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Abstract: This work aims at assessing the applicability of a screening-oriented device dedicated to the establishment of increasingly complex phase diagrams of phase change materials. A thermography-based method has recently been proven to allow the detection of phase transitions of organic materials for multiple samples at a time. The phase transition detection capability of the infrared thermography method is here evaluated for metal systems based on well-referenced materials commonly employed in DSC calibration (pure sample of Gallium and a mixture of Gallium and Indium). The detected transitions are compared to literature data and DSC measurements. All transitions documented in the literature could be retrieved by thermography, and liquidus transitions are validated with DSC measurements. The encouraging nature of the results is discussed, and avenues for improving the method are considered.

Keywords: infrared thermography; phase transition; metal alloy; characterization method

1. Introduction

In the frame of energy transition, thermal energy storage (TES) is recognized as one of the key elements to optimize the use of available energy resources, especially renewable ones which are intermittent by nature. Latent heat energy storage provides great energy densities with the smallest temperature differences between storing and releasing heat. This technology relies on Phase Change Materials (PCMs) which can be either inorganic (e.g., metal alloys, salts, and salt hydrates) or organic compounds such as paraffin waxes, fatty acids or esters, and polymeric materials (e.g., polyethylene glycol). While PCMs are already used for TES from waste heat and solar energy [1], they could also benefit from numerous applications at low to medium temperatures ($-10\,°C$ to $200\,°C$) such as thermal comfort in buildings, transport, textile, cooling in electronics, waste heat recovery in industrial processes, etc. To reach this goal, it is necessary to design advanced PCMs with enhanced performance/cost ratio.

To explore the phase-change and the thermal behavior of blended PCMs (organic-organic, inorganic-organic) could offer additional degrees of freedoms to tailor thermo-dynamic as well as kinetic properties and cost-effective performances of PCMs with respect to the applications, i.e., TES applications at low to medium temperatures requiring heating/cooling. The originality of our approach lies in the use of thermal imaging techniques for the study of phase equilibria and melting/crystallization phenomena of multi-component systems.

The thermal behavior and melting temperature of PCMs can be tailored using blends instead of single-component PCMs. Finding blends without solidification interval (i.e.,

with congruent melting or eutectic), with respect to the performance, is of great importance. Phase diagrams are the road map to select blends with the desired melting temperature and solidification behavior. Unfortunately, the thermal properties of multi-component PCMs and their phase diagrams are not always available. The most common methods used to establish the material phase diagrams (Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), X-ray powder Diffraction (XRD) [2–7]) are very time consuming (the samples being characterized one by one successively, the establishment of the phase diagram of a binary system can take weeks to months) and poorly adapted to screening procedures.

An innovative infrared thermography (IRT) method has recently been employed for the rapid screening of organic phase change materials in order to find suitable candidates for a latent heat thermal energy storage application [8–11]. It enabled the estimation of phase diagrams of fatty acid binary systems in a single short experiment. In comparison with other standard methods commonly used for the determination of phase diagrams, this IRT method allows detecting phase transitions in a large number of samples at a time (tested for up to 100 simultaneous samples so far).

The method relies on the simultaneous observation using an infrared detector of a multitude of samples deposited on a thermally conductive plate, each with their own composition, submitted to a slow heating ramp. Each pixel records a temperature and emissivity-dependent signal whose behavior can be monitored. An abrupt shift in the trend of the signal of a pixel belonging to a sample can be associated to the occurrence of a phase transition. The detection of transitions can then be made for as many samples as can fit within a frame. The phase change characterization process is consequently reduced by a factor corresponding to the number of samples on the plate in comparison with traditional single-sample methods. Indeed, current standard methods are yet deemed time-consuming and poorly adapted to the fast-paced industrial environment. In that frame, the IRT method constitutes an interesting alternative particularly fit for the aimed applications but also in materials science [7,12], especially in metallurgy given the omnipresence of metal alloys in most industries [13–15] and the need for material screening.

The IRT method has been extensively used and validated for the study of phase transitions of organic materials including systems of sugar alcohols [16], fatty acids [9,10], and fatty alcohols [11]. Given the promising results obtained, it is interesting to investigate its applicability to inorganic materials which could allow the rapid screening of blended PCMs, the development of a large material library, the study of the phase transitions of multicomponent PCMs and the establishment of their phase diagrams.

In this work, the applicability of the IRT method, a high-throughput characterization technique, for the detection of phase transitions in metal alloys is explored for a pure sample of Gallium (Ga) and a mixture of Gallium and Indium (In). The results of this preliminary study are compared with Differential Scanning Calorimetry (DSC) measurements and experimental data extracted from literature.

2. Materials and Methods

2.1. Materials

The phase transition detection capability of the IRT method for metal alloys is assessed for two samples: pure Ga and a Ga-In mixture. The CAS number and general information of the two pure used materials are presented in Table 1.

The choice of materials for the proof of applicability is motivated by three main factors. First, the materials to be studied and the phase diagram for their binary system must be well-known and reliably documented. Then, the type of phase diagram and the nature of occurring transitions must have been encountered and successfully depicted with the IRT method in previous studies. Finally, all occurring transitions must occur within the temperature range which the IRT method has been validated for.

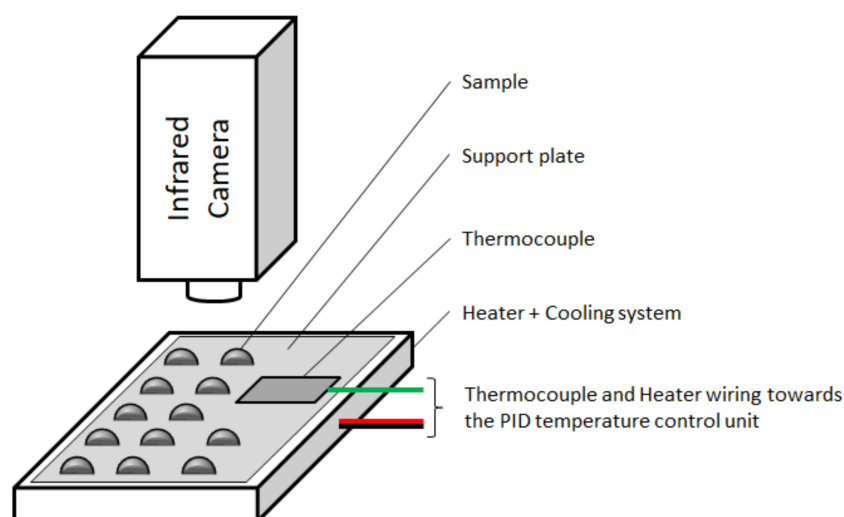**Table 1.** General information about the studied metals.

Metals	Acronym	CAS Number	Supplier	Purity [1] (%)	Melting Temperature [1] (°C)
Gallium	Ga	7440-55-3	Setaram	>99.999%	29.8
Indium	In	7440-74-6	Setaram	>99.995%	156.6

[1] As given by the supplier.

Indium and Gallium, being commonly used for the calibration of DSC, are well-known materials, and the phase diagram of their binary system is well described [17]. Their phase diagram is identified as a eutectic phase diagram [7] whose form is similar to the one retrieved with IRT for binary system of sugar alcohols [8]. In addition, all occurring transitions are within the 0–200 °C range which the IRT method has already been validated for. In consequence, to prove the applicability of the IRT method for the transition detection in metal alloys, the goal is to retrieve phase transition data of a simple pure Ga sample and for a Ga-In mixture presenting at least the two types of transitions reliably documented for this system (namely, the liquidus transition and the eutectic transition). The molar fraction for the mixture of Gallium and Indium was selected within a range between 50 mol% and 60 mol% of In. This composition range is chosen both (i) because transitions are occurring in a temperature range that does not challenge the validity domain of the method (0–200 °C) and are far enough apart to ease the data interpretation in this context of proof of applicability and (ii) because the molar fraction of both compounds are high enough to be considered a multi-component mixture. After weighing both compounds using a Mettler Toledo weighing scale (Mettler Toledo, Bordeaux, France) with a 0.03 mg uncertainty, the Ga-In mixture obtained has been established at 54.9 mol%In–45.1 mol%Ga.

2.2. IRT Method

The IRT method has first been described by Palomo et al. [8] and further developed in several instances [9–11]. Figure 1 shows a scheme of its experimental setup. The functioning principle of the method is similar to Differential Thermal Analysis (DTA).

Figure 1. Scheme of the experimental setup.

The proposed method consists in simultaneously observing, using a X6580SC FLIR (Wilsonville, OR, USA) infrared camera, the melting of a large number of small samples of the studied system with different compositions. To do so, the samples are deposited in droplet form on a flat metal substrate and heated at a slow and constant speed (heating ramp of 1 °C/min). The temperature profile in the experiment is set as a slow heating ramp of 1 °C/min in order to minimize the temperature difference between the supporting plate

and the samples. This temperature is controlled and monitored through a heating/cooling system consisting of a heating plate, a cooling heat exchanger, and PID temperature controller adjusting the load of the heating plate according to the temperature difference between the setpoint and the temperature given by a thermocouple attached to the support plate. The PID coefficients used for temperature control in this work are: proportional gain K_p = 31.85, integral gain K_i = 1.30, and derivative gain K_d = 194.67.

During the previous studies carried out, it was observed that the signals recorded by the infrared camera show first order discontinuities when a sample crosses a transition line. As the phase transition process is isothermal, discontinuities in the evolution of the infrared signal of a sample correspond to a change in the thermal emissivity and the temperature of the sample. This is the basis of the proposed phase diagram establishment method.

The signal of a sample then consists of as many individual signals as there are pixels for a sample. Reliably detecting a transition within such a large cluster of data is challenging. Therefore, before the interpretation of the results, two steps are required.

First, an image treatment is applied to distinguish samples from the background (segmentation) and to sort individual samples (labeling). A visualization of the image treatment process can be seen in Figure 2. Raw infrared images are extracted following the experiment. Those images cannot be interpreted as is, as they contain the data of several samples simultaneously but also data belonging to the background (such as the support plate and the thermocouple in Figure 2a). A segmentation process based on shape detection and contrast level enables the dissociation between samples and background as can be seen in Figure 2b. From there, samples are individually labelled according to their position on the images (Figure 2c) to facilitate the data treatment process.
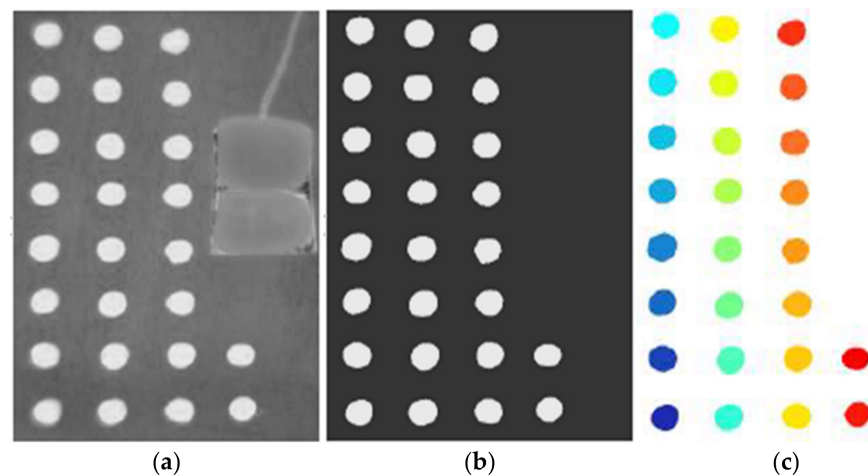

Figure 2. Steps of the image treatment process: (**a**) raw infrared image; (**b**) distinction between samples and background through segmentation; (**c**) identification of individual samples through labeling.

Following the image treatment step, a mathematical process of Singular Value Decomposition is implemented. This process is commonly used when dealing with large multi-variables datasets [18] and has many applications in image processing. In this case, it allows separating the time-dependence and space-dependence of the problem and highlights trend variations in the signal. The SVD of the signals of sample can be expressed as in Equation (1).

$$S = U\Sigma V^t \tag{1}$$

where S is a matrix containing n_i rows and n_t columns (where n_i is the number of pixels constituting the sample and n_t the number of frames of the infrared movie), U an $n_i \times n_i$ matrix containing the space-eigenfunctions along the rows, V an $n_t \times n_t$ matrix containing the time-eigenfunctions along the rows, and Σ an $n_i \times n_t$ diagonal matrix containing the eigenvalues along the diagonal.

The transition detection is then made based on the observation of time-eigenfunctions (related to the time or temperature dependence of the signal). Eigenfunctions are given a rank according to their contribution to the raw data (the lower the rank, the higher the contribution). The rank of the eigenfunctions considered varies depending on the application. The first rank always represents the average evolution of the signals and subsequent ranks highlight deviations from it. In this work, the transition detection is made based on the third and fourth eigenfunctions. A detailed explanation of the process and its application to phase transition detection is available in [8]. The measurement uncertainty for the determination of transition temperature has been estimated at $\pm 1.5\,^\circ$C in [11] through repeated measurements on known materials, comparison with standard methods and accounting for sources of error.

2.3. DSC Validation

The phase transition detection made with the IRT method is compared with DSC measurements made with a DSC 131 provided by SETARAM (KEP Technologies, Caluire-et-Cuire, France). For each sample, two heating/cooling samples are performed: one fast cycle at a 5 °C/min rate to ensure a good thermal contact between the sample and the crucible and to delete any previous thermal history of the samples; one slow cycle at a 1 °C/min matching the heating rate of the IRT experiment. Prior to the measurements, the DSC has been calibrated with Gallium (Purity: 99.999%), Indium (Purity: 99.995%), Tin (Purity: 99.999%), and Lead (Purity: 99.999%) in order to validate the measurement accuracy in the 29–330 °C range. Consequently, the temperatures of the phase transitions were measured with an uncertainty of $\pm 0.5\,^\circ$C. The DSC is cooled with a ventilation system at room temperature meaning that temperatures below 20 °C cannot be reached. Therefore, transitions occurring below 20 °C for the samples cannot be retrieved with DSC and be extracted from literature in the following results. In addition, the interpretation of the DSC curve is made according to the guidelines from [19] stating the transitions temperatures are associated to onset temperatures when applicable and to peak temperatures otherwise.

3. Results & Discussion

Figure 3 shows the evolution of the third and fourth time-eigenfunctions as well as the DSC curve for a sample of pure Gallium (Figure 3a) and for a sample of 54.9 mol%In-45.1 mol%Ga (Figure 3b). It should be mentioned that because the DSC can only be cooled down to room temperature, the eutectic transition for the mixture cannot be retrieved with DSC. Therefore, the heating curve does not present a clear baseline. Hence, it has been decided to compare IRT results to the DSC cooling curve. In the case of non-eutectic alloys, this choice does not drastically impact the transition temperature as they rarely exhibit supercooling tendencies. For the IRT method, the abrupt variations that could be associated with phase transitions are highlighted by blue dashed lines and an etiquette indicating the corresponding temperature. A red dashed line is used for the transitions detected with DSC.

For the pure Gallium sample, the melting temperature is measured at 30.1 °C with our DSC. Anderson et al. [17] compiled all phase transition data for the Ga-In binary system. The average melting temperature for pure Gallium is there stated at 29.8 °C which is within acceptable tolerance from our measurement. Figure 3a shows that a transition is detected around 31.6 °C with the IRT method. However, slightly overestimating, this value is rather acceptable considering the estimative nature of the method which is primarily designed for fast measurements. Another possible transition is detected around 23.4 °C. This transition could not be retrieved with DSC measurements and is not mentioned in available literature data. According to Figure 3b, it appears that a transition has also been detected around this temperature for the mixture sample. This transition temperature is also inconsistent for this composition which would indicate that the variation in the time-eigenfunctions around this temperature is most likely due to an unexpected event. This event could be related to an unwanted phase formation (e.g., oxide, hydroxide, reaction with the substrate) during

the experiment or a potential isolated malfunction of the experimental setup. In order to understand this phenomenon, additional chemical analyses (such as X-ray diffraction measurements) must be performed. For the 54.9 mol%In–45.1 mol%Ga sample, the liquidus temperature is measured at 71.1 °C with the DSC. The IRT method appears to detect a transition around 69.3 °C which would once again be a satisfactory approach. In [17], a sample of 55.6 mol%In–44.4 mol%Ga shows a liquidus temperature of 70.8 °C which is in line with both of our measurements. Although the eutectic transition could not be retrieved with our DSC measurement, literature [17] positions this transition around 15.3 °C. Our IRT experiment detects a transition around 16.5 °C which is a fairly close estimation given the purpose of the method.
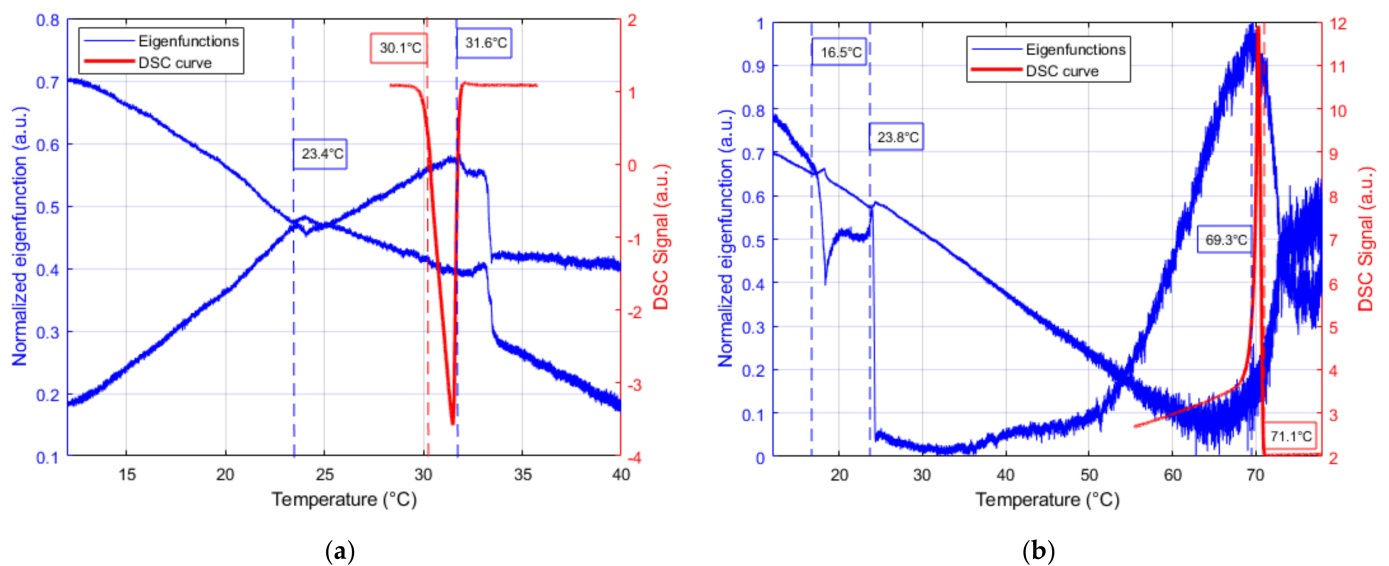

Figure 3. Third and fourth time−eigenfunctions (blue) and DSC curve for: (**a**) the sample of pure Gallium; (**b**) the Gallium−Indium mixture.

4. Conclusions

The IRT method has been applied for the phase transition detection of metals for the first time. For both the pure sample of Gallium and the Gallium-Indium mixture, all transitions documented in literature have been retrieved with the method within an acceptable temperature range for a preliminary approach. The IRT method has so far been able to characterize phase transitions of up to a hundred of organic samples at a time, achieving in a few hours what standard methods can do in weeks. Given the present results, it appears evident that the method could eventually be able to reach similar levels of performance for phase transition characterization in metallurgy.

Although the occurrence of a variation could not be identified with certainty, it is no doubt that with some improvements, the accuracy and reliability could be enhanced. Further works will consist in designing and equipping the current device with a controlled atmosphere cell, making it possible to work either under vacuum or with inert atmospheres at a controlled pressure which will help preventing the potential appearance of parasitic transitions. The objective also being to establish the limits of application of the proposed method, a few well-known systems will be studied, increasing gradually the complexity of the phase diagram (starting with binary systems and increasing the number of compounds afterwards). These first results for metallic alloys being encouraging, the applicability of IRT method will then be assessed using several not yet tested systems (e.g., polymers, metals, salts, organic-inorganic hybrids).

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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