

Research Article

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Compositional and thermophysical study of Al–Si- and Zn–Al–Mg-based eutectic alloys for latent heat storage

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Abstract: In this study, the eutectic temperature and latent heat of Al–Si- and Zn–Al–Mg-based eutectic alloys were determined using differential thermal analysis (DTA) and differential scanning calorimetry measurements in order to identify eutectic alloys for latent heat storage in the eutectic temperature ranges of 450–550 and 300–350°C. First, the eutectic compositions of the Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn alloys were identified using scanning electron microscopy with energy-dispersive X-ray spectroscopy and DTA in two steps. In the second step, metallographic analysis was repeated until a uniform eutectic microstructure was obtained. Thermophysical analysis revealed that the eutectic temperatures of several types of Al–Si- and Zn–Al–Mg-based eutectic alloys were within the targeted temperature ranges with relatively high latent heat. These results confirmed that Al–Si- and Zn–Al–Mg-based eutectic alloys have suitable properties as phase change materials for use in the 300–350 and 450–550°C temperature ranges.

Keywords: latent heat storage, eutectic composition, eutectic temperature and latent heat, PCM, eutectic alloy

1 Introduction

Renewable energy sources do not emit greenhouse gases during power generation and, as a result, are being promoted as a measure against global warming. Among these, solar and wind power have become the main power

sources. However, the amount of electricity generated by solar and wind power changes drastically depending on the weather, which results in disruption in the electric power grid [1,2]. Therefore, thermal power, for which the amount of electricity generated can be adjusted easily, is used to minimize the discrepancy between the electricity supply and demand. However, with the increase in solar and wind power generation in recent years, the adjustment ability of thermal power cannot easily keep up with the variability in the amount of power supplied by these renewable sources. Accordingly, there is a growing demand for a system that facilitates the adjustment of the amount of electricity generated by thermal power plants. Heat storage systems are considered a promising solution because they present several advantages over other systems in terms of cost and energy efficiency [3].

A suitable type of thermal storage material must be selected to maximize the storage capacity of the heat storage system. Latent heat storage materials, called phase change materials (PCMs), have superior properties, such as high heat density, isothermal reaction when storing and releasing heat, high durability for repeated use, and sufficient availability [4]. Among various thermal storage materials, eutectic alloys have favorable properties, such as higher thermal conductivity than inorganic salts, higher energy density than pure metals because of the formation of an intermetallic phase, and less segregation than non-eutectic alloys [5,6]. Figure 1 shows reasonable candidates for eutectic alloys in the eutectic temperature range of 250–600°C [7]. For the construction of high-efficiency heat storage systems, a suitable PCM for each temperature range is required to store the heat from steam at various temperatures. At 500–600°C, Al–Si-based eutectic alloys have been attracting attention as representative PCMs [8,9]. These PCMs are superior in terms of their energy density and cost. Most Al die-cast alloys, whose composition is close to that of Al–Si eutectic alloys, are used in the engines of petrol cars [10]; thus, a large surplus and price reduction of scrap is anticipated as electrification progresses. At 300–350°C, the Zn–Al–Mg eutectic

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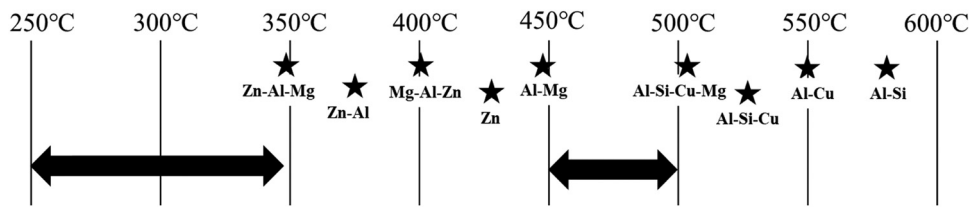


Figure 1: Representative eutectic alloys for PCMs (plots represent eutectic temperatures of each alloy).

alloy shows a high volumetric energy density. In addition, the composition of the Zn die-cast alloy is similar to that of this eutectic alloy; thus, recycling of scrapped materials is expected to reduce the costs of Zn–Al–Mg eutectic alloys. However, as shown in Figure 1, in which plots represent eutectic temperatures of each alloy, no eutectic alloy candidates have been reported in the temperature ranges of 250–350 and 450–500°C.

With this background, the objective of this study is to explore and evaluate new eutectic alloy PCMs in the above-mentioned temperature ranges. Eutectic alloys with a lower eutectic temperature were investigated by adding an additive element to the Al–Si–Cu–Mg and Zn–Al–Mg alloys. Zn and Sn were selected as the additive elements for the Al–Si–Cu–Mg and Zn–Al–Mg eutectic alloys, respectively. These elements are expected to lower the eutectic temperature because of their lower melting temperatures. Furthermore, because these elements are contained in die-cast alloys as impurities, the cost of their addition is expected to be lower.

Eutectic temperature and latent heat are affected by phase equilibrium in the alloy because those values resulted from the balance of chemical potential of phases. In previous research studies about multinary alloys, phase transition temperature and precipitated phases are surveyed using thermal analysis and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), which indicated that those are effective and reliable tools for the investigation on phase equilibrium of multinary alloys [11–13].

Therefore, in this study, eutectic compositions of Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn were identified. In addition, the eutectic temperature and latent heat were clarified for all Al–Si- and Zn–Al–Mg-based eutectic alloys to perform a unified evaluation of these eutectic alloys as PCMs.

2 Materials and methods

Fifteen grams of metal reagents with 3–6 N purity were mixed at a predetermined composition in a graphite

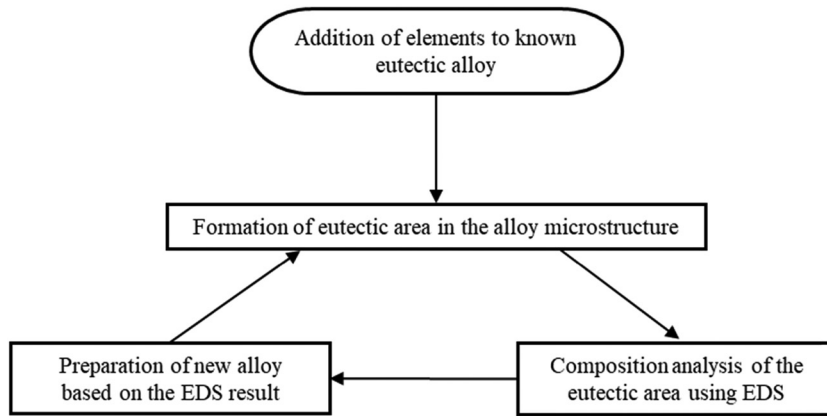
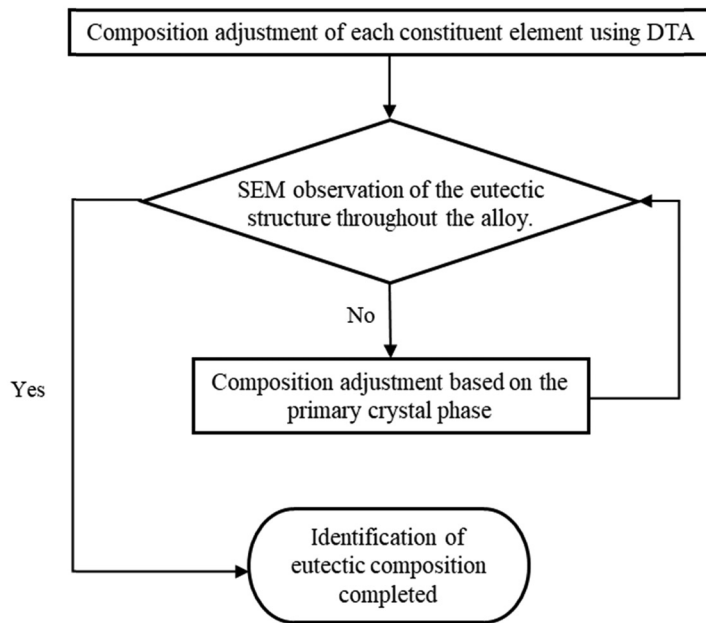
crucible and melted in an induction heating furnace. To prevent the oxidation of the metal, the furnace was evacuated and purged with argon. When the mixture contained volatile elements, melting was conducted in two steps: melting of non-volatile elements followed by melting of the alloy with volatile elements added at a lower temperature. This process is aimed at preventing the loss of volatile elements during melting. Inductively coupled plasma optical emission spectroscopy analysis confirmed that the composition was nearly identical before and after pre-melting. The pre-melted sample was cut and crushed for SEM-EDS and thermophysical analysis, respectively.

2.1 Identification of the eutectic composition

Although the eutectic composition is often identified through calculations, it was experimentally determined in this study. The identification method was divided into two steps, namely, STEP 1: rough estimation using SEM-EDS analysis and STEP 2: precise adjustment of the composition. A flowchart of the process is shown in Figure 2. Table 1 shows the eutectic compositions of Al–Si–Cu–Mg and Zn–Al–Mg before the addition of Zn and Sn, respectively. The detailed methodology for each step is described below, taking the case of the Al–Si–Cu–Mg–Zn alloy as an example.

In STEP 1, an Al–Si–Cu–Mg eutectic alloy with an appropriate amount (~5 mass%) of Zn was prepared. Metallographic observation of the alloy through SEM analysis confirmed that the eutectic and primary phases existed in distinguishable form in the microstructure. Then, the composition of the eutectic part of the alloy was analyzed using EDS. When the distinction between the primary and eutectic phases in the alloy was unclear, the aforementioned processes were repeated to improve the accuracy of the obtained composition.

In STEP 2, the concentrations of the constituent elements of the alloy were adjusted. First, two samples were prepared, wherein the concentration of Al was changed

STEP 1STEP 2**Figure 2:** Flowchart of the eutectic composition identification process.**Table 1:** Eutectic compositions of Al–Si–Cu–Mg and Zn–Al–Mg

Alloy	Eutectic composition (mass%)	Reference
Al–Si–Cu–Mg	Al–6.0Si–28.0Cu–2.2Mg	[7]
Zn–Al–Mg	Zn–3.7Al–2.4Mg	FactSage

by approximately $\pm 2\%$, while the ratio of the other elements was constant. Next, these three samples (original composition and $\pm 2\%$ varied compositions) were analyzed using differential thermal analysis (DTA). Because these analyses were conducted with a constant sample

mass and temperature rise rate, the difference in the shape of the resulting DTA curve reflects the difference in the melting behavior. In principle, eutectic alloys do not have a solid–liquid coexistence temperature range and dissolve homogeneously at the eutectic temperature. Therefore, a more eutectic-like sample can be selected by comparing the DTA curves based on the following criteria: (1) a DTA curve with a single peak for melting and (2) a narrower peak width. By repeating this semi-quantitative evaluation, the concentration of Al in the Al–Si–Cu–Mg–Zn alloy was optimized to be closer to the eutectic composition. Next, with the concentration

of Al fixed, the concentration of Cu was optimized in the same way, followed by the optimization of Si and Zn concentrations. After adjusting the concentrations of all the constituent elements, SEM images of the sample with the obtained composition were obtained. If no primary phase was detected in the alloy, the composition was determined to be a eutectic composition of Al–Si–Cu–Mg–Zn. Otherwise, the concentration was adjusted finely depending on the stoichiometry of the primary phase.

The eutectic composition of Zn–Al–Mg–Sn was also identified using the same method as Al–Si–Cu–Mg–Zn.

2.2 Measurement of eutectic temperature and latent heat

The eutectic temperatures of the eutectic alloys were measured using DTA with a temperature gradient of $10 \text{ K} \cdot \text{min}^{-1}$ in an argon atmosphere. Powdered samples and alumina used as reference materials were placed in alumina pans. Differential scanning calorimetry was used to measure the latent heat with a temperature gradient of 5 K/min in an argon atmosphere. Aiming to enable relative comparison with Al–Si–Cu–Mg–Zn or Zn–Al–Mg–Sn alloy, another Al–Si-based or Zn–Al–Mg-based alloy was measured. The compositions of the alloys other than Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn are shown in Table 2.

3 Results and discussion

3.1 Identification of eutectic composition

The obtained eutectic compositions are listed in Table 3. Finally, the obtained melting curve is shown in Figure 3, in which both melting curves are unity.¹ Figure 4 shows SEM images of Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn alloys with these compositions. The microstructure of the alloy was fine and uniform, which is consistent with the characteristics of eutectic alloys. Therefore, eutectic compositions of the two multinary alloys were successfully determined using this method. EDS analysis of these eutectic alloys confirmed that Zn was present in dispersion without

Table 2: Eutectic compositions of Al–Si-based and Zn–Al–Mg eutectic alloys

Alloy	Eutectic composition (mass%)	Reference
Al–Si	Al–12.6Si	[7]
Al–Si–Cu	Al–5.0Si–27.5Cu	[7]
Al–Si–Cu–Mg	Al–6.0Si–28.0Cu–2.2Mg	[7]
Zn–Al–Mg	Zn–3.7Al–2.4Mg	FactSage

Table 3: Obtained eutectic compositions of Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn

Elements	Al–Cu–Mg–Si–Zn (mass%)	Zn–Al–Mg–Sn (mass%)
Al	54.4	4.1
Cu	24.6	—
Mg	4.8	3.8
Si	7.3	—
Sn	—	6.9
Zn	8.8	85.2

forming compounds in Al–Si–Cu–Mg–Zn eutectic alloy, while Sn formed Mg_2Sn in Zn–Al–Mg–Sn eutectic alloy.

3.2 Measurement of eutectic temperature and latent heat

The measured eutectic temperatures of the Al–Si- and Zn–Al–Mg-based alloys are listed in Table 4. The values reported in previous studies are listed next to those obtained in the present study. The results of the present study are nearly identical to those of previous studies. This agreement indicates the accuracy of the measurements. Thus, as for Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn, whose eutectic temperatures have not been reported, the measured values are reliable. The eutectic temperatures of Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn alloys are 483 and 331°C , respectively, which are 24 and 12°C lower, respectively, than those of the Al–Si–Cu–Mg quaternary eutectic alloy and Zn–Mg–Al ternary eutectic alloy, respectively.

The measured latent heat values are presented in Table 5. The previously reported values are listed next to those obtained in the present study. The obtained values are in agreement with the reported values. Although the latent heat and melting temperature often have a proportional relationship, Al–Si–Cu–Mg showed a higher latent heat than Al–Si–Cu despite the lower eutectic temperature. This result shows that Al–Si–Cu–Mg achieved thermal gain

¹ Note that there is a small peak in the graph of Zn–Al–Mg–Sn that originates from the eutectoid reaction $(\text{Al}) \rightarrow (\text{Al}) + \text{Mg}_{11}\text{Zn}_{11} + (\text{Zn})$ [7].

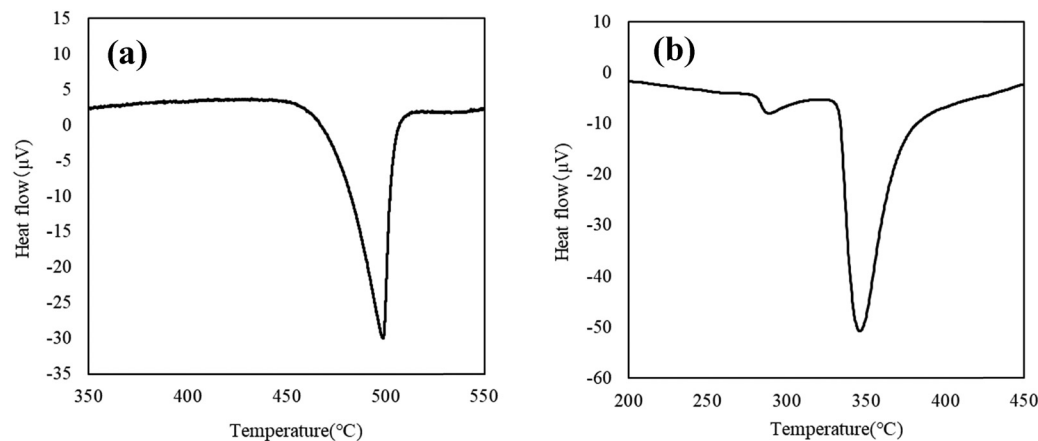


Figure 3: Melting curve of alloys with obtained eutectic compositions. (a) Al-Si-Cu-Mg-Zn and (b) Zn-Al-Mg-Sn.

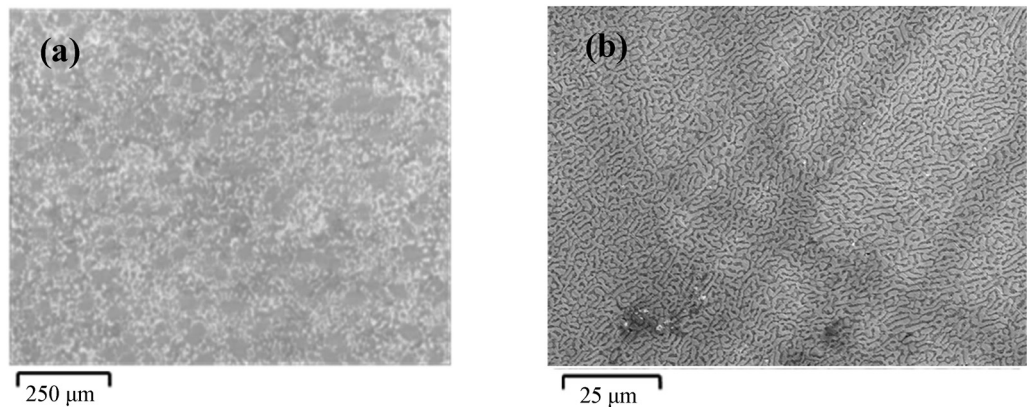


Figure 4: SEM image of alloys with obtained eutectic compositions. (a) Al-Si-Cu-Mg-Zn and (b) Zn-Al-Mg-Sn.

Table 4: Eutectic temperature, measured in this research and literature values

Alloy	Eutectic temperature (°C)		Reference
	Measured	Literature	
Al-Si	578	577	[7]
Al-Cu-Si	520	525	[7]
Al-Cu-Mg-Si	507	507	[7]
Al-Cu-Mg-Si-Zn	483	—	—
Zn-Al-Mg	343	340	FactSage
Zn-Al-Mg-Sn	331	—	—

through the addition of Mg to Al-Si-Cu, which is attributed to the low formation enthalpy of the intermetallic phase or the high mixing enthalpy of Al-Si-Cu-Mg.

Based on the results obtained in this study, the relationship between the eutectic temperature and latent heat of the eutectic alloy is shown in Figure 4. Al-Si and Al-Si-Cu-Mg exhibit a higher latent heat than other eutectic alloys.

According to Richard’s law, the latent heat per mole of pure metal is proportional to the melting temperature. Subsequently, pure metals and eutectic alloys were compared to evaluate the thermal gain attributable to alloying. The latent heat per mole and melting or eutectic temperatures of the representative pure metals and eutectic alloys are plotted in Figure 5. All the Al-Si- and Zn-Al-Mg-based eutectic alloys showed higher slopes than the pure metals,

Table 5: Latent heat

Alloy	Latent heat (J·g ⁻¹)		Reference
	Measured	Literature	
Al-Si	440	462–560	[14–17]
Al-Cu-Si	361	364	[18]
Al-Cu-Mg-Si	422	374	[18]
Al-Cu-Mg-Si-Zn	321	—	—
Zn-Al-Mg	137	132	[19]
Zn-Al-Mg-Sn	137	—	—

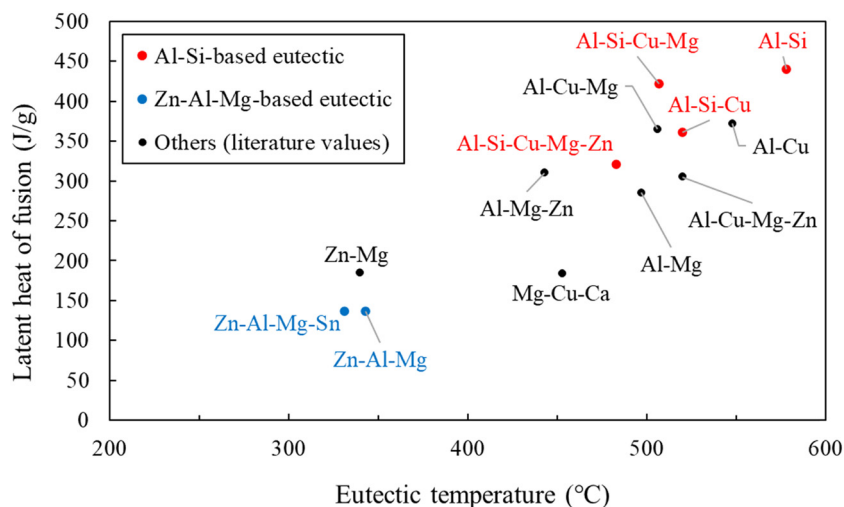


Figure 5: Eutectic temperature and latent heat per weight.

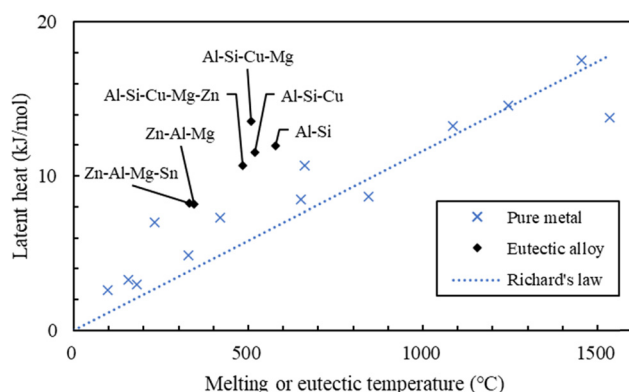


Figure 6: Richard's law and eutectic alloys.

except for those with special crystal structures. To investigate the reason for the especially high latent heat of Al-Si-Cu-Mg, enthalpy evaluations were performed for each eutectic alloy state. As shown in Figure 6, the enthalpy difference is roughly related to the latent heat of the pure metals and eutectic alloys, the enthalpy of mixing, and the formation enthalpy of the compound phases in the eutectic alloy. Hence, the thermal gain from alloying is attributable to the formation enthalpy of the compound phases or the enthalpy of mixing. The constituent compound phases and thermal gains calculated

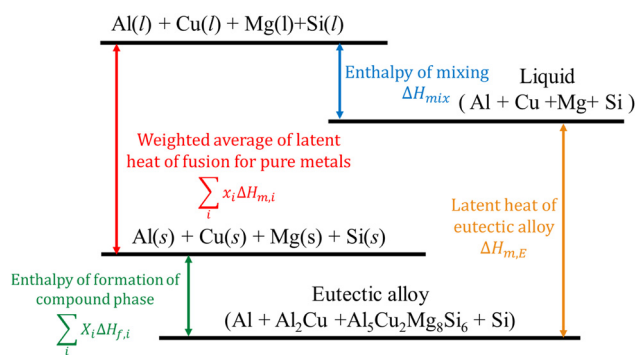


Figure 7: Enthalpy relation between each state for Al-Si-Cu-Mg (x_i : eutectic composition, X_i : quantity of compound phase in eutectic alloy).

from the formation enthalpy [20] for Al-Si-Cu-Mg and Al-Si-Cu are listed in Table 6. The two calculated values showed that the thermal gain resulting from compound formation was almost equal for the two alloys. Considering the enthalpy relation shown in Figure 6, the difference in latent heat between Al-Si-Cu and Al-Si-Cu-Mg is attributed to the difference in the enthalpy of mixing. This suggests that Mg increased the mixing enthalpy of the Al-Si-Cu alloy and the latent heat of Al-Si-Cu-Mg, although further discussion is required.

Table 6: Enthalpy of the formation of compound phases in 1 mol eutectic alloy

Alloy	$\Delta H_{f, Al_2Cu}$ (kJ)	$\Delta H_{f, Al_5Cu_2Mg_8Si_6}$ (kJ)	$\sum_i X_i \Delta H_{f,i}$ (kJ)
Al-Si-Cu	-2.15	—	-2.15
Al-Si-Cu-Mg	-2.13	-0.063	-2.19

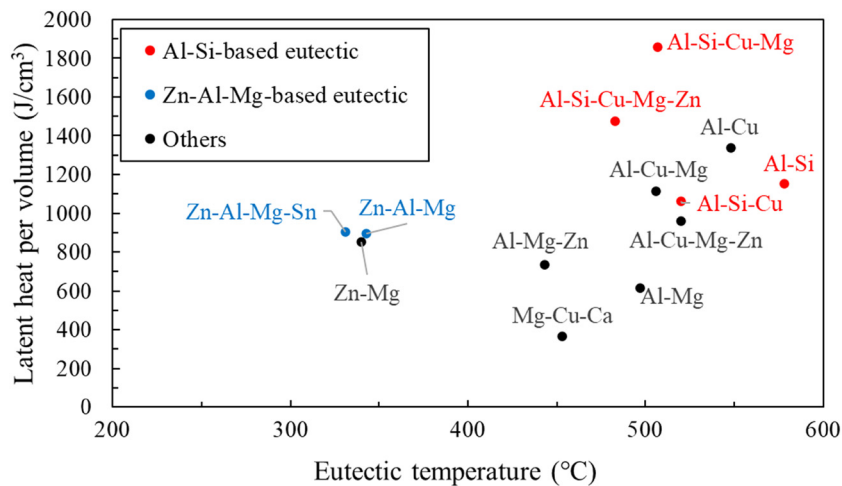


Figure 8: Eutectic temperature and volumetric latent heat.

Considering in the same way, Zn is solid-soluble when added to Al–Si–Cu–Mg eutectic alloy and does not hardly form new compound, which is consistent with the lower latent heat of Al–Si–Cu–Mg–Zn eutectic alloy. In contrast, since Sn forms Mg_2Sn when added to Zn–Al–Mg eutectic alloy, it prevents a latent heat loss, despite the expected effect on Sn addition to lower the latent heat.

The volumetric latent heat of an alloy is critically important for its practical use as a PCM because the total heat capacity of the heat storage system depends on it. To investigate the practicality of the Al–Si- and Zn–Al–Mg-based alloys, the volumetric latent heat was calculated. For alloys without measured density values, the volumetric latent heat values were estimated from the data of other alloys. The eutectic temperature and volumetric latent heat are plotted in Figure 7. Among several kinds of eutectic alloys, Al–Si–Cu–Mg-, Al–Si–Cu–Mg–Zn-, and the two Zn–Al–Mg-based eutectic alloys showed the highest latent heat of melting among the metallic PCMs in the respective melting temperature ranges. Because the volumetric latent heat was strongly affected by the density of the alloy system, it was confirmed that the latent heat of the heavy-element-containing alloy tended to be higher (Figure 8).

4 Conclusions

- (1) The eutectic compositions of Al–Si–Cu–Mg–Zn and Zn–Al–Mg–Sn alloy were identified experimentally. The metallographic structure of the alloys with the obtained composition exhibited the characteristics of

a eutectic alloy. Therefore, a eutectic composition was successfully identified using this method. Furthermore, these eutectic alloys were suitable PCMs for the targeted temperature ranges of 250–350 and 450–500°C for each alloy.

- (2) For evaluating the Al–Si- and Zn–Al–Mg-based eutectic alloys as PCMs, the eutectic temperature and latent heat were clarified. All the Al–Si-based eutectic alloys were found to be promising practical PCMs. Notably, Al–Si–Cu–Mg exhibited a high latent heat. For Zn–Al–Mg-based eutectic alloys, although the latent heat was not high, a high volumetric thermal density was expected because of their high density.

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Data availability statement: Data would be available with the permission by a project, JPNP16002.

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