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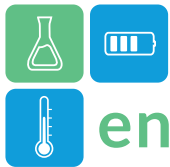
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Metallic phase change material (PCM) for high temperature applications, selection, synthesis and characterisation.

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High heat of fusion metal alloy phase-change materials (PCMs) within the 700-800°C temperature range are chosen for integration with ceramic refractories, forming the core component of a thermal energy storage (TES) unit. Applications targeted by this EU-HEATERNAL project are the steel, aluminium and ceramics industries. The selected PCMs, are a key component of a novel TES prototype consisting of a composite including metal alloy PCMs contained within ceramic refractory bricks. This innovation aims to enhance energy density by 350%, surpassing traditional ceramic bricks, and aims for rapid implementation by 2030. The project targets a 50kWh prototype (TRL5) and up-scaled storage system models connected to factories. This presentation delves into the phase change material selection process and criteria specific to the 700-800°C temperature range, highlighting the impact of synthesis and dendrite growth on latent heat measurements of Cu.Si based PCMs.

Keywords: Metallic alloys, Characterization, TES, PCM

Introduction

The selection of PCMs for thermal energy storage is made after revising the materials characteristics and their storage capacity -i.e. melting temperature, heat transfer and so on [1]. Latent heat storage (LHS) is an efficient method of storing thermal energy in which a phase-change material (PCM) stores or releases heat during an isothermal solid-to-liquid or liquid-to-solid phase transition [2]; compared to sensible storage, it enables higher volumetric energy densities.

Based on previous research [3], it was observed that alloys have higher latent heat of fusion than pure metals thanks to their higher entropy of mixing.

The combination of refractory materials and Phase Change Materials (PCMs) in the HEATERNAL thermal energy storage system (TESS) achieves a synergistic blend of sensible and latent heat storage. In the pursuit of optimizing efficiency and stability through repeated cycles, compatible combinations are explored by examining existing ceramic formulations designed for use with metal alloys.

A preliminary selection of PCM composite metal alloys for an operating temperature range of 700°C - 800°C is reported in this context. The selection

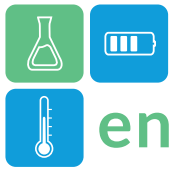
process is guided by key performance indicators (KPIs) such as cost, heat storage capacity (> 400 kWh/m³), proven lifetime (> 1000 hours), low energy & CO₂ footprint, non-toxicity, safety, and ease of recyclability.

Based on the above factors, the chosen metals for evaluation include Al, Cu, Fe, Si, Mn, and Ti, along with their respective alloys. This study centres on the selection, synthesis, and optimization of characterization techniques aimed at maximizing the latent heat of these materials, especially in the temperature range of 700-800 °C.

Methodology

Initial CALPHAD Screening

A preliminary assessment using the CALPHAD approach, utilizing FactSage Thermochemical Software allowed us to determine theoretical liquidus projection phase diagrams. This analysis enabled the prediction of the expected enthalpy of fusion within the temperature range of 700-800°C (see Figure 5). However, it should be considered that even if FactSage can offer a theoretical database regarding



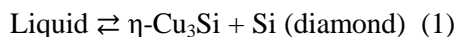
the thermophysical characteristics, depending on the selected databases, some discrepancies between the results and literature have been noted.

Metal alloy synthesis

The Cu-Si system has been the subject of previous research because of its important applications in technology [4–7]. The binary alloy provides great thermophysical characteristics, due to the strong heat storage capacity of silicon and the superior thermal conductivity of copper. As a result, Cu-Si alloys that melt at temperatures higher than 650°C are excellent TES materials [8]. The metals used in synthesis were ordered from HMW Hauner GmbH & Co. KG Gewerbering 36 as granules with a purity of 99.999% and diameter of 1-5 mm.

In the context of this limited abstract, the binary eutectic composition of $\text{Cu}_{83}\text{Si}_{17}$ with a theoretical melting point of 809.1 °C and enthalpy of fusion of 232.6 J/g has been selected.

The expected reaction is as follows[7],



The eutectic alloys $\text{Cu}_{83}\text{Si}_{17}$ (%wt) were prepared by three synthesis methods: solid-state, blowtorch and rapid inductive synthesis.

Solid-State Synthesis Method:

Pure Cu (granules 99,99%, HMW Hauner) and pure Si (granules 99,99%, HMW Hauner) were **weighed to a total of three grams** and placed in graphite crucibles within a tube furnace (carbolite). The samples were heated at 10 K/min from room temperature to $T=1200$ °C, under a nitrogen flow (80mL/min) and held isothermally for 3 hours.

Blowtorch Synthesis:

Approximately two grams of metals were placed in an alumina crucible. After, the samples were heated using a blowtorch, until reaching a molten state. Borax powder flux was added to ensure the homogeneity and to prevent oxidation. The molten alloy was carefully transferred to a graphite crucible for rapid cooling and recovery.

Rapid Inductive Synthesis:

Metals in the appropriate ratio were heated in a 30 μL alumina crucible coated with graphite. The crucible was placed within a quartz tube connected to primary

vacuum (10^{-3} mbar), an induction heater was used to heat the alloys to an estimated temperature of ($\geq 1600^\circ\text{C}$) in $\sim 10\text{s}$.

Simultaneous thermal analysis(STA):

The thermal analysis was performed using a STA 449 F3 JUPITER (Netzsch), where each sample was placed in alumina crucible (30 μL), heated at $10^\circ\text{K}/\text{min}$ and thermally cycled three times between 900°C and 700°C . The samples were under a nitrogen flow (80mL/min) to prevent oxidation. The sample mass ranged from 42-240 mg.

Scanning Electron Microscopy (SEM):

Scanning electron microscopy (SEM) was performed using an FEI QUANTA 250, working between 5 and 30 kV, and operated in high vacuum mode. The SEM is equipped with Schottky field emission gun and Everhart-Thornley detector for (secondary electrons).

Results

DSC results for the 83% Cu copper-silicon binary (Figure 1) revealed notable differences among synthesis methods. The DSC analysis showed two separate peaks, suggesting a slightly off-eutectic composition, maybe due to partial oxidation under air so weighing errors or partial completion of the targeted alloy. Larger total masses used in the blowtorch and furnace synthesis reduce the proportional uncertainty, however these DSC results don't demonstrate any heterogeneity.

The induction sample presented the highest latent heat at approximately 178.9-210.6 J/g, suggesting it is closer to the eutectic point.

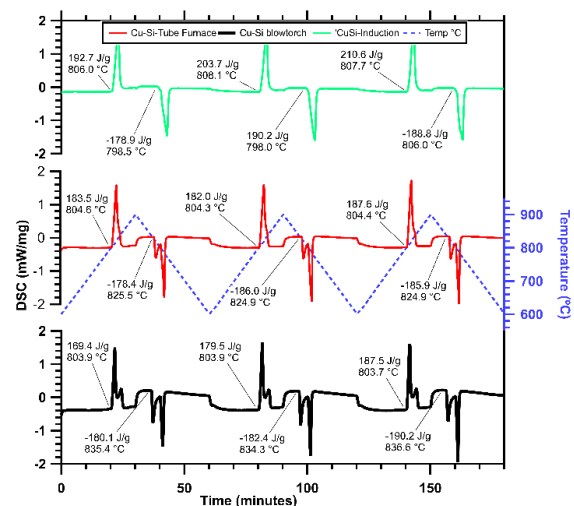


Figure 1: DSC thermograph results of Cu-Si binary alloy synthesised via (top):induction:(middle)tube furnace:(bottom) Blowtorch.

The SEM observations of the samples revealed various microstructures, as it can be seen in Figure 2, Figure 3, and Figure 4. Notably present in each composition are characteristic dark dendrites, featuring an atomic composition of 1.46% Cu and 98.54% Si, existing within a $\text{Cu}_3\text{Si}-\eta''$ matrix. This matrix, comprising 78.67% Cu and 21.33% Si, signifies a eutectic reaction. Figure 2 displays a composition with larger dendrites dispersed sparingly throughout the sample as observed in other works [4]. In Figure 3, larger dendrites are observable, while Figure 4 show a significant proportion of smaller dendrites and a porous structure. These dendrites are indicative of samples exposed to rapid cooling, a result of the small sample size in the DSC crucible and immediate removal of the heat source as the induction heater is switched off.

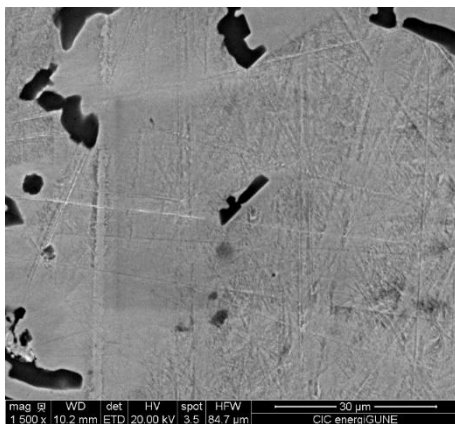


Figure 2: SEM image of $\text{Cu}_{83}\text{Si}_{17}$ eutectic composition synthesised by blowtorch method

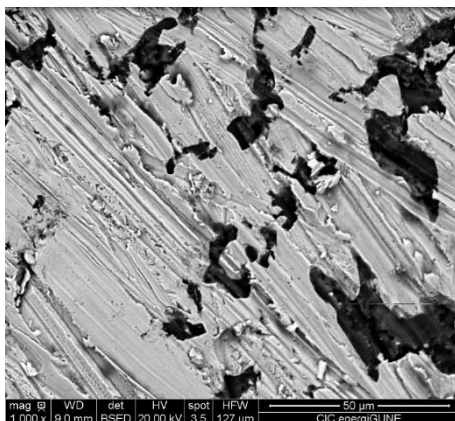


Figure 3: SEM image of $\text{Cu}_{83}\text{Si}_{17}$ eutectic composition synthesised by furnace method

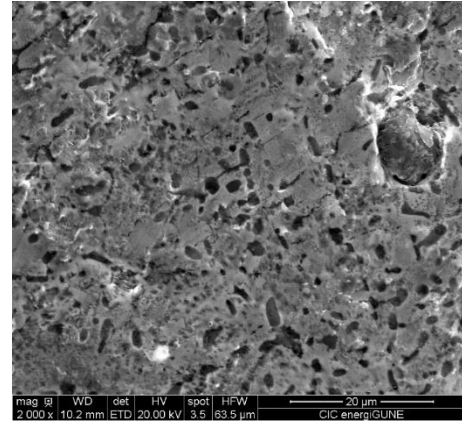


Figure 4: SEM image of $\text{Cu}_{83}\text{Si}_{17}$ eutectic composition synthesised by induction method.

The finer dendritic structures, evident in SEM images, contribute to an increased solid-liquid interface per unit volume. This heightened interface, where latent heat is absorbed or released during solidification, can result in a potentially higher latent heat in alloys with smaller dendrites. Additionally, the refined microstructure associated with smaller dendrites impacts the distribution of phases and atom arrangement, further influencing variations in latent heat compared to alloys with coarser dendritic structures [9].

Conclusions

The binary eutectic $\text{Cu}_{83}\text{Si}_{17}$ emerges as a promising high enthalpy phase change material suitable for incorporation into HEATERNAL PCM ceramic composite bricks.

During the preliminary stages of latent heat analysis in PCM selection, it is crucial to exercise caution in the choice of synthesis methods. Variations in latent heat recordings may be attributed to incomplete eutectic formation or the influence of dendritic growth. As a key component of the HEATERNAL TES system it is important to consider the effects on the measurement of latent heat when up-scaling to a larger system.

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References

- [1] S. Khare, M. Dell'Amico, C. Knight, S. McGarry, Selection of materials for high temperature latent heat energy storage, *Solar Energy Materials and Solar Cells* 107 (2012) 20–27. <https://doi.org/10.1016/j.solmat.2012.07.020>.
- [2] R. Fukahori, T. Nomura, C. Zhu, N. Sheng, N. Okinaka, T. Akiyama, Thermal analysis of Al–Si alloys as high-temperature phase-change material and their corrosion properties with ceramic materials, *Applied Energy* 163 (2016) 1–8. <https://doi.org/10.1016/j.apenergy.2015.10.164>.
- [3] X. Li, H. Wang, H. Wang, S. Kim, K. Esfarjani, Z. Ren, G. Chen, Metallic Composites Phase-Change Materials for High-Temperature Thermal Energy Storage, in: *American Society of Mechanical Engineers Digital Collection*, 2013. <https://doi.org/10.1115/ES2013-18395>.
- [4] L. Soldi, A. Laplace, M. Roskosz, S. Gossé, Phase diagram and thermodynamic model for the Cu–Si and the Cu–Fe–Si systems, *Journal of Alloys and Compounds* 803 (2019) 61–70. <https://doi.org/10.1016/j.jallcom.2019.06.236>.
- [5] X. Yan, Y.A. Chang, A thermodynamic analysis of the Cu–Si system, *Journal of Alloys and Compounds* 308 (2000) 221–229. [https://doi.org/10.1016/S0925-8388\(00\)00983-X](https://doi.org/10.1016/S0925-8388(00)00983-X).
- [6] K. Sufryd, N. Ponweiser, P. Riani, K.W. Richter, G. Cacciamani, Experimental investigation of the Cu–Si phase diagram at $x(\text{Cu}) > 0.72$, *Intermetallics* 19 (2011) 1479–1488. <https://doi.org/10.1016/j.intermet.2011.05.017>.
- [7] B. Hallstedt, J. Gröbner, M. Hampl, R. Schmid-Fetzer, Calorimetric measurements and assessment of the binary Cu–Si and ternary Al–Cu–Si phase diagrams, *Calphad* 53 (2016) 25–38. <https://doi.org/10.1016/j.calphad.2016.03.002>.
- [8] Y. Ge, N. Sheng, C. Zhu, Macroencapsulated Cu Si phase change material by in situ alloying formation for high temperature thermal energy storage over 800 °C, *Journal of Energy Storage* 72 (2023) 108258. <https://doi.org/10.1016/j.est.2023.108258>.
- [9] R. Trivedi, W. Kurz, Dendritic growth, *International Materials Reviews* (1994). <https://doi.org/10.1179/imr.1994.39.2.49>.

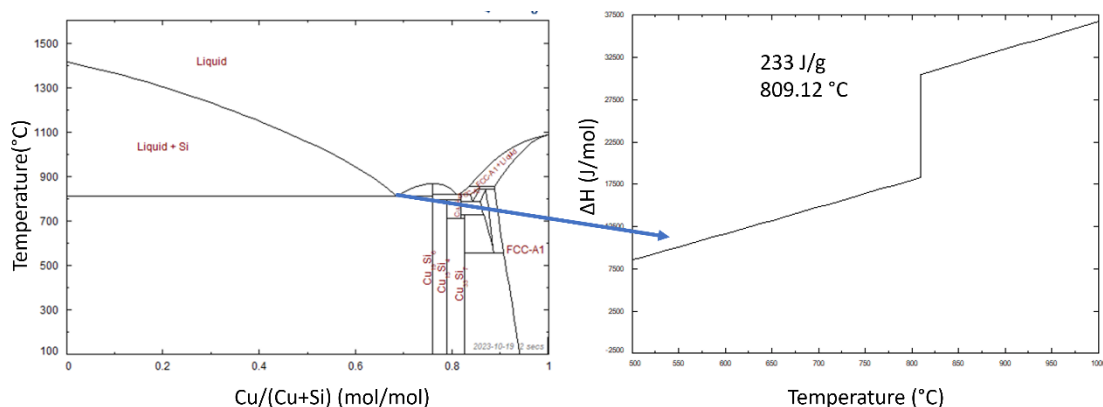


Figure 5: CALPHAD calculations of the copper – silicon binary system generated using FACTSage databases FTlite and ELEM the calculated enthalpy of the eutectic $\text{Cu}_{83}\text{Si}_{17}$ (wt%) is highlighted