International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 2, Feb 2012, Page 131
DOI: 10.1007/s12613-012-0527-0

Modifying agent selection for Al-7Si alloy by Miedema model

Zhong-wei Chen, Cui-ying Ma, and Pei Chen

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China
(Received: 13 January 2011; revised: 1 February 2011; accepted: 8 February 2011)

Abstract: To determine the modifying agents for Al-7Si alloys, microstructure observation and mixing enthalpy analysis using Miedema model for Al-7Si alloy with additions of different rare earth elements were performed, and the effects of rare earth elements on the modification of eutectic silicon morphology were investigated. The results of mixing enthalpy analysis show that these four rare earth elements, La, Sm, Pr, and Ce, which have the large negative mixing enthalpies with Si, can be selected as modifying agents for eutectic silicon morphology. The element with the largest negative mixing enthalpy is Ce. Furthermore, the microstructures indicate that these four elements can effectively modify the eutectic (α)Al-Si crystals in Al-7Si alloy, and the most effective one is also Ce. Differential scanning calorimetry (DSC) results show that the eutectic temperature depressions due to the additions of modifying agents are the important reasons for the modification of eutectic (α)Al-Si crystals.

Keywords: aluminum alloys; silicon alloys; modifying agents; rare earth elements; microstructure; enthalpy

[*This work was financially supported by the Research Fund of the State Key Laboratory of Solidification Processing (No.42-QP-009), the Open Fund of the State Key Laboratory of Solidification Processing in NWPU (No.201009), the Fundamental Research Fund of Northwestern Polytechnical University (No.JC200929), and the 111 Project of China (No.B08040).*]

1. Introduction

Due to lightweight, high strength, good corrosion resistance, and good castability characteristics [1], Al-7Si hypoeutectic casting alloys are widely used in the aerospace and automotive industries. With the low cooling rate of equilibrium solidification of Al-7Si alloy, the microstructure exhibits the primary (α)Al dendrite and acicular eutectic crystals. Coarse and acicular eutectic silicon crystals are the threshold for fracture in the tension environment [2], and they are considered as a disadvantage for the mechanical properties. Therefore, it is very important that the morphologies of eutectic silicon crystals in Al-7Si hypoeutectic alloy change from the coarse and large acicular to the fine and globular-fibrous [3-5].

Modification of eutectic Si crystals can be achieved in two different ways, the chemical modification (addition of certain elements) and the quench modification (change of cooling rate) [1, 3]. It has been found that adding a modifier is the most popular and effective method. Several elements are known to cause the chemical modification. For example, Sr, Na, Ba, Ca, B, and Sb are the most commonly used in the industry, and the additions of rare earth elements are also reported to cause the modifications [3-6]. However, the effective parameter for the modifying agent selection of Al-7Si alloy is still controversial. Conventional parameters for the modifying agent selection in the Al-7Si alloy, such as crystal structure, lattice constant, melting point, and the atomic radius ratio (r/r_{Si}), have been widely reported, but their validity is still debatable [7]. For example, the melting points of Na (97.72°C) and Sr (770°C) are less than 982°C, which is reported as the effective melting point for selecting a modifying agent for Al-7Si alloy [8]. However, Na and Sr are considered as the effective modifying agents for Al-7Si alloy. In addition, rare earth elements with different crystal structures and lattice constants from the eutectic phase of Al-7Si alloy are also reported for chemical modification of the eutectic Si phase [1, 5-7]. Another suggested parameter of modification for Al-7Si alloy is the r/r_{Si}. It is suggested

Corresponding author: Zhong-wei Chen E-mail: chzw@nwpu.edu.cn

that the atoms of modifying agents are absorbed on the growth steps of the silicon solid-liquid interface. According to the impurity induced twinning model [9], the growth twin appears at the interface when r/r_{Si} exceeds 1.65 [10]. However, it is not clear whether the growth twin is an effective mechanism for the modification of eutectic Si crystals [7, 11].

Considering the reactions between modification agents and eutectic Si, a new parameter, the mixing enthalpy calculated by Miedema model [12], was introduced to select the effective modifying agent in this paper. To the further investigation of mixing enthalpy, rare earth elements with large negative mixing enthalpies and different crystal structures and lattice parameters to those of Si were selected as modifying agents for Al-7Si alloy [8, 13].

2. Experimental

The base Al-7Si alloy used in the experiments was A356 alloy ingots. The nominal composition of the base A356 alloy is given in Table 1.

Table 1. Composition of A356 alloy wt%

Si	Mg	Fe	B	Sn	Ti	Al
7.22	0.392	0.142	0.016	0.031	0.115	balance

The as-received commercial A356 ingots were primarily prepared from the same batch to avoid any undesired deviation from some minor elements. The commercial A356 alloy ingots were cut into smaller pieces and melted in a SiC crucible using a 12-kW electric resistance furnace. The SiC crucible was preheated to 400°C, and then the alloy was heated up to 750°C and carefully skimmed to remove the dross and other impurities. Pure La, Ce, Pr, and Sm bulks and Al-10wt% Sr master alloy, which were wrapped in aluminum foils, were added to adjust the chemical composition, respectively, and the melts were held at 750°C for 30 min. The rare earth element composition and designation of alloys are shown in Table 2 analyzed by ICP. The 0.03wt% Sr addition was used as a reference which was the conventional treatment used to modify the eutectic silicon morphology of A356 alloy. The permanent mold was preheated to 300°C before casting. The melts at 720°C were poured into the permanent mold. The microstructure of each sample was observed by scanning electron microscopy (SEM). The thermal behaviors during solidification were evaluated by differential scanning calorimetry (DSC) with a diamond crucible under the pure nitrogen atmosphere at the rate of 100 mL·min^{-1}. The heating rate and cooling rate were 5°C·min^{-1}. The heat effects associated with the phase transformation reactions can be isolated by subtracting the base line of reference.

Table 2. Rare earth element composition and alloy designation

Designation of alloy	I	II	III	IV	V	VI
Adding elements / wt%	A356	Sr 0.03	Ce 0.80	La 0.28	Pr 0.15	Sm 0.20

3. Results and discussion

3.1. Mixing enthalpy

Miedema *et al.* proposed the Miedema model to calculate the mixing enthalpy of Al-Si alloys [12]. They considered that the boundary condition could cause the alloyage effect when materials transform from pure metals to alloys. There are two factors that affect the boundary condition, the chemical potential for the electronic charge (ϕ^*) and the electron density at the boundary of a Wigner-Seitz atomic cell (N_{WS}).

Considering above, Miedema *et al.* suggested that the mixing enthalpy of element A dissolved in element B ($\Delta H_{[A \text{ in } B \text{ (interface)}]}$) can be expressed as

$$\Delta H_{[A \text{ in } B \text{ (interface)}]} = \frac{2V_A^{2/3}}{(N_{WS}^{-1/3})_{av}}\left[-P(\Delta\phi^*)^2 + Q(\Delta N_{WS}^{1/3})^2\right] \quad (1)$$

where $V_A^{2/3}$ is the molar surface area of element A, $(N_{WS}^{-1/3})_{av}$ the average of $N_{WS}^{-1/3}$ about elements A and B, P and Q the proportionality constants of the model (Q/P= 9.4), respectively. When elements A and B are both the transition elements, P=14.1; when one of them is the transition element, P=12.3; and when both of them are not the transition elements, P=10.6.

To select the modifying agents for the Al-7Si alloy, $\Delta H_{[X \text{ in Si (interface)}]}$ was calculated by Eq. (1), where X is the modification element. The results of calculation and the conventional parameters for several modifying agents and alloying elements are summarized in Table 3.

In Table 3, the elements Sr and Ca, which have the modification effects [1, 3, 11], not only have the similar crystal structures, lattice constants, and atomic radius ratios with Si, but also have the large negative mixing enthalpies with Si. Similarly, the elements Cu and Mg, which are not the modification agents according to the published literature, not only

Table 3. Effective parameters of modifying agents and alloying elements for Al-7Si alloy

Element	Group	Crystal structure	Melting point / °C	Lattice constant / pm	$\Delta H_{[X \text{ in Al (interface)}]}$	$\Delta H_{[X \text{ in Si (interface)}]}$	r/r_{Si} [14]
Si	4A	Cubic	1420	574.7	—	—	—
La	Rare earth	Hex	920	375.0	–81.49	–178.0	1.59
Ce	Rare earth	Face cubic	804/799	363.0	–93.80	–205.0	1.56
Pr	Rare earth	Hex	935	364.8	–81.57	–177.8	1.56
Sm	Rare earth	Rhomb	1072	362.9	–81.56	–180.0	1.54
Sr	2A	Face cubic	769	608.5	–46.00	–143.0	1.63
Ba	2A	Body cubic	725	502.8	–45.70	–150.0	1.85
Ca	2A	Face cubic	839	559.0	–57.20	–142.8	1.68
Mg	2A	Hex	649	320.9	13.68	–50.7	1.37
Cu	Transition	Face cubic	1083	361.5	–1.07	–3.7	1.00

have the different crystal structures, the different lattice constants, and the atomic radius ratio with Si less than 1.65, but also have the small negative mixing enthalpies with Si. Therefore, it is suggested that, for the four rare earth elements, La, Sm, Pr, and Ce, the large negative mixing enthalpies with Si can be selected as an effective parameter for modifying agents according to thermodynamics, even though these rare earth elements have the different crystal structures, the different lattice constants with Si, and the atomic radius ratio with Si less than 1.65.

3.2. Microstructure of modified alloys

To validate the effects of four rare earth elements on the morphology of eutectic silicon crystals, Ce, La, Pr, and Sm elements were added to A356 alloy, respectively, and 0.03wt% Sr was also added as a reference. Fig. 1 shows the unmodified microstructure and 0.03wt% Sr modified structure of A356 alloys. In the unmodified alloy, the morphology of eutectic Si crystals is a typical flake and acicular plate. In Fig. 1(b), the eutectic Si crystals are modified to the fine fibrous or spherical shapes, which show the fully modifying effect. Fig. 2 shows the modified microstructures of adding Ce, La, Pr, and Sm, respectively, which have the large negative mixing enthalpies with Si. Because the element Ce has the largest negative mixing enthalpy with Si, the morphology of eutectic Si crystals modified with Ce is similar to that of the one modified with Sr.

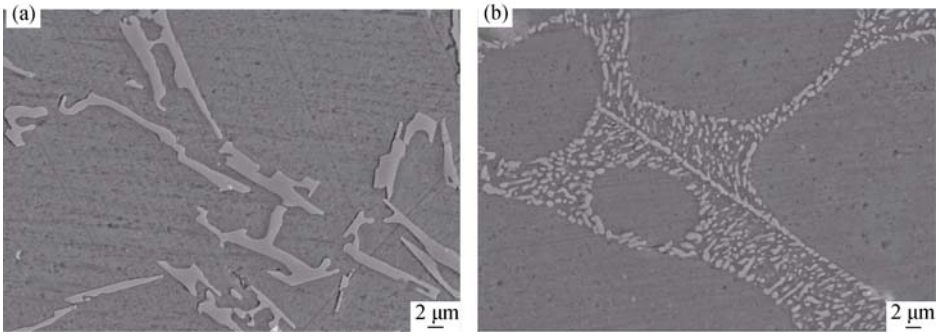

Fig. 1. Microstructures of A356 alloy: (a) unmodified; (b) modified with 0.03wt% Sr.

With regards to the mechanism of eutectic modification, Lu and Hellawell [9] proposed an impurity induced twinning theory. They considered that the modified silicon fibers contained more twins than the unmodified silicon. One theory is that the modifier atoms are absorbed onto the growth steps of the silicon solid-liquid interface, and it is supported by the observation that the modifiers become concentrated in the silicon phase, not in the aluminum phase. In this paper, thermodynamics was considered. Comparing the values of $\Delta H_{[X \text{ in Al (interface)}]}$ and $\Delta H_{[X \text{ in Si (interface)}]}$ in Table 3, the mixing enthalpies of modifying agents (Sr, Ce, La, Pr, and Sm) with Si have the larger negative values than those with Al. Therefore, the affinity of rare earth elements with Si is bigger, and they coalesce more easily with Si to restrain the growth of eutectic Si. This is similar to the results of Lu and Hellawell [9]. In Fig. 2, the morphologies of eutectic Si crystals modified with rare earth elements show more fine fibrous and spherical shapes. The element Ce has the largest negative mixing enthalpy with Si, and the finer spherical morphology of eutectic Si modified with Ce is shown in Fig.

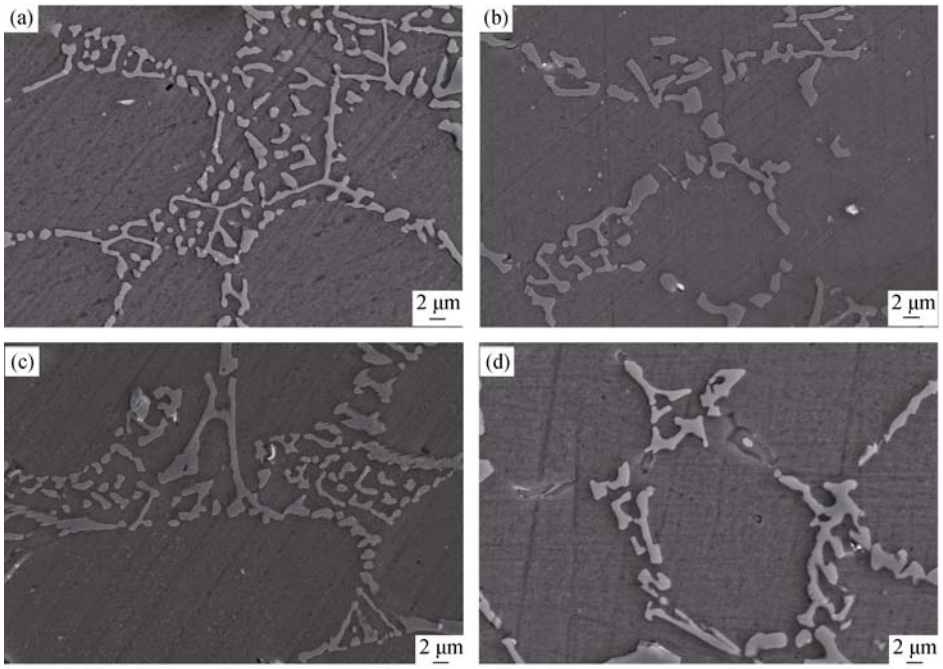

Fig. 2. Microstructures of A356 alloy with different modification agents (wt%): (a) 0.80 Ce; (b) 0.28 La; (c) 0.15 Pr; (d) 0.20 Sm.

2(a). With the modified microstructures, it can be confirmed that these elements (Ce, La, Pr, and Sm), selected by their mixing enthalpies with Si, have the effective modification results.

3.3. DSC traces

To investigate the reason of modification with elements having the large negative mixing enthalpies, the eutectic temperature depression of each modified alloy was measured. The large negative mixing enthalpy means the low melting temperature and the strong affinity between two elements, so eutectic temperature depression is a general phenomenon for the modification of eutectic Si crystals. Fig. 3 shows the DSC results for samples of unmodified (I) and modified (II-VI) alloys during solidification. A similar trend in DSC plots is observed for each alloy, and Table 4 shows the temperature depressions of the initial eutectic point and peak eutectic point of each modified alloy. The additions of Sr and rare earth elements can decrease the temperatures of the initial eutectic point and crystallization in the eutectic reaction, and the temperature depressions are greater than 2°C. In other words, the eutectic-phase crystallization takes place under the proper undercooling, and increasing the undercooling is considered to be the result of modification. This is consistent with the findings by Nogita *et al.* [3-6]. They investigated the solidification mode of eutectic phase in Al-7Si cast alloys by electron back-scatter diffraction and found that the eutectic nucleation mode was strongly dependent on the additive elements. It is suggested that the eutectic Si phases are modified as a result of the activation of some other nucleation sites for the eutectic cells under a certain undercooling. So, the decrease of eutectic temperature in the modified Al-7Si alloy approaches to the undercooling levels of eutectic Si crystals morphological transition, which are changed from flake-like to fibrous. If the eutectic Si crystals nucleate and grow at a temperature lower than the eutectic temperature of the Al-Si alloy by adding an element with the large negative mixing enthalpy with Si, the growth kinetics of eutectic Si crystal changes, and finally the eutectic crystals are modified. Therefore, the eutectic temperature depressions, which result from the addition of

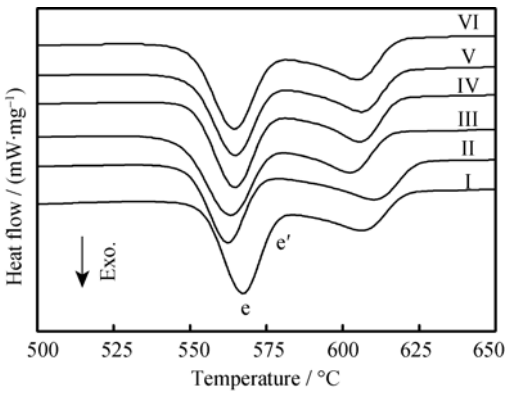

Fig. 3. DSC traces of solidification in modified A356 alloys, where e is the peak of the Al-Si eutectic and e′ is the initial point of the Al-Si eutectic.

Table 4. Temperature depressions of the initial eutectic point and peak eutectic point for each modified alloy

Designation of alloy	Initial eutectic point temperature / °C	Temperature depression of the initial eutectic point / °C	Peak eutectic temperature / °C	Temperature depression of the peak eutectic / °C
I	577.5	—	567.3	—
II	572.0	5.5	562.2	5.1
III	574.7	2.8	563.0	4.3
IV	575.1	2.4	564.5	2.8
V	575.5	2.0	564.6	2.7
VI	575.3	2.3	564.4	2.9

modifying agents, are the main reason for the modification of eutectic (α)Al-Si crystals.

4. Conclusions

(1) Based on the mixing enthalpy calculated by the Miedema model for A356 alloy, four rare earth elements (Ce, La, Pr, and Sm), having the large negative mixing enthalpies with Si, are tested as modifying agents. The element with the largest negative mixing enthalpy is Ce.

(2) Microstructures of the modified alloys show that, in addition to the crystal structure and lattice parameter, a large negative mixing enthalpy with Si is an additional effective parameter for the selection of modifying agents for Al-7Si alloys. Among the four rare earth elements, the addition of Ce to Al-7Si alloy shows the best effect on the modification of eutectic Si crystals.

(3) The eutectic temperature depressions of the modified alloys are larger than 2°C, which is the main reason for the modification of eutectic Si crystals.

References

[1] Y.C. Tsai, C.Y. Chou, S.L. Lee, *et al.*, Effect of trace La addition on the microstructures and mechanical properties of A356 (Al-7Si-0.35Mg) aluminum alloys, *J. Alloys Compd.*, 487(2009), No.1-2, p.157.

[2] C.Y. Chou, S.L. Lee, and J.C. Lin, Effects and deformation characteristics of cross-channel extrusion process on pure Sn and Al-7Si-0.3Mg alloy, *Mater. Chem. Phys.*, 107(2008), No.2-3, P.193.

[3] K. Nogita and A.K. Dahle, Effects of boron on eutectic modification of hypoeutectic Al-Si alloys, *Scripta Mater.*, 48(2003), No.3, p.307.

[4] Y.C. Lee, A.K. Dahle, D.H. StJohn, and J.E.C. Hutt, The effect of grain refinement and silicon content on grain formation in hypoeutectic Al-Si alloys, *Mater. Sci. Eng. A*, 259(1999), No.1, p.43.

[5] A.K. Dahle, K. Nogita, S.D. McDonald, *et al.*, Eutectic modification and microstructure development in Al-Si alloys, *Mater. Sci. Eng. A,* 413-414(2005), p.243.

[6] A. Knuutinen, K. Nogita, S.D. McDonald, and A.K. Dahle, Modification of Al-Si alloys with Ba, Ca, Y and Yb, *J. Light Met.*, 1(2001), No.4, p.229.

[7] H.S. Kang, W.Y. Yoon, K.H. Kimc, *et al.*, Effective parameter for the selection of modifying agent for Al-Si alloy, *Mater. Sci. Eng. A*, 448-451(2007), p.334.

[8] J.Y. Chang, I.G. Moon, and C.S. Choi, Refinement of cast microstructure of hypereutectic Al-Si alloys through the addition of rare earth metals, *J. Mater. Sci.*, 33(1998), No.20, p.5015.

[9] S.Z. Lu and A. Hellawell, The mechanism of silicon modification in aluminum-silicon alloys: impurity induced twinning, *Metall. Trans. A*, 18(1987), No.10, p.1721.

[10] B.J. Ye, C.R. Looper, D.Y. Lu, and C.S. Kang, An assessment of the role of rare earth in the eutectic modification of cast aluminum-silicon alloys, *AFS Trans.*, 93(1985), p.533.

[11] M.M. Makhlouf and H.V. Guthy, The aluminum-silicon eutectic reaction: mechanisms and crystallography, *J. Light Met.*, 1(2001), No.4, p.199.

[12] F.R. de Boer, R. Boom, W.C.M. Mattens, *et al.*, *Cohesion in Metals: Transition Metal Alloys*, North-Holland Physics Publishing, Netherlands, 1988, p.1.

[13] K. Nogita, A. Knuutinen, S.D. McDonald, and A.K. Dahle, Mechanisms of eutectic solidification in Al-Si alloys modified with Ba, Ca, Y and Yb, *J. Light Met*., 1(2001), No.4, p.219.

[14] P. Wang and G.C. Li, *Crystallography Course*, National Defense Industry Press, Beijing, 2006, p.121.