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Ferrosilicon Alloys for High-Temperature Latent Heat Thermal Energy Storage: Thermophysical Properties and Containment Strategies

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Abstract – Latent Heat Thermal Energy Storage (LHTES) based on metallic Phase Change Materials (PCMs) represents a promising solution. Among these materials, ferrosilicon (FeSi) alloys stand out due to their exceptionally high volumetric latent heat, exceeding 1 MWh/m^3, and their ability to operate at temperatures far above those of conventional LHTES systems. Such high temperature operation enables higher theoretical Carnot efficiencies and supports emerging solid state thermophotovoltaic (TPV) concepts, a framework currently being explored within the EU-funded SUNSON project.

This work evaluates the thermophysical properties of available PCMs with a particular focus on the FeSi system and its ternary derivatives zfor high-temperature PCM applications. Attention is given to near-eutectic compositions such as FeSi57 (57 wt% Si), which exhibit a narrow phase transition temperature range of less than 50 °C. Key parameters governing PCM performance, including working temperature, latent heat and density are reported.

A critical challenge in the industrial application of metallic PCMs is the containment of highly reactive liquid phases. Graphite is an attractive and cost-effective refractory option, but its interaction with molten silicon introduces both challenges and potential advantages. This review synthesizes current research on the thermodynamic stability of the resulting silicon carbide (SiC) layer and its potential to act as a self-passivating barrier. The performance of ceramic-coated graphite systems is compared against established non-reactive containment materials used in the silicon industry, such as Si_3N_4 and BN, along with emerging approaches such as microencapsulation.

Overall, Fe–Si-based alloys combined with optimized containment strategies, such as BN-coated graphite represent a promising route toward scalable high temperature thermal energy storage systems.

1. INTRODUCTION

The transition toward renewable energy sources such as solar and wind is essential for reducing greenhouse-gas emissions and achieving a decarbonized energy system. However, the intermittent character of these resources creates a persistent mismatch between energy generation and energy demand. Reliable and scalable energy storage is therefore required if large fractions of renewable electricity are to be integrated into future energy systems (Ramos et al., 2022). Thermal Energy Storage (TES) is one of the main technological pathways to address this challenge because excess electricity or heat can be stored as thermal energy and later returned to the process or converted back into power when required.
Within TES, Latent Heat Thermal Energy Storage (LHTES) has attracted considerable attention because it exploits the enthalpy of phase transformation in a phase change material (PCM) (Fatahi et al., 2022; Imran Khan et al., 2023; Jiao et al., 2023). In comparison with sensible heat

storage, LHTES offers higher energy density and a comparatively narrow operating temperature interval during charging and discharging.

To maximize energy conversion efficiencies and energy density, recent advancements have focused on high temperature LHTES systems operating well beyond 1000 °C. At these temperatures, the stored heat can be efficiently converted back into electricity on demand using thermophotovoltaic (TPV) energy converters. TPV devices are advanced solid-state converters that produce electricity directly from the radiant heat (photons) emitted by the high-temperature storage system. Because they lack moving parts, are compact, and are perfectly suited for high temperatures, TPV systems represent a highly promising heat-to-power conversion technology for high temperature LHTES applications (Datas et al., 2022).

The selection of a suitable PCM for this temperature range is, however, far from trivial. Organic PCMs, salt hydrates, and many common inorganic storage media are either thermally unstable or chemically unsuitable above approximately 1000 °C. As a consequence, attention has shifted toward refractory salts, oxides, and metallic or metalloid systems (Fernández et al., 2017; Imran Khan et al., 2023; Zhao et al., 2020). Among the latter, silicon-rich alloys stand out because silicon has a very high latent heat of fusion, high thermal conductivity, and a melting point that overlaps well with high temperature storage targets.

In this context, Fe–Si-based alloys have emerged as especially promising candidates. By alloying silicon with iron, the volumetric latent heat can remain high while the density increases and the severe expansion of pure silicon on solidification can be partly mitigated. Near-eutectic Fe–Si compositions also exhibit relatively narrow melting intervals, which is advantageous for LHTES operation. At the same time, the containment problem remains a central bottleneck, because molten Si-rich alloys react with most refractory materials, can infiltrate porous substrates, and may cause rapid vessel degradation (Imran Khan et al., 2023; Jiao et al., 2022; Ma et al., 2014; Zhao et al., 2020).

The present paper therefore reviews two tightly coupled topics: the thermophysical properties of Fe–Si-based high-temperature PCMs and the containment strategies required for their practical implementation. Particular emphasis is placed on FeSi57 and related Fe–Si–B, Fe–Si–Mn, and Fe–Si–Cr alloys, as well as on the role of graphite, SiC, Si_3N_4, and BN as candidate containment materials.

2. Thermophysical Properties of PCMs

2.1 Selection criteria for phase change materials

The criteria traditionally used to assess low-temperature PCMs (Abhat, 1983) remain highly relevant at high temperature, although additional constraints arise from the operating environment (Fernández et al., 2017; Imran Khan et al., 2023; Zhao et al., 2020).

Thermodynamic criteria

- The PCM should have a melting point within the desired operating temperature range. For FeSi-based PCMs intended for use in thermophotovoltaic systems, the ideal temperature range is approximately 1200 °C or higher (Datas et al., 2025).
- High latent heat is required to achieve high energy density. In this work, PCM performance is evaluated on a volumetric basis rather than a gravimetric one (Fernández et al., 2017).

- A high specific heat capacity is also beneficial, as it increases the total amount of energy that can be stored.
- High thermal conductivity is important in order to minimize temperature gradients during charging and discharging.
- Congruent melting is desirable so that the solid and liquid phases have the same composition, thereby avoiding segregation and changes in melting behaviour during cycling.
- Small volume changes during the phase transition are important in order to minimize mechanical stress on the containment vessel. This is a particularly critical property for silicon-rich systems, as silicon can expand by up to 9% upon solidification.

Kinetic criteria

- Supercooling during solidification should be avoided; otherwise, the operating temperature may vary from cycle to cycle.

Chemical criteria

- The material should be chemically stable under the intended operating conditions.
- It should not react with or corrode the containment vessel, as containment remains one of the main challenges for high-temperature metallic PCMs (Imran Khan et al., 2023; Jiao et al., 2022; Ma et al., 2014; Zhao et al., 2020).
- It should possess low volatility at operating temperatures to prevent excessive vapor pressure so the PCM does not evaporate or increase the mechanical stress in a closed system.
- If possible, the material should also be non-toxic, non-flammable, and non-explosive.

Economic criteria are also undoubtedly important, but these will not be further discussed here.

2.2 Candidate high temperature PCMs

In the LHTES literature, temperatures of 600–700 °C are often classified as high temperature (Imran Khan et al., 2023; Jayathunga et al., 2024; Prieto et al., 2022; Yang et al., 2025), since conventional steam turbines for power generation typically have upper operating limit of around 700 °C (Nomoto, 2017; Wright et al., 2004). Temperatures above 1000 °C, however, are generally classified as ultra-high temperature (UHT) and pose substantially greater challenges in terms of materials stability and system design. Under these conditions, many conventional PCMs, such as organic paraffins, fatty acids, and salt hydrates, become thermally unstable. Consequently, candidate materials are largely limited to inorganic salts, oxides, and metallic systems.

Salts and oxides

Table I reports a list of salts and oxides that have melting points above 1000 °C and high latent heat, making them possible candidates as PCM. Fluoride salts are frequently discussed for high-temperature TES because the strong ionic bonding associated with fluorine leads to relatively high melting points and substantial latent heat (Misra, 1988). Nevertheless, toxicity, corrosivity, and materials compatibility remain important drawbacks. Oxides and silicates are often chemically stable and in some cases inexpensive, but many exhibit lower effective thermal conductivity and can form viscous liquids or glassy phases that complicate heat transfer and cycling. Metallic and metalloid PCMs, by contrast, offer rather higher thermal conductivity and can be tuned over a wide temperature range, but they are highly corrosive and present containment challenges in the molten state.

Table I. Inorganic oxides and salts PCM candidates with working temperature above 1000 °C reported in the literature.

PCM Composition	Melting Point	Gravimetric Latent Heat	Solid Density	Volumetric Latent Heat
	°C	J/g	g/cm³	kWh/m³
Magnesium Fluoride (MgF_2) **(Allison, 2013; Cárdenas and León, 2013)**	1263	938-942	3.15	821-824
Calcium Fluoride (CaF_2)**(Allison, 2013; Cárdenas and León, 2013)**	1418	380-391	3.18	336-345
Barium Fluoride (BaF_2)**(Allison, 2013; Cárdenas and León, 2013)**	1320-1368	119-133	4.89	162-181
Strontium Fluoride (SrF_2) **(Allison, 2013; Cárdenas and León, 2013)**	1440-1477	231-236	4.24	272-278
Sodium Metasilicate (Na_2SiO_3)**(Allison, 2013; Cárdenas and León, 2013)**	1088	424	1.749	206
Beryllium Oxide (BeO)**(Allison, 2013; Batutis, 1961)**	2548	3160	3.01	2642

Magnesium fluoride is one of the most promising fluoride candidates as shown in table I because of its combination of high latent heat and melting point. In literature it often appears in several eutectic formulations, reducing the working temperature to below 1000 °C while maintaining substantial storage density (Birchenall and Riechman, 1980; Imran Khan et al., 2023; Kenisarin, 2010; Misra, 1988). However, additional work is still required to validate its long-term cycling stability and containment compatibility under realistic TES conditions.
Among oxides , although some compounds have high melting point, they usually possess low gravimetric latent heat under 200 J/g and densities below 5 g/cm3 (Cárdenas and León, 2013), and may produce highly viscous melts with poor heat-transfer characteristics. Sodium metasilicate has a melting point and latent heat that make it conceptually relevant as a PCM, but translating slags or slag-like systems into practical latent-heat media remains difficult because of low thermal conductivity, glass formation, and complex melting behavior. Beryllium oxide has excellent thermophysical properties (Batutis, 1961) but is included only for completeness because its toxicity makes it unsuitable for practical implementation in addition to its very high melting temperature.

Metallic or metalloid PCM
Metallic PCMs have always been an interesting but extremely challenging system: they can be virtually engineered for any working temperature, they crystallize naturally very easily, they

have high thermal conductivity. On the other hand, molten metals are very reactive, especially with oxygen and the containing vessel.
Table II presents a list of potential PCMs. The containment will be discussed in the next section of this work.

Table II. Representative metallic and metalloid high temperature PCM candidates reported in the literature.

PCM Composition	Melting Point	Gravimetric Latent Heat	Solid Density	Volumetric Latent Heat
	°C	J/g	g/cm³	KWh/m³
Silicon (Si)(Homa and Sobczak, 2019; Jiao et al., 2019; Olesinski and Abbaschian, 1984)	1414	~1800	2.330	1150
Boron (B)(Allison, 2013; Olesinski and Abbaschian, 1984)	2077-2092	4644	2.080	2683
Copper (Cu)(Allison, 2013; Sheng et al., 2022)	1063-1085	207 - 210	8.960	514
Si-3.25B (Datas et al., 2020)	1389	1069 - 1853	2.300	693 - 1205
FeSi57 (Lo Biundo et al., 2025a)	1213	930	4.067	1050
Fe-26Si-9B (Polkowski et al., 2025b)	1196 - 1264	834	4.422 (liquid)	1020
Fe-46Si-5B (Polkowski et al., 2025b)	1173 - 1196	960	3.800 (liquid)	1064

Among metallic PCMs, pure silicon is an ideal high temperature storage PCM. At 1414 °C, silicon transforms from a diamond FCC crystal structure to a liquid with metallic character (Eustathopoulos et al., 1999) and exhibits a latent heat of fusion of approximately 1800 J g^{-1}. Despite its moderate density relative to other metals such as iron or copper, its volumetric latent heat remains around 1000–1150 kWh m^{-3}, which is high for a single-component PCM (Datas et al., 2018; Homa and Sobczak, 2019). Silicon is also attractive because both the solid

and liquid phases have comparatively high thermal conductivity, to the extent that molten silicon has even been proposed as a heat-transfer fluid (Amy et al., 2021).
The main drawback of pure silicon is the large volume expansion on solidification of 9%. This expansion can generate severe mechanical stress on the crucible during discharge and may cause cracking or catastrophic failure of the vessel. Alloying offers a way to reduce this problem while preserving much of the latent-heat advantage of silicon.

Boron has an even higher latent heat, reaching above 4600 J/g or 2500 kWh/m³ due to its icosahedral crystalline structure, but its melting point above 2000 °C, high cost, and difficult purification make it unattractive as a standalone.

Several transition metals have been considered as candidate PCMs because of their availability, density, and melting temperature. Among them, copper is often discussed in the literature as a possible phase change material (Datas et al., 2022; Gil et al., 2010; Li et al., 2013; Ma et al., 2014; Sheng et al., 2022). Pure copper melts at slightly above 1085 °C. Its gravimetric latent heat is relatively low, at around 210 J g^{-1}; however, its high density (approximately 8.96 g cm^{-3} in the solid state) results in a volumetric latent heat of about 514 kWh m^{-3}, corresponding to roughly half that of silicon. Copper is particularly attractive because of its excellent thermal conductivity, which supports rapid charging and discharging and enhances heat transfer from the heat source into the bulk PCM. This reduces the risk of localized overheating and helps maintain a more uniform melting front. Additionally, copper is more inert towards the surroundings, compared to many other metallic PCMs.

The Binary Fe-Si System and Near-Eutectic Compositions
When it comes to candidate metallic phase change materials (PCMs), the iron-silicon (Fe–Si) binary system stands out. Silicon provides excellent latent heat, while iron adds density and helps counteract the volume expansion issues common with pure silicon. Near congruent melting compositions are particularly of interest because they keep the phase transition in a narrow temperature range, which is a requirement for efficient latent-heat storage (Fernández et al., 2017; Zhao et al., 2020).

Looking at the Fe–Si phase diagram, most of the phase diagram in figure 1 has solidus between 1200–1400 °C reaching the temperature needed for thermophotovoltaic (TPV). FeSi57, close to the Fe3Si7 phase field, has been reported to provide an energy-storage capacity of approximately 1.05 MWh m^{-3} while operating in the 1150–1250 °C interval, together with a very small volume change on solidification (reported as approximately −0.4%) (Lo Biundo et al., 2025a). This combination of high volumetric latent heat, a narrow phase transition temperature, and almost zero volume change makes FeSi57 one of the most promising Fe–Si proposed options for high temperature LHTES.

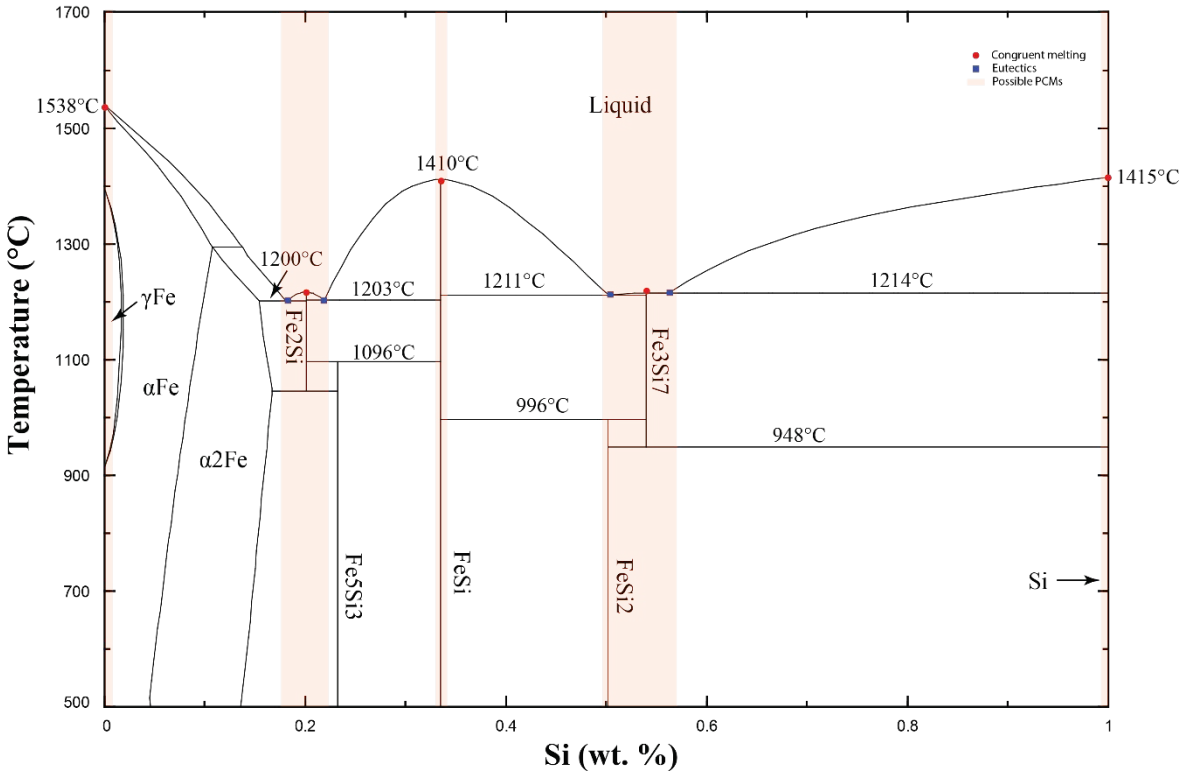

Figure 1. FeSi phase diagram calculated with FactSage. The area near the congruent melting phases and eutectic points are interesting for application as PCM since most of the energy stored is concentrated in a narrow phase transition range. **(Lo Biundo, 2026)**

Further studies have explored the addition of ternary alloying elements to the Fe-Si system to identify new PCM compositions with higher latent heat or tailored operating temperatures. The Fe-Si-B system has gained significant interest, primarily due to the intrinsically high latent heat of boron. In particular, the eutectic composition Fe-26Si-9B (wt.%) has been proposed as a viable PCM (Jiao et al., 2022), showing a latent heat of 1020 kWh/m³ (Polkowski et al., 2025b). Similarly, the Fe-46Si-5B composition has a latent heat of 1064 kWh/m³.

In addition, the Si-B system has been assessed. Its eutectic composition, Si-3.25B, undergoes a 9% volume expansion during solidification (Datas et al., 2020), posing mechanical constraints similar to pure silicon. While this expansion can be suppressed by incorporating 20 wt.% boron, such an addition shifts the liquidus temperature above 1700°C (Jiao et al., 2019).

Beyond boron, the addition of Cr, Ti, and V was calculated utilizing FactSage. These thermodynamic calculations have identified several promising ternary candidates, including Fe-24Si-11B, Fe-34Si-38Cr, Fe-34Si-43Cr, Fe-36Si-14V, Fe-34Si-10V, and Fe-38Si-20Ti. Nevertheless, empirical validation of these theoretical compositions remains to be conducted (Lo Biundo et al., 2025b).

3. Containment Strategies and Refractory Materials

Containment is one of the defining challenges for PCMs above 1000 ◦C and especially for metallic ones. At these temperatures, silicon rich alloys and halide salts are aggressively corrosive, dissolving, reacting and infiltrating most used materials (Mohan et al., 2019). The long term containment, along thermocycles of melting and freezing, does not depend on the stability of the PCM itself, but on the container-liquid interaction.

The important interfacial phenomena to consider are wetting, chemical reaction (thermodynamic and kinetic), interdiffusion, infiltration in pores or cracks and thermomechanical damage caused by the phase transition (Dezellus and Eustathopoulos,

2010). These effects often affect each other: a reactive melt may lower the contact angle, penetrate a porous body, form a new interfacial phase, and embrittle the container during thermal cycling due to difference in expansion. This paper will focus primarily on metallic silicon-based alloys and recent advancements in their storage technology.

3.1 Refractory metals

Refractory metals used in the aerospace industry such as molybdenum, tungsten, tantalum, and niobium are often considered for high-temperature applications because of their high melting points, mechanical strength, and fabrication potential. In fact, they are used in molten-salt systems below 1000 °C (Kenisarin, 2010). For silicon-rich PCMs and fluorides, however, refractory metals are generally unsuitable because they form silicides and fluorides without developing a passivation layer.

When molten silicon is in contact with a refractory-metal surface, compounds such as $MoSi_2$, WSi_2, or $TaSi_2$ are formed. Tests with silicon in molybdenum crucibles have shown that the metal continuously dissolves into the melt until catastrophic failure. The resulting silicide layer is not truly passivating and cannot prevent further corrosion (Batutis, 1961). For LHTES system that need to withstand thousands of cycles, refractory metals are therefore not considered viable containers for silicon-rich PCMs.

3.2. Oxide ceramics

Oxide ceramics such as silica (SiO_2), alumina (Al_2O_3), and magnesium oxide (MgO) have suitable melting temperature, but they are unfit to store the silicon based alloys. First, oxides will react to make a slag according to the reaction

$$2\underline{MeO}+Si=\underline{SiO2}+2Me$$

where the underscored oxides will form a slag and the metal will dissolve in the PCM.
Second, silicon is known to react with silica according to the equation

$$SiO_2(s) + Si(l) = 2SiO(g)$$

Due to the gas formed, in sessile drop experiments the melt is observed to "oscillate" on the substrate (Drevet and Eustathopoulos, 2012; Jiao, 2020).
The Si/MgO and the Si/Al_2O_3 systems show contact angles of respectively 88° and 86°, and react at the interface, dissolving Mg and Al in the melt and forming silica (Yuan et al., 2004). Thus, oxide ceramics are not suitable for the storage, both for a "pollution" of the melt and the generation of slag and gasses.

3.3. Non-oxide ceramics: SiC, Si_3N_4, BN and graphite

Silicon carbide (SiC)
SiC is inert when in contact with pure silicon, as carbon solubility in silicon is low, at ppm levels. According to sessile-drop studies the contact angle for Si/SiC is in the range of 30–50°, indicating good wetting(Eustathopoulos et al., 1999; Li and Hausner, 1992a). This indicates a good chemical compatibility and favors the infiltration of the melt if the substrate is too porous (Israel et al., 2010). When iron is present, the interfacial behavior depends on alloy composition. Iron-rich melts can react more actively with SiC, dissolving it into silicon and precipitating carbon., while silicon rich ones will form SiC in contact with graphite according to the Si+C=SiC equation. The equilibrium threshold depends on the temperature and SiC stability is achieved for melts above 20 wt% Si at 1200 °C or 30 wt% at 2000 °C as shown in figure 2 [To be published (Lo Biundo et al., 2026)].

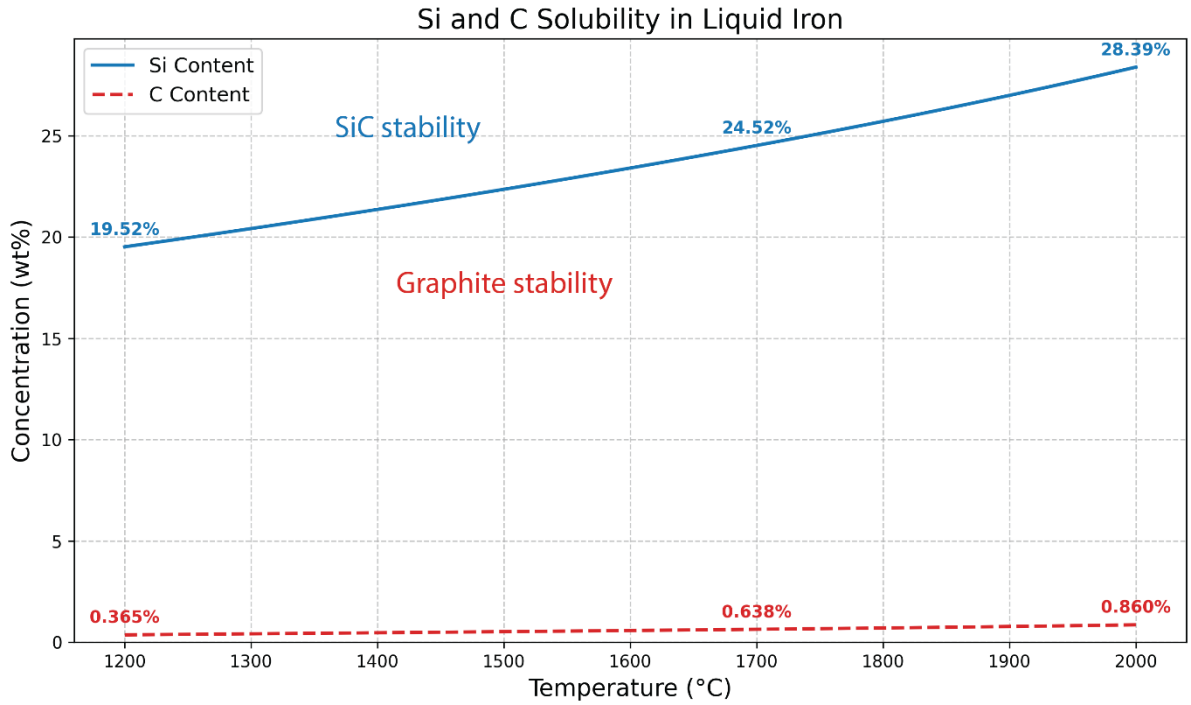

Figure 2. Calculated equilibrium concentrations in (wt%) in liquid iron on SiC substrate using FactSage. (Lo Biundo, 2026)

Silicon nitride (Si_3N_4*)*

Si_3N_4 has been used in the silicon industry because it is non-wetting toward molten silicon. While it is considered non wetting and non reactive, the performance of Si_3N_4 is highly sensitive to oxygen partial pressure and local interfacial chemistry, and complete wetting has been reported under some low-oxygen condition due to the formation of a oxynitride (SiN_xO_y) layer (Li and Hausner, 1992b), exhibiting contact angles from 90° to 40° since the layer eventually evaporates reacting forming SiO (Jiao, 2020).

The addition of boron in the PCM can change its behaviour. For boron containing alloys, higher contact angles of 143° have been reported for FeSiB/Si_3N_4, due to the formation of BN at the interfacial layer (Jiao et al., 2022). The boron nitride formed at the interface is chemically inert and non wettable, improving the barrier properties.

Boron nitride (BN)

Hexagonal BN is another important non-oxide ceramic for silicon-rich systems. For pure silicon, BN generally exhibits non-wetting behaviour, with high contact angles between 90°–145°(Polkowski et al., 2018). However, pure silicon can also dissolve BN during prolonged exposure, forming silicon borides and progressively degrading the barrier (Polkowski et al., 2018). At higher temperature and after repeated cycling, the contact angle decreases.

In boron-rich Fe–Si–B alloys, the thermodynamic driving force for BN dissolution is suppressed because the melt already contains boron (Jiao, 2020). BN is non-wetting over multiple cycles and therefore acting as an efficient barrier. Its main limitation is mechanical rather than chemical: BN is brittle and difficult to use as a standalone structural containment material on a large scale.

Graphite (C)

Graphite is an excellent refractory material, as it withstands easily high temperatures. It reacts with silicon containing melts forming SiC. The Si/SiC system is, in fact, a good description of

the reactive wetting of the Si/C system, where SiC is formed at the interface. According to (Israel et al., 2010), the infiltration of the melt into the porous structure is reaction-limited by the formation of SiC; it follows a linear trend with time and is directly related to the spreading velocity on the surface. These velocities depend heavily on the morphological features of the graphite: the total porosity, the dimension of the pores, and the degree of pore closure, with smaller, closed pores performing significantly better. The high wettability Si/SiC of the system promotes creep along the crucible walls and capillary infiltration into its pores. For this reason, a closed-pore graphite variant like isostatic graphite will perform much better, whereas extruded graphite, which is more porous and features an open-pore structure, is less suitable. Moreover, while graphite can be used because it forms an inert, self-healing SiC layer, the initial interaction involves two distinct mechanisms that alter the PCM composition. First, carbon dissolves directly into the molten PCM. Second, the graphite chemically reacts with the PCM to form the interfacial SiC layer, consuming silicon in the process.

3.4 Container design

A promising candidate as a vessel is graphite crucible coated internally with boron nitride. In this design, a thin BN layer gives the graphite non reactive and non wetting properties towards the Fe–Si melts. If the BN coating is locally damaged or scratched, the exposed graphite will react with the silicon present in the melt to form an inert SiC layer, which acts as a self-healing backup barrier and suppresses further damages. This vessel would benefit on the availability of graphite availability, price and structural strength and use BN as a layer that can last multiple cycles.

For such design to be effective, there are some requirements. First the graphite should not have open porosity, and a denser graphite generally is better at containing the melt and forming a stable SiC layer (Israel et al., 2010). Second the BN layer needs to be adherent to the substrate to postpone the degradation as much as possible during thermocycling. Third, graphite and the other ceramics discussed here are not stable in oxygen atmosphere in the intended temperature range: graphite turns into CO and CO_2 gas and so does the BN, releasing N_2 and forming B_2O_3 which has a "low" melting point of 450 °C. Si_3N_4 and SiC, on the other hand, behave much like BN, where N_2 and CO_2 volatilize, but the resulting SiO_2 oxide can protect the material from further oxidation.

Overall, a BN-coated graphite container appears to be a practical compromise between chemical resistance, mechanical robustness, machinability, and cost. Its success, however, depends on the combined optimization of graphite microstructure, BN coating quality, alloy composition, and operating atmosphere.

3.5. Encapsulation of PCMs

A prominent alternative is the encapsulation of PCM in a shell in order to have a solid material that is easier to handle and has some advantages, like a high surface to volume ratio that improves the charging and discharging and reduces stresses by thermal gradients since the beads are smaller (Imran Khan et al., 2023). An example is the Al-Si PCM growing a self healing Al_2O_3 oxide shell on the PCM droplets, making them inert and easy to use (Nomura et al., 2019) and some studies on the encapsulation of FeSi57 were done, promoting the formation of an SiO_2 layer using microsilica (Polkowski et al., 2025a).

Encapsulating the PCM eliminates direct contact between the liquid melt and containment wall, mitigating crucible corrosion issues. The resulting system behaves like a solid-state material that exhibits a spike in its "effective specific heat capacity" at the phase change temperature.

Despite these benefits, several drawbacks remain. The additional encapsulation step introduces manufacturing complexity and higher costs, while also penalizing the system's

overall latent heat capacity. Operational risks include potential particle leakage and complex manufacturing scalability. Additionally, while individual particle heat transfer can be constrained by the shell, submerging the encapsulated PCMs in a dynamic heat transfer fluid can actually boost the system's effective thermal conductivity rather than decreasing it. This topic, therefore, constitutes a research gap, where a new type of easy to handle and efficient high temperature PCM could be used.

Table III. Studies on microencapsulation of PCMs at high temperature

PCM@capsule	Melting Point	Latent Heat	Encapsulation Mechanism
	°C	J/g	
$FeSi57@SiO_2$	1229	890	Ultrasonic atomization to form spherical cores, which are subsequently coated with nano SiO2 and fired to form a layer. (Polkowski et al., 2025a)
$Cu@Al_2O_3$	1063	210	Copper powders are mixed with a CMC gel binder to form a non-densified core. This binder decomposes and leaves behind internal voids. When the copper melts, this porous medium accommodates the liquid's expansion. (Sheng et al., 2022)
Cu@Fe (FeO)	1090	24.6	This core-shell structure naturally forms through the liquid phase separation of undercooled Fe-Cu immiscible alloys during aerodynamic levitation processing. Fe rapidly oxidizes forming a protective FeO (Ma et al., 2014)
NaF@C	988	192 J/g	NaF particles are encapsulated in a resole-type phenolic resin, that then is cured and carbonised to form a carbon shell. (Jiang et al., 2022)
NaCl- Al_2O_3 @SiC@Al_2O_3	800-850	Not specified	Double-layer encapsulation where an intermediate SiC powder layer isolates the highly corrosive molten salt, and the bulk outer Al_2O_3 shell provides strength and oxygen protection (Liao et al., 2024)
Al-Si@Al_2O_3	577	273–301	Two-step fabrication involving a boehmite treatment (boiling) and high-temperature heat oxidation to grow a protective Al_2O_3 shell on the droplets (Nomura et al., 2019)

4. CONCLUSIONS

This work has evaluated the potential of Fe–Si-based alloys as phase change materials for ultra-high-temperature latent heat thermal energy storage, together with the associated challenges of containment and material compatibility.

Among candidate PCMs operating above 1000 °C, metallic systems offer advantages in terms of thermal conductivity and energy density. Silicon-rich materials are particularly attractive due to their exceptionally high latent heat of fusion. However, the large volume expansion of pure silicon during solidification represents a significant limitation for practical implementation.

Alloying with iron provides a solution to mitigate the volume expansion. The Fe–Si system, especially near-eutectic compositions such as Fe–57Si, combines high volumetric latent heat (~1000 kWh m^{-3}), a narrow phase transition interval, and minimal volume change. These characteristics make Fe–Si alloys among the most promising candidates for high temperature LHTES, particularly in combination with thermophotovoltaic conversion technologies.

The containment of molten silicon-rich alloys remains the primary challenge. Refractory metals are unsuitable due to continuous silicide formation, while oxide ceramics suffer from chemical reactivity leading to SiO evolution. Non-oxide ceramics offer improved performance, although each material presents limitations: SiC provides chemical stability but is highly wettable; Si_3N_4 and BN exhibit non-wetting behavior but are sensitive to environment and mechanical constraints. Graphite, while reactive, can form a passivating SiC layer that contributes to system stability.

A graphite vessel coated with boron nitride provides a combination of mechanical robustness, non-wetting behavior, and self-healing capability through SiC formation at coating defects. The biggest drawback of graphite is the need for a non-oxidizing environment.

Encapsulation strategies represent an alternative approach to avoid the melt-container interaction. Although there is active research in this field, there is a lack of technological maturity for temperatures above 1000 °C, particularly for silicon-based alloys.

Future work should focus on the coupled optimization of alloy design, interfacial stability, and container engineering to enable reliable and scalable high temperature thermal energy storage systems.

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