Suitability of aluminium copper silicon eutectic as a phase change material for thermal storage applications: Thermophysical properties and compatibility

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Abstract
Latent thermal storage in metals can overcome many issues related to the temporal or spatial intermittency of heat resources, particularly in the provision of heat in electric vehicles. Alloys that are energy dense and thermally conductive are most attractive for thermal storage applications. The eutectic alloy, Al-25% Cu-6% Si (wt%) has been identified as an optimal metallic phase change material melting in the temperature range 508°C to 548°C. Through differential scanning calorimetry, light flash analysis and long-term reaction experiments, the thermal and compatibility characteristics of this alloy are experimentally determined. Graphite and alumina are observed as compatible housing materials for the alloy after 2 weeks at 550°C. Reaction depth and products at the interface with iron and stainless steel are identified with energy-dispersive X-ray spectroscopy and electron backscatter diffraction analysis. A volumetric energy density of 0.7764 ± 0.0178 kWh/L was calculated for an operating range of 160°C to 660°C from the measured properties, suggesting the material is an excellent candidate for thermal storage in electric vehicles.

KEYWORDS
Al-cu-Si system, compatibility, metallic phase change material, thermal storage

1 | INTRODUCTION

The continuous provision of heat is necessary for many facets of modern life. Examples include maintaining a safe and comfortable environment for people or in the stable generation of electricity in a thermal power plant. Plentiful heat has often been generated through the conversion of chemical energy of a fuel in a combustion process. Unfortunately, excessive consumption of fuel in industrialised nations has led to the globally significant environmental issue of anthropogenic climate change. Alternative renewable energy sources, photovoltaics, solar thermal and wind power, for example, often face the problem of intermittency. Thermal storage materials overcome intermittency by storing heat.

Heat can be stored in a number of ways. The most intuitive method of heat storage is by increasing the temperature of a material, also known as sensible heating. Here, the heat capacity of a material provides the proportionality between heat stored per kilogram and
temperature. A higher heat capacity leads to more energy being stored per degree of temperature. Heat may also be stored latently in a phase transformation, like melting. A phase transformation occurs at a constant temperature for a pure element, pure compound or at specific compositions in a mixture (eutectic or congruent isomorphous minima/maxima).\textsuperscript{1} When referring to melting, the amount of energy is referred to as the latent heat of melting, or equivalently, the (latent) heat of fusion. Metals have a relatively large heat capacity and undergo phase transformations with large heats of fusion. For convenience, metals appropriate for thermal storage will be referred to henceforth as metallic phase change materials (mPCM)s.

The rate at which heat can be stored and liberated depends on the system and on properties inherent to the material. Thermal diffusivity and conductivity are material properties characterising the rate at which heat can move within a solid or static liquid material. mPCMs have exceptional thermal conductivity and diffusivity when compared to other common thermal storage materials such as molten salts, paraffins and thermal oils.\textsuperscript{2} Pure or eutectic composition mPCMs are preferred over other compositions due to their ideally isothermal melting behaviour. This provides higher cycling stability with minimal phase separation and provides a large proportion of the stored heat at a single temperature, simplifying heat transfer system design.

Our group at the German Aerospace Centre (DLR) has been investigating Al-based alloys for vehicle applications since 2016.\textsuperscript{3} The binary eutectic Al-12.7 wt% Si has been previously investigated with a melting temperature of 577°C.\textsuperscript{4-7} The ternary Al-Cu-Si system has been selected as it has comparable thermal properties to the binary Al-Si with a lower melting temperature of about 522°C.\textsuperscript{2} Additionally, this ternary system has shown superior corrosion resistance compared to Al-Cu and Al-Si alloys.\textsuperscript{8}

Our previous findings show the Al-25.4% Cu-6.1% Si (wt%) (rounded to Al-25% Cu-6% Si [wt%] in the rest of the article) eutectic to be optimal in energy density (both gravimetric and volumetric) and in cost per kWh of latent heat for the temperature range 508°C to 548°C.\textsuperscript{2} Given its apparent optimal properties for a temperature range relevant to many applications, the thermal properties and compatibility of the eutectic should be determined to enable implementation.

Several articles have identified the eutectic and sought to characterise its thermal properties. The potential of this alloy as an mPCM was first identified by Farkas and Birchenall in 1983.\textsuperscript{5} In the aluminium copper silicon system, they identified a eutectic at 30% Cu and 5% Si by mass. The identified melting point was 571°C. Huang et al.\textsuperscript{10} specifically addressed an alloy with composition Al-27% Cu-5.25% Si (wt%), measuring heat capacities and the latent heat of fusion. They used a differential scanning calorimeter (DSC) and an Isothermal Copper-Block Calorimeter (ICC) measuring a heat of fusion at 365.6 and 395.7 kJ/kg, respectively. The heat capacity was reported as 0.875 kJ/kg K in the solid state and 1.437 kJ/kg K in the liquid state. In 2011, Cheng et al.\textsuperscript{11} released an article presenting thermal properties and corrosion mechanics of various aluminium alloys. The closest composition they measured was Al-29.3% Cu-8.5% Si (wt%) with a solidus temperature of 452.2°C, a liquidus temperature of 513.6°C and a heat of fusion of 114.7 kJ/kg. Becattini et al.\textsuperscript{12} built a pilot-scale demonstrator for adiabatic compressed air storage with Al-26.5% Cu-5% Si (wt%) as the storage material. They measured a melting range of 509°C to 527°C, a heat of fusion of 404 kJ/kg, a heat capacity of 1.004 and 1.103 kJ/kg K in the solid and liquid, respectively. They also measured the density and thermal diffusivity. The entire Al-Cu-Si system has been treated by many researchers. Three recent works\textsuperscript{13-15} contained compositions and temperatures of the relevant eutectic. A summary of these investigations is given in Table 1 and a liquidus projection calculated with the database TCAL5 noting the eutectic composition is given in Figure 1.

Storage materials undergoing a melting transformation must be contained in a housing material. Housing materials should be machinable or formable to an appropriate shape, be reasonably priced and unreactive with the storage material and the environment. Though mPCMs may be attractive due to their thermal properties, they react with many potential container materials.\textsuperscript{7}

There are few papers concerning the compatibility of the Al-25% Cu-6% Si (wt%) eutectic. However, Becattini et al.\textsuperscript{12} recently observed the behaviour of Al-26.5% Cu-5% Si (wt%) with 304 stainless steel after several thermal cycles. The authors found that the PCM leaked through either the welding seams or insertions for thermocouples and planned to undertake detailed analysis on the growth of intermetallic layers. Thus, implying the observation of a notable reaction.

The compatibility of the pure or binary constituents of the eutectic are more commonly explored in literature and give a strong indication of expectations for the ternary. A major report was published by Birchenall et al.\textsuperscript{17} It covered several topics on heat storage in eutectic alloy transformation. Compatibility experiments were performed for several combinations of mPCM and container. The reaction layer growth of several molten metals was recorded as a function of time up to 3 weeks when in contact with SS304 and SiC. This led to the conclusion that silicon carbide was a preferred container material for aluminium and copper rich alloys.\textsuperscript{17} They also found that aluminium rich alloys were prone to attacking SS304 and
SS316L containers. The compatibility of the Al-12wt%Si eutectic was experimentally investigated by Fukahori et al. Alumina, aluminium nitride and silicon nitride all showed high corrosion resistance in their experiments. A thorough treatment of the impact of Si addition to Al on its attack of iron-carbon steel was published by Springer et al. Silicon was found to slow the corrosion of mild steel by liquid aluminium. The work identified many reaction phases also found in this work. A recent publication by Dindi et al. analysed the compatibility of eutectic Al-Si alloy with BN coated stainless steel containers undergoing thermal cycling. The coating was observed to inhibit reaction over 720 thermal cycles, but cracking was observed.

The objective of this paper is an in-depth characterisation of thermophysical properties including melting temperature, heat capacity, latent heat, thermal diffusivity and conductivity as well as compatibility of the Al-25% Cu-6% Si (wt%) eutectic. The novelty of this paper lies in thermophysical property measurement over a wide temperature range in the solid and liquid states leading to practical models. A detailed study of reaction behaviour for four different potential housing materials, provides evidence sufficient to make recommendations for appropriate container materials, enabling engineering decisions and distinguishing this paper from previous work.

2 | EXPERIMENTAL METHODS

2.1 | Sample material

The Al-25% Cu-6% Si (wt%) alloy was purchased from IME Aachen and had a measured composition of 66.84 wt% Al, 23.54 wt% Cu, 9.02 wt% Si and 0.59 wt% other impurities (the majority of which was Zn). The silicon content of the sample alloy was slightly higher than the eutectic composition predicted by CALPHAD calculations with the TCAL5 database. Estimates from the same thermodynamic database suggest that the slight difference in composition has a negligible impact on density, heat capacity, heat of fusion and, solidus and liquidus temperature.

2.2 | Gravimetric analysis

Density was determined at room temperature using traditional gravimetric analysis. Cylindrical samples of
samples were then placed into transparent sapphire crucibles and loaded into the Netzsch LFA 467 HT Hyper-Flash. Before each run the furnace was evacuated and flushed three times with argon (purity 5.0). Experiments took place under the same argon flowing at 50 L/min.

The LFA experiments were performed over three different runs. In the first run, the thermal diffusivity of four samples was measured from room temperature to 450°C in steps of 50°C. After the first run, the samples and sapphire crucibles were examined visually for signs of damage. The second run with the same four samples started at 600°C and had variable steps decreasing down to room temperature. Five measurements per sample per temperature step were taken for these two runs. One final run was performed, starting at 650°C and utilising finer steps down to room temperature but with only one new sample. Three measurements were made at each temperature for the final run. Measurements heating from room temperature and cooling from the melt represent the wide range of heat treatments expected in application.

2.5 | Static pellet reaction experiment

To experimentally investigate the operational compatibility of Al-25% Cu-6% Si (wt%) long-term static crucible reaction experiments were undertaken. Here, cylindrical pellets of approximately 800 mg were placed inside crucibles of different potential housing materials and held at approximately 600°C for 2 weeks. The experiment volume was evacuated to 1 × 10⁻⁵ mbar before loading with approximately 300 mbar of Argon (99.993 mol% purity) serving as a static inert environment during the experiment. Crucibles of alumina, graphite, iron and stainless steel were utilised. The graphite and alumina crucibles were baked at 600°C under vacuum for 8 h prior to the experiment to remove any volatile compounds. The crucible composition, dimensions and manufacturer information are given in Table 2.

Following the reaction experiment, the crucible and sample pairs were examined. The mass change over the experiment was found to be negligible in all cases. The lid was removed from the crucibles before the crucibles were set in a conductive epoxy (PolyFast; Struers, Copenhagen, Denmark). The fixed crucible and sample were then cut in half and the cross-section ground and polished to a sufficient smoothness for scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD). SEM micrographs were taken and EDX/EBSD analysis was performed on representative points and areas. EDX line and mapping scans were also taken to visualise the distribution of elements through the mPCM-crucible interface.
# RESULTS AND DISCUSSION

## Thermophysical property characterisation

The density of Al-25% Cu-6% Si (wt%) was determined to be 3344.3 ± 1.7 kg/m³ at room temperature (approximately 25°C). The low uncertainty in this measurement is probably optimistic as deviations in geometry and the presence of pores are overlooked. This value was larger than the predictions from the CALPHAD database TCAL5,16 3249 kg/m³ at the nominal composition or 3194 kg/m³ at the sample material composition (66.84% Al, 23.54% Cu, 9.02% Si and 0.59% other impurities [wt %]). The difference may be attributed to limitations in the thermodynamic model.

The solidus and liquidus temperatures were determined by extrapolating the characteristic peak temperatures for six different samples with various heating rates (5-20 K/min) to a heating rate of zero (shown in Figure 2). The solidus temperature was taken as the average of the onset temperature for all heating runs, this is shown in Figure 3A. As proposed by Illers,27 a linear relation between peak temperature and the square root of the product of heating rate and sample mass ($\sqrt{\beta \cdot m}$) was assumed, plotted in Figure 3B. The solidus temperature of the Al-25% Cu-6% Si (wt%) eutectic was determined to be 520.04 ± 1.95°C (maximum possible error). The liquidus temperature was measured as 528.46 ± 6.11°C based on 1.96 times the SE of the linear regression. Within error bars. The two temperatures nearly agree. The produced sample shows characteristics of a near eutectic alloy.

The specific heat of fusion is equal to the area under the peak of a DSC curve measuring heat capacity. The heat of fusion was found to be 381.26 ± 15 kJ/kg. Here the uncertainty is the maximum possible error of the five measurements. This value is within experimental uncertainty of past measurements10 but considerably lower than predictions from CALPHAD.2

The heat capacity of Al-25% Cu-6% Si (wt%) was determined in the solid and liquid states. The data are plotted in Figure 4. A comparison to the heat capacity calculated from the thermodynamic database is also given with the two magenta lines.16 The lines are for the nominal composition Al-25.4%Cu-6.1%Si (wt%) and the sample composition (Al-23.54wt%Cu-9.02 wt% Si). The experimental results have the same trend as the thermodynamic database, but the absolute values differ greater than the 95% confidence interval in the measurement. The difference cannot be attributed to the samples slightly different composition, indicating a limitation in the thermodynamic database.

A Shomate function was fit to the solid and a linear function to the liquid state data, resulting in the coefficients given in Table 3. The temperature range for the solid heat capacity model should be observed. It is recommended that a constant heat capacity of 0.73 kJ/kg K, corresponding to the last model prediction, be used for temperatures lower than 100°C.

The solid heat capacity measurements are lower than those of Becattini et al.12 The measurements conform to expectations based on the constituent solid phase behaviour. As the melting point (400°C-500°C) is approached

| Crucible material | Composition, wt% | Diameter (outer), mm | Height (outer), mm | Manufacturer |
|-------------------|------------------|----------------------|-------------------|--------------|
| Alumina           | >99.5% Al₂O₃     | 12.8 (16)            | 13.8 (15)         | Friatec AG   |
| Graphite          | C (<20 ppm ash)  | 13 (16)              | 13 (15)           | Mersen France Gennevilliers S.A.S (machined in house) |
| Armco iron        | >99.85% Fe       | 12.6 (16)            | 13.4 (15)         | HKM Stahl GmbH (machined in house) |
| Stainless steel   | SS304            | 12.6 (16)            | 13.4 (15)         | Hans-Erich Gemmel & Co. GmbH (machined in house) |

![Figure 2](https://example.com/figure2.png)
the heat capacity of solid aluminium shows an excess specific heat. Brooks and Bingham\textsuperscript{28} attributed this to the formation of lattice defects and an increasing contribution from the anharmonic behaviour of the lattice. As aluminium is the majority component of the solid eutectic alloy, this behaviour should also be expected. A slightly decreasing linear behaviour of $c_p$ above the melting point was observed. Observations by McDonald\textsuperscript{29} showed a constant behaviour of aluminium $c_p$ with temperature in the liquid state. Given the small temperature range of data in the liquid state, the $c_p$ was modelled as constant.

The energy density of the alloy can be determined from the measured density, heat of fusion and heat capacity. The latent energy density is $0.1059 \pm 0.004$ kWh/kg or, on a volumetric basis, $0.3542 \pm 0.0139$ kWh/L. If the operating range of $160^\circ C$ to $660^\circ C$ is considered, the energy density is $0.2322 \pm 0.0178$ kWh/kg or $0.7764 \pm 0.0178$ kWh/L volumetric. The volumetric energy density measured is within experimental uncertainty of that predicted in our survey paper.\textsuperscript{2} This energy density is comparable to other aluminium alloys for example, Al-33.3wt%Cu at $0.716$ kWh/L or Al-12.5wt%Si at $0.708$ kWh/L.

The thermal diffusivity of Al-25\% Cu-6\% Si (wt\%) was determined in both the solid and liquid states. The diffusivity was observed to decrease with temperature up to the melting point of the solid alloy. The behaviour appears slightly non-linear. Measurements near the melting point were subject to large scatter due to the latent heating impacting the temperature-time output of the LFA. The diffusivity dropped from near 45 to 15 mm$^2$/s over the melting transformation before increasing again with temperature. The liquid thermal diffusivity was measured up to $650^\circ C$ and the behaviour appears linearly increasing over this range. The behaviour and absolute values correspond to the work of Becattini et al.,\textsuperscript{12} slightly higher at low temperatures. The data and fit are plotted in Figure 5, the coefficients of the curve fit are presented in Table 4.

The thermal conductivity of the alloy can be calculated as the product of the heat capacity, density and thermal diffusivity. However, the density of the alloy was only measured at $25^\circ C$, not over the entire temperature range. The relative change in density from TCAL5 was
used to extrapolate the room temperature measurement. The relative change in volume over the melting transformation and the volume expansivity of the solid phases and liquid phase were calculated from the thermodynamic database TCAL5 from Thermo-Calc Software. The values were then applied to the measured room temperature density to provide an estimate at temperature dependent density. This is shown in Figure 6.

The behaviour is approximately linear until near to the melting point. As a liquid the density is predicted to decrease linearly. Coefficients for these linear fits are provided in Table 5.

The product of the heat capacity, thermal diffusivity and the CALPHAD extrapolated density measurement led to a high order polynomial. The complexity of this was reduced to give a linear estimate at the thermal conductivity of the eutectic, shown in Figure 6. The calculated value is less than that of Becattini et al.\textsuperscript{12} almost certainly due to our lower heat capacity measurement. The coefficients are shown in Table 6.

The calculated conductivity from the measured properties and the database density should be used with caution. The accuracy of the density calculated using CALPHAD methods has not been experimentally verified by the authors. Additionally, the measurement uncertainties are compounded through the calculation procedure. Accurate measurements of density with a different technique could improve this calculation, or a direct measurement of conductivity using a different technique.

The addition of copper to the alloy does not significantly improve the thermal diffusivity or conductivity from pure aluminium\textsuperscript{30} or Al-Si eutectic alloy.\textsuperscript{31} This can be attributed to two factors; the addition of copper adds an extra phase to the microstructure resulting in further grain boundaries and the fact that the Cu does not exist in its high conductivity face centred cubic metallic phase, rather it exists in the intermetallic Al\textsubscript{2}Cu.

3.2 Compatibility experiments

After 2 weeks at approximately 600°C, no reaction was observed between Al-25% Cu-6% Si (wt%) with alumina and graphite crucibles but a strong reaction was observed with iron and stainless steel crucibles. This observation
was confirmed with SEM and EDX analysis on cross sections of the four reaction experiments. Line scans revealed the dissolution of the crucible and the penetration of the mPCM pellet by the container constituents in the iron and steel experiments.

No reaction occurred at the interface between the alumina crucible and Al-25% Cu-6% Si (wt%). The pellet did not adhere at all to the crucible following the experiment and was removed prior to SEM analysis. SEM micrographs reveal the eutectic structure of the alloy with some primary silicon observable. EDX point, line and mapping scans show no impact of the crucible on the mPCM (Figure 7).

The compatibility observed corresponded to expectations from equilibrium phase diagram between the constituents of Al-25% Cu-6% Si (wt%) and Al₂O₃. Reduction of Al₂O₃ to the other possible oxides (SiO, SiO₂, CuO, Cu₂O, CuAlO₂, Cu₃A₂O₄) is not energetically favourable. No solubility or intermediate phase was expected for the temperatures set in the reaction experiment.

Similarly, no reaction was observed at the interface between the eutectic alloy and the graphite crucible. The pellet did not stick to the crucible surface and was again easily dislodged. The eutectic microstructure was observed in SEM analysis, again with some relatively large primary silicon crystals. Carbon was not observed to dissolve into the mPCM, the crucible was unaffected and no new carbide phases were observed in the SEM images nor through EDX analysis. Representative EDX maps are shown in Figure 8.

Two mixed carbides of Al, Si and C are stable in the experiment temperature range according to equilibrium calculations. Neither was observed. It is likely that the activation temperature for these carbides to form was not attained. These observations conform to those of Inoue and Yamaguchi who found that, from ball milled aluminium, silicon and graphite powders, Al₄C₃ and SiC form above 800°C and Al₄SiC₄ only formed above 1106°C. Several other authors also reported similar observations. It is unlikely that a lower temperature quaternary carbide, also involving copper, would form at temperatures up to that selected in this works reaction experiments. Thus, graphite is considered a compatible container for Al-25% Cu-6% Si (wt%) with operating temperatures below 600°C. The bulk liquid melt in contact with solid graphite is probably compatible up to 800°C.

A reaction was observed at the interface between the alloy and the iron crucible. The iron crucible underwent considerable dissolution and reaction to a maximum depth of 390 μm. EDX point, line and mapping revealed the extent of dissolution and the phases formed. Iron was observed to diffuse throughout the entire mPCM volume, forming several intermediate compounds as layers and discrete inclusions.

Figure 9A shows the cross section of an Fe crucible with the alloy Al-25% Cu-6% Si (wt%). The bright area at the
bottom is the Fe crucible, labelled 0. Moving upwards, regions of different material can be distinguished. Three layers are labelled (No 1, 2 and 3) in Figure 9A, the borders between them are wavy and not well defined (wavy interface between crucible 0 and Layer 1). A large horizontal crack splits Layer 1 into two sections. Layer 3 is formed of
large blocks (3 and 4). These regions can also be found in
the upper region of Figure 9A, which otherwise shows typi-
cal features of the Al-25%Cu-6%Si (wt) alloy. These features
are CuAl2-dendrites (5), eutectic regions (6) of the Al phase,
CuAl2 and small Si platelets. Also visible in the micrograph
are large, lengthy Si platelets (7). The EDX maps of
Figure 9C,D demonstrate the penetration of iron into the
mPCM and the corrosion of iron by the aluminium.

A thin layer was observed at the interface between
Layers 1 and 2. The layer, approximately 10 μm in width,
was accompanied by a row of precipitates on the side of
Layer 1. The intermediate layer was rich in Si, Fe and
Cu. The precipitates had a greater proportion of Si and
Fe. The crystal structure of the precipitates could not be
determined by EBSD analysis although the diffraction
pattern had high quality.

An EDX line scan was performed along the yellow
line in Figure 9A. The results for Al, Cu and Fe,
normalised to total counts per pixel, are given in
Figure 9B. The layers can be distinguished clearly at the
step changes in Fe concentration. Quantitative data for
the concentrations was measured separately by averaging
over representative areas in the respective layers or pre-
cipitates. A local analysis of crystal structures was also
carried out with EBSD analysis using phase matching
with 11 Kikuchi lines. Crystals in different orientations
were tested with this procedure. The crystal structures
were characterised by Strukturbericht-type and their
space group number. The quantification and most likely
phase for each numbered region are given in Table 7.

A reaction was also observed in the experiment
involving Al-25% Cu-6% Si (wt%) and stainless
The steel (304) was attacked by the mPCM, penetrating to a depth of approximately 170 \( \mu m \). SEM and EDX analysis revealed the dissolution of iron and chromium throughout the mPCM volume and the composition of several reaction layers and precipitates.

Figure 11 shows the reaction cross section of a 304 stainless steel crucible with Al-25% Cu-6% Si (wt%) alloy. The crucible in the micrograph (Figure 11A) on the left and bottom is in light grey. Large black areas are holes filled with embedding material during metallographic preparation. In the lower left corner of the crucible, the dissolution of the crucible by the melt can be clearly observed. Layers of different material can be found next to the bottom of the crucible. Horizontal cracks probably formed during cooling of the melt. The solidified melt shows several different phases. The position of an EDX line scan is given by the yellow vertical line. As with the iron crucible, the EDX maps of Figure 11C,D demonstrate the penetration of iron into the mPCM and the consumption of the steel crucible.

The data show clearly that typical elements of the crucible (Fe, Cr, Ni) can be found in the lower reaction layers (No 1, 2 and 3 in Figure 11A). As in the iron crucible, the reaction layers do not act as barriers to diffusion of the crucible constituents into the melt. Iron, chromium and nickel were found above the reaction layers. For example, the precipitate 4 (with the shape of a large block) and 5 contain a large amount of Fe supplied by the dissolved crucible.

The layers are not homogeneous, instead they have an internal structure. In the case of Layer 2, this structure consists mainly of two phases and the morphology is coarse enough to be resolved by EDX measurements. The compositions of the two phases are given in Table 8, noted as “2a in layer 2” and “2b in layer 2”. The composition of the bright phase (2a) is similar to the composition of the block-shaped precipitate labelled 4. The slightly differing morphology may be explained by the presence of chromium in phase 2a.

| Layer   | Chemical Composition | Phase Description                                      |
|---------|----------------------|--------------------------------------------------------|
| No 0 (crucible) | Fe: 99.45, Al: 0.39, Si: 0.16 | Fe bcc, SG 229                                        |
| No 1 (Layer 1) | Fe: 70.71, Cr: 27.83, Al: 0.59 | FeAl2-type, SG 63                                      |
| No 2 (Layer 2) | Mn4Al14(Al0.5Si0.5)4Si-type | Mn4Al14(Al0.5Si0.5)4Si-type, SG 200                   |
| No 3 (Layer 3) | Cu3FeAl7-type | Cu3FeAl7-type, SG 128                                  |
| No 4 | | Cu3FeAl7-type, SG 128                                  |
| No 5 (dendrite) | CuAl2-type | CuAl2-type, SG 140                                    |
| No 6 (black area in eutectic) | Si: 99.53, Al: 0.05 | Si, SG 227                                             |
| Intermediate 1-2 in Figure 10 | Al13Fe4-type | Al13Fe4-type, SG 124                                   |

*Note: Data are given in atomic percent. The measured data have been calibrated using measurements of an Al-25% Cu-6% Si (wt%)-as cast alloy. The measured values for silicon have been multiplied by a factor of 0.5275. The values of the other elements have been recalculated according to their composition and to achieve 100 at%.*

**Figure 10** Detailed view on Al-25% Cu-6% Si (wt%)/Fe reaction cross section with detector for forward scattered electrons (FSC). There is an intermediate layer of around 10 \( \mu m \) thickness accompanied by a layer of precipitates. The location of Figure 10 is indicated in Figure 9A (zoom). The grain structure of the layers is clearly visible due to imaging by the FSC-detector.
The second phase “2b in layer 2” appears dark in Figure 11A and seems to extend further into Layer 3. This impression is supported by a comparison of the compositions of Phase 2b and Layer 3, which are very similar. The crystallographic phases found in the Layers 1-3 of the stainless-steel crucible correspond to the phases found in the Layers 1-3 of the Fe crucible; however, the chemical composition is altered by Cr and Ni from the steel crucible. It is quite remarkable that the sequence of layers starting from the crucible is reversed: the lowest layer 1 is in both cases the FeAl$_2$$_8$-type. In the iron crucible, this is followed by the Mn$_4$Al$_{14}$(Al$_{0.5}$Si$_{0.5}$)$_4$Si-type and finally the Cu$_2$FeAl$_7$-type. For the stainless steel crucible, the first layer is followed by a mixed layer of these two mentioned phases. Layer 3 is then of Mn$_4$Al$_{14}$(Al$_{0.5}$Si$_{0.5}$)$_4$Si-type alone. In the EDX line scan, these features can be recognised by the higher level of Fe in Layer 3 (vicinity of the crack). The blocks are similar in composition and have the same crystal structure in both cases (Cu$_2$FeAl$_7$-type).

A detailed micrograph of the alloy is given in Figure 12. The alloy Al-25% Cu-6% Si (wt%) seems not strongly altered in this area by the dissolution of the steel crucible, eutectic structure consisting of the phases labelled No 7 and No 8 plus thin platelets (9) in different orientations. According to EDX measurements (Table 8), the respective phases are determined as Al$_2$Cu, Al and Si. A low amount of Ni can be found in the Al$_2$Cu-phase. However, in addition to the “usual” phases of Al-25% Cu-6% Si (wt%), precipitates which contain a considerable
amount of Cr and Fe are found (10). The influence of the element Ni supplied by the crucible can be observed in the vicinity of larger areas of the Al$_2$Cu-phase (11). The region labelled by No 12 has a similar composition as No 11, but several percent of the Al have been replaced by Ni and the crystal structure is altered into the (Cu$_{0.80}$Ni$_{0.20}$)$_{2.53}$Al$_{3.5}$-type.

Long-term static reaction tests revealed the compatibility behaviour of alumina, graphite, iron and stainless steel 304 when placed in contact with molten Al-25% Cu-6% Si (wt%) for 2 weeks. Alumina and graphite appeared to show no reaction at all with the alloys. If alumina could be manufactured into an appropriate shape and remain intact through operational mechanical and thermomechanical stress, then it is recommended as a compatible housing material. Graphite showed potential in experiments and would prove an affordable housing if the formation of carbides in the application, due to temperature excursions or relative motion for example, could be avoided. Iron and 304 stainless steel showed significant dissolution of the crucible material and the formation of many intermediate compounds in complex layered structures. Iron and steel cannot be recommended as container materials for this alloy.

3.3 | Summary

For convenience, the measurements and models are summarised in Table 9.
4 | CONCLUSION

The ternary eutectic alloy Al-25% Cu-6% Si (wt%) is a promising metallic phase change material and appears optimal in the temperature range 508°C to 548°C. The melting point, latent heat of fusion and room temperature density of the alloy were determined experimentally. An energy density of 0.7764 ± 0.0178 kWh L was calculated from the measured properties over an operating range of 160°C to 660°C. The temperature dependent thermal conductivity of the alloy was calculated from DSC measurements of heat capacity, light flash measurements of thermal diffusivity and calculated values for density. The eutectic was found to be compatible with alumina and graphite, but not iron and stainless steel (304 grade) after 2 weeks at 600°C. Graphite and alumina are recommended as housing materials. An in-depth EDX and EBSD analysis revealed the corrosion depth and the reaction products at the interface where reaction occurred.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors

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REFERENCES

1. Lane GA. Solar Heat Storage: Volume II: Latent Heat Material. Boca Raton, FL: CRC Press; 2018.
2. Rawson AJ, Kraft W, Gläsel T, Kargl F. Selection of compatible metallic phase change materials and containers for thermal storage applications. J Energy Storage. 2020;32:101927.
3. Kraft, W and MK Altstedde. Use of metallic phase change materials (mPCM) for heat storage in electric- and hybrid vehicles. 6th Hybrid and Electric Vehicles Conference 2016.
4. Kraft, W, Altstedde MK, Kainz T, DuoTherm - ein neuartiges thermisches energiespeichersystem am beispiel batterieelektrischer stadtbusse, VDI Wissensforum - Thermanagement in Elektromotorisch Angetriebenen PKW 2017.
5. Kraft, W, Jilg V, Klein Altstedde M, Lanz T, Vetter P, Schwarz D. Thermal high performance storages for use in vehicle applications. 2nd ETA Conference, November 22-23, 2018; Berlin, Germany 2019. p. 66-79.
6. Kraft, W, Stahl V, Vetter P, Thermal high performance storages for electric bus heating - overview on the current state of development. ENERSTOCK 2021.
7. Rawson AJ, Gläsel T, Nowak B, Boon D, Stahl V, Kargl F. The compatibility of metallic thermal storage materials and housing materials: a computational survey and accelerated reaction
experiments. In: Chen X, Zhong Y, Zhang L, et al., eds. Energy Technology 2020: Recycling, Carbon Dioxide Management, and Other Technologies. Cham, Switzerland: Springer International Publishing; 2020.
8. Awe S, Seifeddine S, AEW J, Lee YC. Development of new Al-cu-Si alloys for high temperature performance. Adv Mater Lett. 2017;8:695-701.
9. Farkas D, Birchenall CE. New eutectic alloys and their heats of transformation. Metall Trans A. 1985;16(3):323-328.
10. Huang ZG, Wu GZ, Xiao SL, Mei SH. Properties of cast Aluminium alloys as thermal storage materials. Cast Metals. 1989; 2(4):203-206.
11. Cheng XM, Chen X, Li YY, Tan YG. Research on the properties of the thermal storage and corrosion of Al-si-cu-mg-Zn alloy. Adv Mat Res. 2011;197-198:1064-1072.
12. Becattini V, Geissbühler L, Zanganeh G, Haselbacher A, Steinfeld A. Pilot-scale demonstration of advanced adiabatic compressed air energy storage, part 2: tests with combined sensible/latent thermal-energy storage. J Energy Storage. 2018; 17:140-152.
13. He CY, du Y, Chen HL, Xu H. Experimental investigation and thermodynamic modeling of the Al-cu-si system. Cal. 2009; 33(1):200-210.
14. Lukas HL, Lebrun N. Al-Cu-Si (aluminium - copper - silicon): datasheet from Landolt-Börnstein - Group IV Physical Chemistry. Light Metal Systems. Part 2. Vol 11A2. Berlin, Germany: Springer-Verlag; 2005.
15. Ponweiser N, Richter KW. New investigation of phase equilibria in the system Al-cu-si. J Alloys Compd. 2012;512(1-2): 252-263.
16. Thermo-Calc Software AB, TCALS Al-Based Alloy Database.
17. Birchenall, CE, Gueceri, SI, Farkas, D, Labdon, MB, Nagaswami, N, Pregger, B, Heat storage in alloy transformations. Report prepared for National Aeronautics and Space Administration. Newark, DE: Delaware University 1981.
18. Fukahori R, Nomura T, Zhu C, Sheng N, Okinaka N, Akiyama T. Thermal analysis of Al–Si alloys as high-temperature phase-change material and their corrosion properties with ceramic materials. Appl Energy. 2016;163: 1-8.
19. Springer H, Kostka A, Payton EJ, Raabe D, Kaysser-Pyzalla A, Eggerle G. On the formation and growth of intermetallic phases during interdiffusion between low-carbon steel and aluminum alloys. Acta Mater. 2011;59(4): 1586-1600.
20. Dindi A, Lopez Ferber N, Gloss D, Rilby E, Calvet N. Compatibility of an aluminum-silicon metal alloy-based phase change material with coated stainless-steel containers. J Energy Storage. 2020;32:101961.
21. European Virtual Institute for Speciation Analysis (EVISA). Instrument Database: Netzsch-Gerätebau GmbH - DSC 404 C Pegasus Thermal Analyzer 2010. http://www.speciation.net/Database/Instruments/NetzschGeratebau-GmbH/DSC-404-C-Pegasus-Thermal-analyzer-i2003 .
22. Shomate CH. A method for evaluating and correlating thermodynamic data. J Phys Chem. 1954;58(4):368-372.
23. Yamaguchi K, Itagaki K. Measurement of high temperature heat content of silicon by drop calorimetry. J Thermal Anal Calorim. 2002;69(3):1059-1066.
24. Chase MW. NIST-JANAF thermochemical tables 2 volume-set. Journal of Physical and Chemical Reference Data Monographs. College Park, MD: American Institute of Physics; 1998.
25. NETZSCH-Gerätebau GmbH. LFA 467 HT HyperFlash® – Light Flash Apparatus https://www.netzsch-thermal-analysis.com/en/products-solutions/thermal-diffusivity-conductivity/lfa-467-ht-hyperflash .
26. Struers, Hot Mounting. 2018.
27. Illers K-H. Die Ermittlung des Schmelzpunkts von kristallinen Polymeren mittels Wärmeflusskalorimetrie (DSC). Eur Polym J. 1974;10:911-916.
28. Brooks CR, Bingham RE. The specific heat of aluminum from 330 to 890°K and contributions from the formation of vacancies and anharmonic effects. J Phys Chem Solid. 1968;29(9): 1553-1560.
29. McDonald RA. Enthalpy Heat capacity, and heat of fusion of aluminum from 366° to 1647° K. J Chem Eng Data, 1967;12(1): 115-118.
30. Ho, CY, RW Powell, PE Liley, Thermal Conductivity of the Elements: A Comprehensive Review. National Standard Reference Data System 1974.
31. Wang Z, Wang H, Li X, et al. Aluminum and silicon based phase change materials for high capacity thermal energy storage. Appl Therm Eng. 2015;89:204-208.
32. Gale WF, Totemeier TC, eds. Thermochemical data. Smithells Metals Reference. 8th ed. Oxford, UK: Butterworth-Heinemann; 2004:1-58.
33. Inoue K, Yamaguchi A. Synthesis of Al4SiC4. J Am Ceram Soc. 2003;86(6):1028-1030.
34. Yokokawa H, Fujishige M, Ujiie S, Dokima M. Phase relations associated with the aluminum blast furnace: aluminum oxycarbide melts and Al-C-X (X=Fe, Si) liquid alloys. Metal Trans B. 1987;18(2):433-444.
35. Viala JC, Fortier P, Bouix J. Stable and metastable phase equilibria in the chemical interaction between aluminum and silicon carbide. J Mater Sci. 1990;25(3):1842-1850.
36. Burkhardt U, Grin Y, Ellner M, Peters K. Structure refinement of the iron-aluminium phase with the approximate composition Fe2Al5. Acta Crystallographica Section B. 1994;50:313-316.
37. Phragmén G. On the phases occurring in alloys of aluminium and copper, magnesium, manganese, iron, and silicon, in J. Inst. Met. 1950;77:489-552.
38. Bown MG, Brown PJ. The Structure of FeCu2Al7 and T(CoCuAl), Acta Crystallographica. 1956;9:911-914.
39. Meetsma A, De Boer JL, Van Smaalen S. Refinement of the Crystal Structure of Tetragonal Al2Cu, J. Solid State Chem. 1989;83:370-372.
40. Bown MG. The Structure of Rhombohedral T(NiCuAl), Acta Crystallographica. 1956;9:70-74.

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