Study on the thermal storage properties of Al-Si-Cu-Mg alloy

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Abstract: Based on thermodynamic calculation technology, the thermodynamic data of six alloys (i.e. Al-Si and Al-Si-Cu-Mg systems) was calculated. The microstructure, phase transformation temperature and latent heat of the Al-4%Cu-12%Mg-7%Si alloy and Al-13%Si alloy were also verified by X-ray diffraction(XRD), scanning electron microscopy/Energy-dispersive system (SEM/EDS) and Differential scanning calorimetry (DSC). The results show that the enthalpy change value of Al-Si-Cu-Mg alloy is larger than that of Al-Si alloy from 800 °C to 400 °C, while its phase transformation temperature is lower. In particular, the enthalpy value of Al-4%Cu-12%Mg-7%Si alloy is 85% higher than that of Al-13%Si near eutectic alloy, and its initial temperature of phase transformation is about 74 °C lower. The former has relatively low phase transformation temperature and over-dimensioned latent heat of phase transformation, displaying the excellent thermal storage property. Therefore, the alloy is a potential solar energy thermal storage material. The results in the paper also indicated that thermodynamic calculation is of value in seeking new potential solar energy thermal storage materials for solar thermal power generation system.

1. Introduction

Energy crisis can promote the rapid development of solar energy utilization technology, so that the study on thermal storage materials features great practical significance. Al alloy materials can achieve the high temperature energy storage of solar energy on solar cookers, with the thermal storage temperature of 650-700 °C. Meanwhile, compared with inorganic salt thermal storage materials, the Al alloys have large thermal storage density, high thermal conductivity and fast thermal exchange speed. Therefore, it is a potential candidate for future thermal storage materials [1].

The thermal storage capacity of materials mainly consists of two aspects: the first one is the latent heat with phase transformation and the other is the sensible heat. In recent years, studies on thermal storage properties of Al alloys mainly concentrate on the latent heat with phase transformation. However, sensible heat is also an important part of materials' thermal storage in practical use and lack of deep views in it.

According to the previous studies, Al-Mg, Al-Si, Al-Si-Mg, Al-Si-Cu and other alloys are widely applied in the high temperature phase transformation thermal storage area. The phase transformation temperature range of Al-Mg alloy is relatively narrow [2], Al-Si-Mg alloy has high latent heat of phase transformation, while Al-Si-Cu alloy has long thermal storage life [3]. Nevertheless, there is few study on Al-Si-Cu-Mg alloy, especially on their comprehensive thermal storage property. In this paper, the energy storage property and microstructure of Al-Si-Cu-Mg alloy were studied by thermodynamic calculation, XRD, SEM/EDS and DSC.
2. Phase diagram calculation and experiment methods

Thermodynamic calculation (CALPHAD) is the most mature and widely used phase diagram calculation technology in the world now [4], which constructs proper thermodynamics model, describes the thermodynamic functions of each phase in the system, and calculates the needed phase diagram data (enthalpy) in accordance with the characteristics and data of each phase in duality and multicomponent system (inc. measured phase diagram data, thermodynamic data, crystal structure data, and metastable phase diagram data). However, a series of unknown parameters in thermodynamic function expressions should be optimized and obtained through thermodynamic calculation software, and with the combination of thermodynamic data and phase diagram data. The thermodynamic database adopted in this paper is cost507 [5], and the calculation software is Thermo_Calc [6]. The calculation is based on the following procedure: (1) calculate the enthalpy of the alloy with given components under different temperatures, with the temperature interval of 1 °C, and temperature scope of 400-800 °C; (2) when the calculation is completed, the diagram and data documents of the calculation results are output; (3) find out the enthalpy with 400 °C and 800 °C from the calculated data documents, to get the enthalpy change.

In order to make comparative analysis, Al-Si alloy, which is a binary near eutectic alloy with commonly accepted good thermal storage performance, is especially selected as the control one. Three kinds of Al-Si and Al-Si-Cu-Mg alloy are calculated, respectively, as shown in Table 1. Then, based on the calculation results, an alloy with good thermal storage property is selected from the Al-Si-Cu-Mg. And its thermal storage property is studied via experiment study, by comparing that of Al-13%Si.

![Table 1. Composition of studied alloys /wt.%](image)

| Sample No. | Si | Cu | Mg | Al |
|------------|----|----|----|----|
| A1         | 7  | -  | -  | Bal.|
| A2         | 13 | -  | -  | Bal.|
| A3         | 20 | -  | -  | Bal.|
| B1         | 7  | 4  | 4  | Bal.|
| B2         | 13 | 4  | 4  | Bal.|
| B3         | 7  | 4  | 12 | Bal.|

In the experiment, the primeval alloy ingredients are melted in the well resistance furnace, and then cast to slab through iron pattern, with the alterant of NaCl+KCl+NaF, and mold discharging agent of Na₂SO₄:ZnO:H₂O=3:12:85.

D/max 2500 VB-type XRD is adopted to analyze the phase of the alloy sample, and the microstructure is observed and analyzed through Philips Sirion200 SEM. DSC analysis is conducted on NETZSCH STA 449C DSC, and powder sample is used to test its latent heat of phase transformation and melting point. The DSC test parameters are as follows: heating temperature scope is 30~700 °C, and heating rate is 20 °C/min; protective medium is nitrogen with 99.999% purity, and current speed is 50 ml/min. Before analysis, high purity aluminum melting point is used to adjust the DSC analysis system.

3. Results and discussion

3.1. Calculation results

Fig. 1 shows the relationship between enthalpy and temperature for Al-Si alloys A1-A3, wherein A2 is near eutectic alloy. The horizontal ordinate represents temperature, with the unit of K, while the longitudinal coordinate represents enthalpy value, with the unit of J. From the diagram, we can get the enthalpy value \( (H) \) with the alloy between 673 K (400 °C) and 1 073 K (800 °C). According to these data, we can calculate the enthalpy value change \( (ΔH) \) of the alloy between 400-800 °C. Besides, we can also obtain the phase transformation temperature \( (T_m) \) area of the alloy, and the data is shown in Table 2.
Figure 1. Relationship between enthalpy and temperature for Al-Si alloys

According to the previous paper [7], the latent heat of phase transformation for Al-13%Si near eutectic alloy is larger than that of Al-22%Si. As shown in Table 2, with the content of Si rising from 7% to 20%, the enthalpy change value of A1-A3 between 400 and 800 °C increases from 458 J g⁻¹ to 605 J g⁻¹. On the other hand, the enthalpy change value rises along with the increasing content of silicon, while without much relationship with eutectic structure.

Table 2. Enthalpy change of the studied alloys between 400-800 °C

| Alloy No. | H (400 °C) J mol⁻¹ | H (800 °C) J mol⁻¹ | ΔH (400-800 °C) J mol⁻¹ | ΔH (400-800 °C) J g⁻¹ | Tm (°C) |
|----------|--------------------|--------------------|-----------------------|----------------------|---------|
| A1       | 109                | 12539              | 12430                 | 458                  | 578-615 |
| A2       | 102                | 14326              | 14224                 | 524                  | 578-596 |
| A3       | 93                 | 16550              | 16457                 | 605                  | 578-701 |
| B1       | 6927               | 34360              | 27433                 | 963                  | 500-574 |
| B2       | 7039               | 32960              | 25921                 | 912                  | 500-574 |
| B3       | 4318               | 31723              | 27405                 | 972                  | 504-610 |

The initial temperature of phase transformation of Al-Si alloy is related to its melting phase. It was once reported that the α-A1 solid solution firstly changes from solid to liquid in Al-Si binary system, and the phase transformation temperature does not differ too much due to the similar structures for α-A1 solid solution with different Si contents [7]. In Table 2, the calculated initial temperature of phase transformation for A1-A3 alloy is the same, which is 578 °C. The results is also pretty close to the measured phase transformation temperature of Al-12.5%Si eutectic alloy, where the temperature is 577.2 °C [8].

Figure 2. Relationship between enthalpy and temperature for Al-Si-Cu-Mg alloys

Fig. 2 shows the relationship between enthalpy and temperature for Al-Si-Cu-Mg alloys B1-B3. Have to state here, the unit of temperature on horizontal coordinate is °C. The corresponding thermodynamic data are also shown in Table 2. The enthalpy change value B3 alloy is the largest (60 J g⁻¹), while its phase transformation temperature is slightly higher than that of B1 and B2 alloy.

Compared with Al-Si binary system alloy (Table 2), Al-Si-Cu-Mg alloy has the larger enthalpy value between 400-800 °C, and with lower phase transformation temperature. Taking A2 alloy (Al-
13%Si) as an example, the enthalpy change value of B3 alloy is 85% higher and, its initial temperature of phase transformation is about 80 °C lower. Therefore, from the above calculation results, we can draw the conclusion that the thermal storage performance of Al-Si-Cu-Mg is better than that of Al-Si alloy and the Al-4%Cu-12%Mg-7%Si alloy displays the best thermal storage performance among the studied alloys.

3.2. Experiment results
Based on the thermodynamic calculations of phase diagram, the microstructure and thermal storage performance for B3 alloy (Al-4%Cu-12%Mg-7%Si) are contrasted with commonly used Al-13%Si binary near eutectic alloy.

3.2.1. Microstructure analysis
SEM structure of Al-13%Si is shown in Fig. 3, which is combined with grey solid solution, grey acicular phase and a few white particles. The length of grey acicular phase is about 25-50 μm. Meanwhile, there are coarse bulk phases in the structure, with the color of grey and the size of about 20 μm. The corresponding EDS results of Al-13%Si are listed in Table 3. Combining the component data and Al-Si binary phase diagram [9], we can confirm that position A is α-Al solid solution, position B is primary silicon, and position C is Al-Fe-Si compound, while needle like phase is eutectic silicon.

As stated in Section 2, the alloy casting process was conducted by iron casting and so the metal cools slowly, hence acicular eutectic but not evenly distributed lamellar eutectic generates as shown in Fig.3.

![Figure 3. Microstructure of Al-13%Si alloy](image)

The microstructure of B3 (Al-4%Cu-12%Mg-7%Si) alloy is shown in Fig.4. There are grey matrix, white second phase structure, a few grey structures and grey-black bulk structure in the alloy. The corresponding EDS and XRD results are showed in Table 3 and Fig. 4, respectively. Based on the EDS and XRD results, we can confirm that the grey matrix in position D is α-Al solid solution, the second phase in position E is Al2Cu, grey structure in position F is Al2CuMg and eutectic silicon structure, while-grey black position G is Mg2Si phase. Al-Si eutectic in microstructure does not have characteristic peak in X ray diffraction test, maybe it is because Al-Si eutectic in B3 alloy is less than the detection limit of diffraction measurement.

| Table 3. EDS results of Al-13%Si and Al-4%Cu-12%Mg-7%Si alloys | at. % |
|------------------|------|
| **Alloy**       | **Position** | **Al** | **Si** | **Cu** | **Mg** | **Fe** |
| Al-13%Si         | A     | 99.32  | 0.68   | -     | -     | -     |
|                  | B     | 1.89   | 98.11  | -     | -     | -     |
|                  | C     | 64.18  | 26.54  | -     | -     | 9.28  |
| Al-4%Cu-12%Mg-7%Si | D     | 96.64  | 0.59   | 1.02  | 1.75  | -     |
|                  | E     | 78.80  | 5.36   | 14.95 | 0.88  | -     |
|                  | F     | 51.55  | 19.12  | 6.07  | 23.26 | -     |
|                  | G     | 6.36   | 29.20  | 0.65  | 63.79 | -     |

The microstructure of B3 (Al-4%Cu-12%Mg-7%Si) alloy is shown in Fig.4. There are grey matrix, white second phase structure, a few grey structures and grey-black bulk structure in the alloy. The corresponding EDS and XRD results are showed in Table 3 and Fig. 4, respectively. Based on the EDS and XRD results, we can confirm that the grey matrix in position D is α-Al solid solution, the second phase in position E is Al2Cu, grey structure in position F is Al2CuMg and eutectic silicon structure, while-grey black position G is Mg2Si phase. Al-Si eutectic in microstructure does not have characteristic peak in X ray diffraction test, maybe it is because Al-Si eutectic in B3 alloy is less than the detection limit of diffraction measurement.
3.2.2. Analysis for latent heat of phase transformation

Fig. 5 is the DSC curves of A2 (Al-13%Si) and B3 (Al-4%Cu-12%Mg-7%Si) alloys. For the Al-13%Si system, the alloys experience the melting phase transformation from 577 °C to 638 °C, and its peak temperature is about 590 °C. And the measured initial temperature of phase transformation (577 °C) is pretty close to that by phase diagram calculation (578 °C, as shown in Table 2). In theory, the transformation temperature of Al-Si eutectic is 577 °C [10], which is the same as the measured and calculated initial temperature of phase transformation. The fact illustrates that the calculation data accords with the tested result perfectly and the calculation methods in this paper are reasonable. In addition, many structures will undergo constant temperature melting at the eutectic temperature of 577 °C in Al-Si system, resulting into a large number of heat absorption, as shown in Fig. 5.

![Figure 5. DSC curve of Al-13%Si and Al-4%Cu-12%Mg-7%Si alloy](image)

The phase transformation temperature of B3 (Al-4%Cu-12%Mg-7%Si) alloy are in range of 503.5 °C-610.3 °C, which is very close to the above calculation results (504 °C-610 °C, as shown in Table 2). As displayed in Fig. 5, DSC curve of B3 alloy includes three endothermic peaks, which are 510.5 °C, 543.3 °C and 591.7 °C, respectively. The melting point of α-Al+Al2Cu+Al2CuMg eutectic is 507 °C, and the melting point of α-Al+Al2Cu eutectic is 548 °C [11]. During the phase transformation process, the Al2Cu phase with low melting point will melt firstly at 510.5 °C, followed by the melting of Al2CuMg at 543.3 °C, and finally the Mg2Si and α-Al solid solution experience melting process, resulting into the endothermic peak at 591.7 °C.

The latent heat and temperature of phase transformation for A2 and B3 alloys can be calculated from DSC curves and listed in Table 4. Compared with A2 alloy, the initial and terminal temperatures of phase transformation for B3 alloy have reduced 74 °C and 27 °C, respectively, and its overall phase transformation temperature is lower. In spite of that the latent heat of phase transformation for B3 alloy is slightly lower than that of A1 alloy, it still reaches 425 J g⁻¹, which is far higher than the
general requirement for metal-matrix phase transformation energy storage materials used in solar thermal power generation system, namely 200 J g\(^{-1}\)\([12]\).

| Table 4. Latent heat of phase transformation for Al-13%Si and Al-4%Cu-12%Mg-7%Si |
|-------------------|-----------------|-----------------|
| Alloy             | Latent heat / J g\(^{-1}\) | Temperature / °C |
| Al-13%Si          | 486             | 577.3–637.7     |
| Al-4%Cu-12%Mg-7%Si| 425             | 503.5–610.3     |

4. Conclusions

To study the energy storage property of Al-Si-Cu-Mg alloy, the thermodynamic data of six alloys (inc. Al-Si and Al-Si-Cu-Mg systems) was calculated. Then the microstructure, phase transformation temperature and latent heat of the Al-4%Cu-12%Mg-7%Si alloy and Al-13%Si alloy were also verified by XRD, SEM/EDS and DSC. The following conclusions can be drawn:

1. The enthalpy change value of Al-Si-Cu-Mg alloy is larger than that of Al-Si alloy from 800 °C to 400 °C, while its phase transformation temperature is lower. In particular, the enthalpy value of Al-4%Cu-12%Mg-7%Si alloy is 85% higher than that of Al-13%Si near eutectic alloy, and its initial temperature of phase transformation is about 74 °C lower.

2. The Al-4%Cu-12%Mg-7%Si alloy have relatively low phase transformation temperature and over-dimensioned latent heat of phase transformation, displaying the excellent thermal storage property. Therefore, the alloy is a good potential solar energy thermal storage material.

3. In the paper, the calculated results are in complete agreement with the measured ones, indicating that the calculation result is reliable and thermodynamic calculation is of value in seeking new potential solar energy thermal storage materials for solar thermal power generation system.

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