results (from the horizontal and vertical disposition of tubes), convection at the macroscopic scale can be discarded as a cause for the phase segregation. It has no relevance in the phase segregation of the U-SN eutectic in the volume range analyzed in this study. However, this conclusion cannot be ensured if considerably larger volumes are used.

Supercooling degree of the U-SN eutectic was determined under different cooling rates, 0.2 °C/min, 3 °C/min (thermal cycling tests) and near to equilibrium conditions. The U-SN eutectic mixture showed supercooling in all the experiments carried out in the study. The thermal cycling assessment determined that the amount of the segregated material per each melting-solidification cycle decreases with increasing the cooling rate. Isothermal crystallization (Section 3.2.2) indicates that there is segregation after one cycle even when near-equilibrium conditions are used (see Fig. 13 d). The cycling tests included in Section 3.1.1 indicate that a higher supercooling degree does not necessarily lead to a higher segregation in the case of the U-SN eutectic mixture, as several authors report to occur in other materials [18,28,29]. According to the observations by Gunasekara [29], the eutectic composition changes due to supercooling, and the change can be calculated by applying the lever rule on the phase diagram for the supercooled phases. If this were the case, a higher phase segregation could be foreseen when a larger supercooling occurs, which did not happen in the experiments carried out in this work. Then, the existence of supercooling does not provide a unique plausible explanation for the occurrence of the phase segregation. In our work, the experiments carried out show that other parameters regarding the eutectic formation as the imposed cooling rate also have great relevance in the segregation of the eutectic mixture.

Even though the supercooling degree and the amount of segregated material do not exhibit a direct cause/effect relationship in the U-SN eutectic, it is certain that the phase segregation occurs due to the inability of the two phases to crystallize together (at the same time) at the eutectic temperature. The isothermal crystallization test (Section 3.2.2) shows that the crystallization in conditions near to equilibrium starts under a supercooling degree of 3 °C (assuming 85 °C as the eutectic melting temperature). XRD determined that the first crystals formed under these conditions were rich in urea, which points out that these primary crystals grow without (apparently) inducing the simultaneous crystallization of the secondary phase to grow coupled together (as initially expected from a eutectic composition). The microscopy observation shows a proeutectic-like microstructure and as a result, it can be inferred that the eutectic mixture presents non-reciprocal nucleation: the primary nucleating phase, i.e. urea, does not promote the crystallization of the secondary phase, i.e. sodium nitrate, to form the binary eutectic.

Several authors had previously identified the non-reciprocal nucleation phenomenon in eutectics and its causes. De Groh [17] highlights that a significant difference in the nucleation barriers for each phase can have a strong effect in the segregation of supercooled eutectics and is likely to result in non-reciprocal nucleation behavior. Kobayashi et al. [34] showed that, in the Al—Si alloys, the ability of a material to nucleate and the influence of one phase in the nucleation of the other one depends on the relative interfacial energies for both involved phases. The supercooling degree depended on the primary phase nucleation-ability. Chiba and Spittle [32] studied the variation of the microstructure with the composition of the systems Al—Sn, Cd—Zn, Bi—Cd, Bi—Sn, and Pb—Sn. Each of these systems presented an anomaly: the poor ability of the primary phase to nucleate the eutectic. Summarizing, these studies show evidence supporting that non-reciprocal nucleation is linked to supercooling, coarser primary phase crystals and a change in the microstructural arrangement.

The nonreciprocal nucleation is a direct cause of the phase segregation presented in the analyzed mixture under the studied experimental conditions. When the original eutectic solid is heated up, the distance between the sodium nitrate micro constituents and the urea crystals (due to their great size) is very large, occasionally too large for part of the material to melt like an eutectic composition, thus preventing complete melting to occur (because part of the eutectic micro-constituents are not in intimate contact). This causes the segregation to take place during melting because some crystals remain unmolten. These crystals are subsequently segregated. This can be seen in Fig. 13 d), which corresponds to the melting at 95 °C of a sample that had previously experienced only one thermal cycle. Solid particles are visibly suspended in the liquid, a white solid is segregated on the top, and a small amount of white particles are segregated on the bottom of the tube. The final melting stage presents a transparent liquid with a solid segregated on the top and some white particles segregated on the bottom.

Besides, the microstructure and the morphology of the crystals formed under different cooling conditions gives a plausible explanation of the relationship between the segregated volume and the cooling rate (Section 3.2.1). The microstructural features obtained in the material solidified under a very low cooling rate (sample 2) have a very large size, thus leading to a large mass segregation per thermal cycle. The distance between the urea and sodium nitrate crystals, i.e. the eutectic spacing, and the size of the primary urea crystals have a direct influence on the proportion of the segregated material produced. The lower the cooling rate, the higher distance between the microconstituents, the higher the segregated volume observed.

When high cooling rates are used, metastable phases are produced (determined by means of HTXRD and shown in Fig. 11). When the adequate temperature is reached and enough heating energy is supplied, the metastable phase spontaneously decomposes to produce small sodium nitrate crystals in a urea matrix, as was directly observed using SEM. This points towards a metastable supersaturated solid solution of urea with sodium nitrate. The decomposition of the metastable phase produces a eutectic microstructure, where very fine precipitates of the sodium nitrate appear in the urea matrix (as shown in Fig. 10). The formation of this metastable phase with the initial eutectic composition explains why the segregated volume is significantly smaller when high cooling rates are employed. Both, a metastable phase with the eutectic composition or its decomposition to form a eutectic microstructure made of fine interpenetrated crystals of the two phases, result in a much closer intimate contact than when slow cooling is applied. As a consequence, high cooling rate produces smaller quantity of segregated material. However, the total suppression of the phase segregation has not been attained under the studied cooling-range because primary urea crystals are always present. In any case, segregation is greatly reduced when high cooling rates are used in the U-SN eutectic mixture, which should be taken into consideration for designing the final application.

The metastable phase has a phase transformation temperature very

close to the eutectic melting point, which greatly hindered its identification by means of DSC, usually being hidden in a wide peak that certainly corresponds to two overlapping peaks, as shown in Fig. 12. The metastable phase does not alter the PCM functioning as both phase change temperatures are in a narrow temperature interval and no significant variation of the melting enthalpy has been determined.

Finally, the segregated materials do not present degradation (provided by the experimental conditions) and, simple and quick mechanical stirring showed to be sufficiently good for regeneration of the original mixture, exhibiting the original thermal properties.

5. Conclusions

The urea and sodium nitrate eutectic mixture suffers phase segregation after repeated melting-and-solidification cycles. This study analyzes the potential causes and the influential parameters in the U-SN eutectic phase segregation. The presented study may serve as a potential hint to the study and characterization of the phase segregation suffered by other PCMs.

The crystallization path followed by the material presents a strong responsibility on the phase segregation. The material showed non-reciprocal nucleation in all the studied conditions. The urea primary crystals and the rejected sodium nitrate could not be in intimate contact any more to melt again as a eutectic mixture, thus producing the segregation of both solid phases when the PCM is heated up to the charging temperature. The results of the study carried out show that not all the eutectic mixtures behave as congruent materials, as it has been broadly assumed and reported by some authors researching eutectic mixtures for their use as phase change materials.

Even if segregation was determined in all the studied experimental conditions, the cooling rate plays an important role in the quantity of segregated material per each melting/solidification cycle. Higher cooling rates showed smaller segregated volume than slower cooling rates. This is due to the microstructural differences obtained. Under low cooling rates, big crystals grow and the distance between the crystals of the two phases is very large. This hinders the intimate contact required for the mixture to behave as a eutectic composition and, as a result a great quantity of segregated material form. High cooling rates reduce this problem.

The complete prevention of the phase segregation of urea and sodium nitrate in the eutectic mixture seems unfeasible. However, it was confirmed that the segregated samples can be recombined by simple mechanical stirring for a short time when the mixture is molten. The thermal properties of the regenerated mixture are similar to those of a fresh eutectic mixture and XRD diffraction confirmed that the phases present were urea and sodium nitrate in the eutectic proportion, thus ensuring the lack of degradation. Therefore, the use of this material as a PCM is feasible if a proper stirring procedure is implemented in the thermal storage system in addition to a correct design of the storage tank that allows high cooling rates to be achieved by the PCM.

Future research on the topic should include the potential use of seeding, nucleating agents or outer stimuli that may produce the reciprocal nucleation and subsequently the crystallization of the mixture in a congruent way.

CRediT authorship contribution statement

Laura Quant: Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft. **Gonzalo Diarce:** Conceptualization, Supervision, Writing – review & editing. **Lourdes Bouzas:** Investigation. **Ana García-Romero:** Conceptualization, Supervision, Funding acquisition, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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