Microstructure Evolution and Performance Improvement of Hypereutectic Al–Mg$_2$Si Metallic Composite with Ca or Sb

Min Zuo *, Boda Ren, Zihan Xia, Wenwen Ma, Yidan Lv and Degang Zhao

School of Materials Science and Engineering, University of Jinan, Jinan 250022, China; rbd18863515609@163.com (B.R.); xzh778888@163.com (Z.X.); mwvdeyouxiang@126.com (W.M.); lyd1169704770@163.com (Y.L.); mse_zhaodg@ujn.edu.cn (D.Z.)

* Correspondence: mse_zuom@ujn.edu.cn; Tel.: +86-531-8276-5317

Received: 21 May 2020; Accepted: 8 June 2020; Published: 15 June 2020

Abstract: In this article, the modification effects on Al–Mg$_2$Si before and after heat treatment were investigated with Ca, Sb, and (Ca + Sb). In comparison with single Ca or Sb, the samples with composition modifiers (Ca + Sb) had the optimal microstructure. The sample with a molar ratio for Ca-to-Sb of 1:1 obtained relatively higher properties, for which the Brinell hardness values before and after heat treatment were remarkably increased by 31.74% and 28.93% in comparison with bare alloy. According to differential scanning calorimetry analysis (DSC), it was found that the nucleation behavior of the primary Mg$_2$Si phase could be significantly improved by using chemical modifiers. Some white particles were found to be embedded in the center of Mg$_2$Si phases, which were deduced to be Ca$_5$Sb$_3$ through X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM) analyses. Furthermore, Ca$_5$Sb$_3$ particles possess a rather low mismatch degree with Mg$_2$Si particles based on Phase Transformation Crystallography Lab software (PTCLab) calculation, meaning that the efficient nucleation capability of Ca$_5$Sb$_3$ for Mg$_2$Si particles could be estimated.

Keywords: Al–Mg$_2$Si composite alloy; chemical modifier; microstructure; Brinell hardness; heterogeneous nucleation behavior

1. Introduction

Recently, aluminum matrix composites (AMCs), especially Mg$_2$Si-particle-reinforced aluminum matrix alloys, have attracted considerable attention due to their high specific strength, excellent wear, and anticorrosion resistance in structural components in the aerospace and automotive fields [1–3]. As an advanced intermetallic compound, Mg$_2$Si possesses excellent properties, including high hardness (4.5 × 10$^4$ N m$^{-2}$), low density (1.99 × 10$^3$ kg m$^{-3}$), low thermal expansion coefficient (7.5 × 10$^{-6}$ K$^{-1}$), and a suitable elastic modulus (120 GPa), meaning it has been regarded as an intriguing candidate for use in structural applications [4,5]. As is known to all, the material performance is closely related to the configuration state [6,7]. Based on this, the question of how to prepare the controllable structural configuration of metallic alloys has been the focus of a number of studies.

As for Al–Mg$_2$Si alloys, the modification and refinement of Mg$_2$Si phases have become especially important topics, in which coarse primary Mg$_2$Si dendrites [8] and Chinese script eutectic Mg$_2$Si [9,10] would seriously weaken the mechanical properties of systems. Over the past few years, many researchers have developed various routes to achieve the optimization effect of the Mg$_2$Si phase, such as melt superheating [11], hot extrusion [12,13], ultrasonic melt treatment [14], rapid solidification [15], and heat treatment [16,17]. Besides these methods, chemical modifier treatments have been found to be much easier to operate with high efficiency, such as with Na [18], Sr [19], Be
China
[20], Gd [21], La [22], and Y [23]. Farahany et al. [24] reported that a Bi additive also had a significant effect on the morphologies of Al_{2}Cu (θ), Al_{3}FeSi (β), and Al_{5}Cu_{3}Mg_{5}Si_{3} (Q) phases, in addition to an excellent modification effect on primary and eutectic Mg_{2}Si in Al–20Mg_{2}Si–2Cu composites. Alizadeh and Mahmudi [25] found that Sb could change the morphologies of Mg_{2}Si particles in Mg–4Zn–2Si alloys from Chinese script to more rounded edge types, resulting in better plasticity for shear deformation.

Based on the references above, it was found that most of chemical modifiers only work on one of the two Mg_{2}Si phases (primary Mg_{2}Si or eutectic Mg_{2}Si), with limited effect. Based on this, the complex modification treatment deserves more attention, owing to the considerable potential for the microstructural optimization of metallic alloys. Lv et al. revealed [26] that primary Mg_{2}Si particles were significantly refined from 95 μm to 10 μm with 2.0% Sb and 0.2% Bi, for which the Brinell hardness was increased up to 134.67 after heat treatment. Based on the rather low planar mismatch δ between (111)_{Mg_{2}Si} and (0001)_{Mg_{3}Sb} of 1.79%, Mg_{2}Si could act as the heterogeneous nucleation site for primary Mg_{2}Si, and with the cooperative absorption behavior of Bi on the growth front, the primary Mg_{2}Si dendrites would be obviously refined. Zha et al. [27] reported that an enhanced synergistic modification effect of Sb and Zr could be obtained for Al–20Mg_{2}Si alloys. Mg_{2}(Sb, Si): particles could serve as the nuclei of primary Mg_{2}Si and Zr, further improving the refinement effect through the decrease of the solidification temperature interval of the primary particles. Researchers still need to do a lot of work to identify the interaction effects between chemical modifiers, such as promotion, inhibition, or no influence.

Recently, the complex additives of Ca and Sb into aluminum alloys containing Mg_{2}Si particles have drawn much attention. Yu et al. [28] revealed that CaSb_{2} particles could serve as heterogeneous nucleation sites for primary Mg_{2}Si and Ca elements adsorbed on the growth front could restrict the growth rate of Mg_{2}Si. Due to the large electronegativity difference between Ca and Sb of 1.05, various Ca–Sb compounds could form. In this paper, the composite modifications of Ca and Sb with different atomic ratios in Al–20Mg_{2}Si alloys were applied in this process. The effects of single Ca and Sb modifiers on the microstructure and mechanical properties of composites before and after heat treatment were also reported. The novel complex modification of Ca and Sb would open significant new opportunities for microstructural control and property enhancement of aluminum alloys containing Mg_{2}Si reinforcements.

2. Experimental Procedures

Commercially pure Al ingot (99.97%), pure Mg ingot (99.89%), and Al–24Si master alloy were used as raw materials to prepare basic Al–12.7Mg–7.4Si alloys, which correspond to Al–20Mg_{2}Si alloys (all compositions are in wt %, unless otherwise stated). Ca in the form of Al–29Ca master alloy and pure Sb ingot (98.25%) was added into Al–20Mg_{2}Si to investigate the interaction effects of modifiers.

Melt modifications of Al–20Mg_{2}Si alloys were carried out as follows. By using an electrical resistance furnace (SG2–7.5–12, Longkou Electric Furnace Factory, Longkou, China), about 300 g of basic alloy was remelted in a graphite crucible (φ94 × 154 mm) (Jinda Crucible Factory, Tianjin, China) at 780 °C for 30 min. Subsequently, single modifier of Ca or Sb and a composite modifier (Ca + Sb) were added into the melt and mechanically stirred with a graphite rod for 10 min in order to obtain uniform dispersion. During the modification process, the melt temperature was monitored by a thermocouple and assisted by a K-model handset thermocouple (Wuxi Ruiwen Automation Instrument Co. LTD, Wuxi, China). Finally, the melt was poured into a permanent mold (70 × 35 × 20 mm) preheated to 200 °C. For the first group of modification treatments, the addition level of Ca was 0.15%. The second group of experiments was used to treat base alloys with various amounts of Sb (i.e., 0.23%, 0.46%, and 0.91%). Thirdly, the interaction influence of the composite modifier (Ca + Sb) on the microstructure of the base alloy was studied. In order to obtain more information, three molar ratios of Ca and Sb were evaluated, including 2:1 (0.15% Ca, 0.23% Sb), 1:1 (0.15% Ca, 0.46% Sb), and 1:2 (0.15% Ca, 0.91% Sb).
The Al–20Mg2Si samples were heat-treated following the T6 procedure, which involves treating the solution at 510 °C for 4 h followed by water quenching and then artificial aging at 175 °C for 8 h. Metallographic specimens were cut from the midsection of each sample and then mechanically ground and polished through standard routines. In order to evaluate the microstructures of alloys, the average sizes of primary Mg2Si particles were obtained from at least ten areas of specimen’s metallograph, and from each area about ten primary Mg2Si particles were chosen. The microstructural characterization of Al–20Mg2Si samples were determined with an optical microscope (4XC, Shanghai Caikon Optical Instrument Co. LTD, Shanghai, China) and a field-emission scanning electron microscope (FESEM) (QUANTA FEG250, FEI, Hillsboro, OR, USA) assisted by an energy-dispersive X-ray spectrometer (EDS) (INCA Energy X-MAX-50X, OIMS, Oxford, UK). The phase compositions of basic alloys were determined using X-ray diffraction (XRD) (D8 ADVANCE, Bruker, Germany) with Cu-Kα in steps of 10°–80°. Meanwhile, the scanning rate and acquisition step were 4°/min and 0.02° (2θ), respectively. Brinell hardness values (HB) of Al–20Mg2Si composite alloys with different chemical modifiers were evaluated by a Brinell hardness tester with an applied load of 612.9 N pressed by a φ5 indenter (HBRVU-1875, Shanghai Materials Testing Instrument Co. LTD, Shanghai, China). For each sample, the hardness values were obtained according to the average value from seven points. The melting and solidification behaviors of alloys were evaluated using differential scanning calorimetry (DSC) (DSC-404, Netzsch Inc., Selb, Germany) under argon flow protection within the range of 200–750 °C at a rate of 10 °C/s. The possible orientation relationships between intermetallic compounds in this system were developed with the Phase Transformation Crystallography Lab software (PTCLab Version 1.19.0) [29].

3. Results and Discussion

Figure 1 shows the typical microstructures of Al–20Mg2Si composite alloys modified with 0.15% Ca. As a typical surface active element, Ca restricts the growth rate of the Mg2Si phase, resulting in significant modification of particles. As the arrows indicate in Figure 1, primary Mg2Si particles were refined from more than 100.0 μm to about 44.1 μm, with standard deviation of 4.7 μm. However, some coarse Mg2Si dendrites were still detected with sizes up to 119.0 μm, as illustrated in Figure 1b. Furthermore, eutectic cell structures were obviously modified, as indicated by ellipses, with eutectic Mg2Si particles changing to short rod-like structures and dots.

Figure 1. (a) typical microstructure of Al–20Mg2Si composites modified with 0.15% Ca; (b) partial enlarged drawing of this sample.

The typical microstructures of Al–20Mg2Si alloys modified with different addition levels of Sb are illustrated in Figure 2. It was found that Sb has an obvious influence on both phases of primary and eutectic structures. With the concentration of Sb increasing from 0.23% to 0.91%, the average sizes of primary Mg2Si particles were 54.2 μm (standard deviation of 4.8 μm), 67.1 μm (standard deviation of 4.0 μm), and 46.7 μm (standard deviation of 4.2 μm), respectively. As indicated by circles in Figure 2a, Mg2Si particles were obtained as corner-sharing octahedrons in three-dimensional spaces. Meanwhile, typical particles with four-petalled structures highlighted by
circles were found, which were obtained from truncated octahedron Mg:Si along (001) planes, as shown in Figure 2c. Due to the enrichment of Al atoms at the center of the [111] planes, the hopper structure of the Mg:Si octahedron was formed. With the addition of Sb increasing to 0.91%, the microstructure of the Al–20Mg:Si composites was further optimized, with the eutectic cell structure being excellently modified.

Figure 2. Typical microstructures of Al–20Mg:Si alloys with different addition levels of Sb: (a,b) 0.23%; (c,d) 0.46%; (e,f) 0.91%.

In comparison with modification efficiencies of single Ca and Sb, composite modifiers (Ca + Sb) with different molar ratios were added into Al–20Mg:Si alloys, such as 2:1, 1:1, and 1:2 ratios. As indicated in Figure 3, it was found that with a molar ratio of Ca-to-Sb of 1:1, the sample possessed better modification and refinement efficiency than the other two samples. In addition to the rather fine spot-like eutectic Mg:Si, primary Mg:Si particles were refined to 27.7 μm with standard deviation of 2.9 μm. With a higher concentration of Sb, the eutectic structure tended to be coarser, as illustrated in Figure 3e,f. The mean size of primary Mg:Si particles shown in Figure 3e was 55.8 μm. Furthermore, coarse flake-like eutectic Mg:Si compounds were also observed in this sample.
Figure 3. Typical microstructures of Al–20Mg2Si alloys modified by the complex modifier (Ca + Sb) with different molar ratios: (a,b) 2:1; (c,d) 1:1; (e,f) 1:2.

In order to get more information, the typical microstructures of these composite alloys after T6 heat treatment were studied and are shown in Figure 4. In comparison with single Sb addition, eutectic Mg2Si compounds with a Ca modifier after heat treatment were finer. By modifying the compositions of Ca and Sb, the microstructures of the Al–Mg2Si alloys after heat treatment were further optimized. As clearly illustrated in Figure 4c–e, the sharp edges of primary Mg2Si polyhedrons became more rounded, with eutectic Mg2Si phases transforming from flakes into fine spot-like shapes simultaneously. The sample modified with 0.15% Ca and 0.46% Sb (molar ratios for Ca-to-Sb of 1:1) possessed the optimal microstructure, meaning that mechanical properties of metallic alloys could be better predicted.
Figure 4. Typical microstructures of Al–20Mg2Si alloys with Ca or Sb modifiers after heat treatment: (a) 0.15% Ca; (b) 0.46% Sb; (c) 0.15% Ca; 0.23% Sb (molar ratio of 2:1); (d) 0.15% Ca and 0.46% Sb (molar ratio of 1:1); (e) 0.15% Ca and 0.91% Sb (molar ratio of 1:2).

Figure 5 shows the Brinell hardness values of Al–20Mg2Si alloys treated with different modifiers. It can be seen that with single addition of Ca and Sb, the Brinell hardness values of as-cast compositions were increased by 4.21%, 9.69%, 5.62%, and 16.0% respectively, compared with the basic alloy. After heat treatment, the Brinell hardness values of alloys were all improved to a certain extent. The samples with complex modifications obtained relatively higher hardness values, especially the one with a Ca/Sb molar ratio of 1:1. The Brinell hardness values of this sample before and after heat treatment were about 93.8 and 110.4, increasing by 31.74% and 28.93%, respectively, in comparison with the bare alloy.
As we all know, the improvement of mechanical properties of metallic alloys is related to the optimization of the microstructure. With the addition of a chemical modifier, the solidification behavior of the Al–20Mg2Si alloys might be influenced, resulting in the evolution of their microstructures. Figure 6 shows the differential scanning calorimetry (DSC) curves of Al–20Mg2Si alloys with different chemical modifiers. As clearly indicated in Figure 6, the precipitation temperatures of primary Mg2Si phases in alloys modified by Ca or Sb were in the range of 675–683 °C with a deviation of 2 °C, which were relatively higher values than that of the bare alloy. The increase in precipitation temperature of the primary phase implies the decrease of the required undercooling temperature, indicating that the nucleation behaviors of primary phases were significantly improved. Furthermore, the initial precipitation temperatures of eutectic Mg2Si phases in these samples were 546, 545, 543, and 542 °C, respectively.
The corresponding XRD patterns of Al–20Mg2Si alloys before and after complex modifications of Ca and Sb are illustrated in Figure 7. In order to obtain clear diffraction peaks for possible compounds containing Ca or Sb, the concentrations of Ca and Sb were increased to about 1% and 3%, respectively, meaning that the molar ratio of Ca-to-Sb still remained at 1:1. Based on the XRD patterns, it could be found that besides Al and Mg2Si phases, some weak diffraction peaks were detected, which were determined to be CaSb3 compounds based on ICSD #002065. As the orange arrows indicate in Figure 7, the diffraction lines exhibited peaks at 32.46°, 34.42°, 35.68°, 49.47°, and 63.62°, corresponding to (222), (420), (203), (304), and (642) reflections of CaSb3 (orthorhombic, Pnma, a = 1.250 nm, b = 0.951 nm, c = 0.829 nm) respectively. The formation of CaSb3 compounds might be the reason for the excellent complex modification efficiency of Ca and Sb in Al–20Mg2Si systems.

Figure 7. XRD patterns of as-cast Al–20Mg2Si alloys: (a) bare sample; (b) modified sample.

The typical FESEM micrograph and corresponding EDS line scanning analyses along A–B are shown in Figure 8. It can be seen that there were some light grey particles embedded in the center of the primary Mg2Si particle. According to the X-ray images for respective elements, enrichment of Ca and Sb elements in the area between the two dotted lines was observed, which was confirmed to be the heterogeneous nucleation site for the primary Mg2Si phase during the solidification process. To obtain more details about this compound, a chemical composition analysis with an EDS test was carried out and is illustrated in Figure 9. From the FESEM image in Figure 9, the existence of light grey particles in the middle of primary Mg2Si particles was proven. Based on the EDS results, the atomic ratio of Ca and Sb elements with light grey particle was about 1.95, which was relatively closed to 1.67 in the CaSb3 phase. In accordance with the XRD analysis, this enrichment of Ca and Sb in the center of Mg2Si provided further evidence of the heterogeneous nucleation effect of CaSb3.
Figure 8. FESEM analysis of primary Mg$_2$Si in Al–20Mg$_2$Si alloys after modification by 0.15% Ca and 0.46% Sb: (a) microstructure; (b–f) the X-ray images for respective elements from A to B, including Al, Mg, Si, Ca, and Sb.
Yuan et al. [30] studied the microstructure refinement of Mg–Al–Zn–Si alloys with Sb and found that the morphological change of MgSi was attributed to Mg2Sb as the nucleation nuclei. As a surface-active element, Ca elements could be adsorbed on the {111} and {100} planes of MgSi particles, restricting the corresponding growth rates of these planes. Based on this, various stages of MgSi-truncated octahedrons enclosed by {111} and {100} lattice planes would be formed. The electronegativity is a typical chemical characteristic, which indicates the ability of an atom to attract other electrons to itself. The larger the difference between the electronegativity parameters of two atoms, the higher the tendency for them to form compounds. In this Al–Mg-Si system, Ca and Sb are likely to react with each other due to the large electronegativity difference of 1.05, resulting in the formation of various stoichiometric compounds [31]. Yu [32,33] investigated the crystallization behavior of primary MgSi in composites with different Ca/Sb molar ratios. In their study, the total mass concentration of Ca and Sb was 0.5%, in which the addition levels of Ca and Sb were determined to be within the range of 0.05%–0.25% and 0.25%–0.45%, respectively. Furthermore, it was found that CaSb2 and CaSb3 could affect the nucleation process of primary MgSi, resulting in the refinement of primary particles.

By using differential thermal analysis (DTA) and microstructure analysis, Niyazova et al. [34] first investigated the binary phase diagram of Ca–Sb and reported that three stable compounds could be formed, including Ca2Sb3, CaSb2, and CaSb. Okamoto [35] further researched the Ca–Sb phase diagram based on new DTA data and negative formation enthalpies of Ca1Sb0.5 and Ca2Sb. In addition, Martinez-Rippoll and Brauer [36] deduced the CaSb phase to be the stoichiometry of CaSb2, and Leon-Escamilla and Corbett [37] refined the crystal structure of CaSb2. Qin et al. [38] studied the thermodynamic modeling of the Ca–Sb system by using first-principles calculations. According to their research, the thermodynamic behaviors of different compounds in the Al–Mg–Si–Ca–Sb system could be discussed as follows. According to XRD and EDS analyses, the nucleation nuclei embedded in primary MgSi particles were deduced to be CaSb2, which could be formed through the following Equation (1):

$$5\text{Ca} + 3\text{Sb} \rightarrow \text{Ca}_3\text{Sb}_3$$  \hspace{1cm} (1)

The standard Gibbs free energy change $\Delta G$ could be obtained through the corresponding Equation (2):

$$\Delta G = -618918 + 207.28T$$  \hspace{1cm} (2)

in which $T$ is the temperature of the liquid melt in degrees Celsius. When the system temperature changed from 700 to 1000 °C, the $\Delta G$ values fell in the range of −411 to −473 kJ/mol, which proved...
the feasibility of this reaction due to the large negative values. In comparison with the formation reaction of CaSb [32], the precipitation of CaSb₃ possesses a much lower ΔG value, meaning a greater tendency for the formation of CaSb₃.

According to the edge-to-edge matching model [39,40], the CaSb₃ phase could act as a potential heterogeneous nucleation site for Mg₃Si particles due to the low mismatch degree, which was obtained using Phase Transformation Crystallography Lab software (PTCLab). The detailed orientation relationships between CaSb₃ and Mg₃Si phases are listed in Figure 10. Based on the calculations, the interatomic spacing misfit between (010)_{CaSb₃} and (01T)_{Mg₃Si} was rather low at 0.08%. Meanwhile, the corresponding interplanar spacing mismatches between (050)_{CaSb₃} / (400)_{Mg₃Si} and (002)_{CaSb₃} / (111)_{Mg₃Si} were merely 2.10% and 4.80%, respectively. From this, the efficient nuclear capability of CaSb₃ for Mg₃Si particles could be estimated, which was further confirmed by the FESEM results shown in Figures 8 and 9.

![Figure 10. The corresponding interatomic spacing and interplanar spacing misfits between CaSb₃ and Mg₃Si phases.](image)

With the co-modification of Ca and Sb, the mechanical properties of Al–Mg₃Si composite alloys were improved, which were attributed to the optimization of the microstructure. As for polycrystalline alloys, the effects of grain size on mechanical properties could be described by the Hall–Patch Equation (3). Based on the Hall–Patch model:

\[
H = H_0 + kD^{1/2}
\]

where \(H_0\) is the hardness of the bulk material, \(k\) is the constant in the relationship with the material characteristic, and \(D\) is the average grain size [41,42]. With the heterogeneous nucleation sites provided by CaSb₃, coarse primary Mg₃Si dendrites were changed into fine particles. Additionally, the eutectic structure was also efficiently modified due to the existence of Ca. Through the efficient refinement of primary Mg₃Si and modification of the eutectic structure, the hindrance ability of the grain boundaries as the obstacles for crack propagation would be significantly improved, resulting in the promotion of mechanical properties.

4. Conclusions

In summary, a novel precipitation behavior control method with (Ca + Sb) was applied for microstructural control and performance improvement of Al–Mg₃Si alloys. The modification mechanism of the complex modifier (Ca + Sb) in this alloy was also investigated.
• In comparison with single Ca or Sb modifiers, the optimum modification effect for the Al–Mg2Si alloy was obtained through the composite addition of (Ca + Sb), especially for the alloy with 0.15% Ca and 0.46% Sb (molar ratio of 1:1), which possessed an optimal microstructure configuration and mechanical properties;

• Through FESEM and XRD analyses, CaSb3 compounds were observed in the center of the primary MgSi particles. Furthermore, the formation feasibility of CaSb3 was also proven by thermodynamic calculation;

• According to DSC analysis, the precipitation of primary MgSi phases in Ca- or Sb-modified alloys was in the range of 675–683 °C, meaning that the precipitation behavior could be improved;

• CaSb3 has a rather low mismatch degree with MgSi particles according to calculations using Phase Transformation Crystallography Lab software (PTCLab). The interatomic spacing misfit between \( \{001\}_{\text{CaSb3}} \) and \( \{01T\}_{\text{MgSi}} \) was rather low at 0.08%. Meanwhile, the corresponding interplanar spacing mismatches between \( \{050\}_{\text{CaSb3}} / \{400\}_{\text{MgSi}} \) and \( \{002\}_{\text{CaSb3}} / \{111\}_{\text{MgSi}} \) were merely 2.10% and 4.80%, respectively;

• Based on these findings, the efficient nucleation behavior of CaSb3 for MgSi particles could be estimated, resulting in the improvement of the microstructure and mechanical properties of composite alloys.

Author Contributions: Conceptualization, M.Z.; data curation, W.M.; formal analysis, Y.L. and D.Z.; investigation, B.R. and Z.X.; project administration, M.Z.; writing—review and editing, M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Natural Science Foundation of Shandong Province (ZR2019MEM019), National Natural Science Foundations of China (51772132), and Shandong Province Higher Educational Youth Innovative Science and Technology Program (2019JKA018).

Conflicts of Interest: The authors declare no competing interests.

References

1. Ram, S.; Chattopadhyay, K.; Chakrabarty, I. High temperature tensile properties of centrifugally cast in-situ Al-Mg2Si functionally graded composites for automotive cylinder block liners. J. Alloy. Compd. 2017, 724, 84–97, doi:10.1016/j.jallcom.2017.06.306.

2. Sun, J.; Li, C.; Liu, X.; Xu, L.; Li, H.; Liu, Y. Investigation on AlP as the heterogeneous nucleus of MgSi in Al–Mg2Si alloys by experimental observation and first-principles calculation. Results Phys. 2018, 8, 146–152, doi:10.1016/j.rinp.2017.11.025.

3. Wu, X.-F.; Wang, Y.; Wang, K.-Y.; Zhao, R.-D.; Wu, F. Enhanced mechanical properties of hypoeutectic Al-10MgSi cast alloys by Bi addition. J. Alloy. Compd. 2018, 767, 163–172, doi:10.1016/j.jallcom.2018.07.070.

4. Mabuchi, M.; Higashi, K. Strengthening mechanisms of Mg Si alloys. Acta Mater. 1996, 44, 4611–4618, doi:10.1016/1359-6454(96)00072-9.

5. Li, G.; Gill, H.S.; Varin, R.A. Magnesium silicide intermetallic alloys. Met. Mater. Trans. A 1993, 24, 2383–2391, doi:10.1007/bf02646518.

6. Zuo, M.; Zhao, D.; Wang, Z.; Geng, H. Complex modification of hypereutectic Al-Si alloy by a new Al-Y-P master alloy. Met. Mater. Int. 2015, 21, 646–651, doi:10.1007/s12540-015-4535-2.

7. Eztapour, H.R.; Chaichi, A.; Sajjadi, S.A. The effect of Al2O3-nanoparticles as the reinforcement additive on the hot deformation behavior of 7075 aluminum alloy. Mater. Des. 2015, 88, 1049–1056, doi:10.1016/j.matdes.2015.09.009.

8. Tebib, M.; Samuel, A.; Ajersch, F.; Chen, X.-G. Effect of P and Sr additions on the microstructure of hypereutectic Al–15Si–14Mg–4Cu alloy. Mater. Charact. 2014, 89, 112–123, doi:10.1016/j.matchar.2014.01.005.

9. Lee, Y.-S.; Cha, J.-H.; Kim, S.-H.; Lim, C.-Y.; Kim, H.-W.; Kim, H.-S. Modification of eutectic MgSi in AlMg5Si2Mn alloy by pre-homogenization deformation treatment with different reduction conditions. Mater. Charact. 2018, 141, 388–397, doi:10.1016/j.matchar.2018.04.045.
10. Wu, X.-F.; Wang, K.-Y.; Wu, F.; Zhao, R.-D.; Chen, M.-H.; Xiang, J.; Ma, S.-N.; Zhang, Y. Simultaneous grain refinement and eutectic MgSi modification in hypoeutectic Al-11MgSi alloys by Sc addition. *J. Alloy. Compd.* **2019**, *791*, 402–410, doi:10.1016/j.jallcom.2019.03.326.

11. Saffari, S.; Akhlaghi, F. Microstructure and mechanical properties of Al-Mg:Si composite fabricated in-situ by vibrating cooling slope. *Trans. Nonferrous Met. Soc. China* **2018**, *28*, 604–612, doi:10.1016/s1003-6326(18)64693-x.

12. Emamy, M.; Yeganeh, S.V.; Razaghian, A.; Tavighi, K. Microstructures and tensile properties of hot-extruded Al matrix composites containing different amounts of Mg:Si. *Mater. Sci. Eng. A* **2013**, *586*, 190–196, doi:10.1016/j.msea.2013.08.026.

13. Ghandvar, H.; Idris, M.H.; Ahmad, N. Effect of hot extrusion on microstructural evolution and tensile properties of Al-15%Mg:Si-xGd in-situ composites. *J. Alloy. Compd.* **2018**, *751*, 370–390, doi:10.1016/j.jallcom.2018.04.131.

14. Bai, G.; Liu, Z.; Lin, J.; Yu, Z.; Hu, Y.; Wen, C. Effects of the addition of lanthanum and ultrasonic stirring on the microstructure and mechanical properties of the in situ Mg 2 Si/Al composites. *Mater. Des.* **2016**, *90*, 424–432, doi:10.1016/j.matdes.2015.10.159.

15. Zhang, J.; Fan, Z.; Wang, Y.; Zhou, B. Hypereutectic aluminium alloy tubes with graded distribution of Mg:Si particles prepared by centrifugal casting. *Mater. Des.* **2000**, *21*, 149–153, doi:10.1016/s0261-0306(99)00100-4.

16. Li, Z.; Li, C.; Liu, Y.; Yu, L.; Guo, Q.; Li, H. Effect of heat treatment on microstructure and mechanical property of Al-10%Mg:Si alloy. *J. Alloy. Compd.* **2016**, *663*, 16–19, doi:10.1016/j.jallcom.2015.12.128.

17. Emamy, M.; Emami, A.; Tavighi, K. The effect of Cu addition and solution heat treatment on the microstructure, hardness and tensile properties of Al-15%Mg:Si-0.15%Li composite. *Mater. Sci. Eng. A* **2013**, *576*, 36–44, doi:10.1016/j.msea.2013.03.066.

18. Emamy, M.; Khoshkideh, R.; Raouf, A.H. The influence of pure Na on the microstructure and tensile properties of Al-Mg:Si metal matrix composite. *Mater. Sci. Eng. A* **2011**, *528*, 4337–4342, doi:10.1016/j.msea.2011.02.010.

19. Jiang, W.; Xu, X.; Zhao, Y.; Wang, Z.; Wu, C.; Pan, D.; Meng, Z. Effect of the addition of Sr modifier in different conditions on microstructure and mechanical properties of T6 treated Al-Mg:Si in-situ composite. *Mater. Sci. Eng. A* **2018**, *721*, 263–273, doi:10.1016/j.msea.2018.02.100.

20. Azarbarmas, M.; Emamy, M.; Alipour, M. Study on fracture behaviour of Al–15%Mg:Si metal matrix composite with and without beryllium additions. *J. Mater. Sci.* **2011**, *46*, 6856–6862, doi:10.1007/s10853-011-5648-8.

21. Ye, L.; Hu, J.; Tang, C.; Zhang, X.-M.; Deng, Y.; Liu, Z.; Zhou, Z. Modification of Mg:Si in Mg–Si alloys with gadolinium. *Mater. Charact.* **2013**, *79*, 1–6, doi:10.1016/j.matchar.2013.02.005.

22. Wang, L.; Guo, E.; Ma, B. Modification effect of lanthanum on primary phase Mg:Si in Mg:Si alloys. *J. Rare Earths* **2008**, *26*, 105–109, doi:10.1016/s1003-0721(08)60047-2.

23. Nedooshan, H.R.J.; Liu, W.; Wu, G.; Bahrami, A.; Pech-Canul, M.I.; Emamy, M. Mechanical and Tribological Characterization of Al-Mg:Si Composites After Yttrium Addition and Heat Treatment. *J. Mater. Eng. Perform.* **2014**, *23*, 1146–1156, doi:10.1007/s11665-014-9900-4.

24. Farahany, S.; Ghandvar, H.; Nordin, N.A.; Ourdjini, A.; Idris, M.H.; Nordin, A. Effect of Primary and Eutectic Mg:Si Crystal Modifications on the Mechanical Properties and Sliding Wear Behaviour of an Al–20Mg:Si–2Cu–xBi Composite. *J. Mater. Sci. Technol.* **2016**, *32*, 1083–1097, doi:10.1016/j.jmst.2016.01.014.

25. Alizadeh, R.; Mahmoudi, R. Effects of Sb addition on the modification of Mg:Si particles and high-temperature mechanical properties of cast Mg–4Zn–2Si alloy. *J. Alloy. Compd.* **2011**, *509*, 9195–9199, doi:10.1016/j.jallcom.2011.06.109.

26. Lv, J.; Dong, H.; Fan, L.; Yu, W.; Li, L. Effects of Bi-Sb Addition and Solution Treatment on Microstructures and Mechanical Properties of Al-20 wt.% Mg:Si Composites. *J. Mater. Eng. Perform.* **2019**, *28*, 3105–3114, doi:10.1007/s11665-019-04081-4.

27. Zhu, J.; Zhou, T.; Zha, M.; Li, C.; Li, J.; Wang, C.; Gao, C.; Wang, H.; Jiang, Q. Microstructure and wear behaviour of Al-20Mg:Si alloy with combined Zr and Sb additions. *J. Alloy. Compd.* **2018**, *767*, 1109–1116, doi:10.1016/j.jallcom.2018.07.032.

28. Yu, H.-C.; Wang, H.; Chen, L.; Liu, F.; Wang, C.; Jiang, Q. Heterogeneous nucleation of Mg:Si on CaSb2 nucleus in Al–Mg–Si alloys. *CrystEngComm* **2015**, *17*, 7048–7055, doi:10.1039/c5ce01271f.
29. Gu, X.-F.; Furuhara, T.; Zhang, W.-Z. PTCLab: Free and open-source software for calculating phase transformation crystallography. J. Appl. Crystallogr. 2016, 49, 1099–1106, doi:10.1107/s1600576716006075.
30. Yuan, G.; Liu, Z.; Wang, Q.; Ding, W. Microstructure refinement of Mg–Al–Zn–Si alloys. Mater. Lett. 2002, 56, 53–58, doi:10.1016/s0167-577x(02)00417-2.
31. Chen, K.; Li, Z. Effect of co-modification by Ba and Sb on the microstructure of Mg:Si/Mg–Zn–Si composite and mechanism. J. Alloy. Compd. 2014, 592, 196–201, doi:10.1016/j.jallcom.2013.12.041.
32. Yu, H.-C. Crystallization of primary Mg:Si in Al-20Mg:Si alloy with various molar ratios of Ca/Sb. J. Alloy. Compd. 2019, 787, 872–881, doi:10.1016/j.jallcom.2019.02.158.
33. Yu, H.-C.; Wang, H.-Y.; Chen, L.; Zha, M.; Wang, C.; Li, C.; Jiang, Q.-C. Spheroidization of primary Mg:Si in Al-20Mg:Si-4.5Cu alloy modified with Ca and Sb during T6 heat treatment process. Mater. Sci. Eng. A 2017, 685, 31–38, doi:10.1016/j.msea.2016.12.080.
34. Niyazova Z.U.; Vakhobov A.V.; Dzhuraev T.D. Phase diagram of the Ca–Sb system. Izv Akad. Nauk SSSR, Neorg. Mater 1976, 72, 1293–1294.
35. Okamoto H. Ca–Sb (Calcium–Antimony). J. Phase Equilib. 1997, 18, 313.
36. Martinez-Ripoll, M.; Brauer, G. The crystal structure of CaSb2. Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1974, 30, 1083–1087, doi:10.1107/s0567740874004304.
37. Leon-Escamilla E.A.; Corbett J.D. Hydrogen in polar intermetallics. Binary pnictides of diveral metals with MnSi3-type structures and their isotypic ternary hydride solutions. Chem. Mater. 2006, 18, 4782–4792.
38. Qin, S.; Liu, S.; Zhang, C.; Xin, J.; Wang, Y.; Du, Y. Thermodynamic modeling of the Ca-In and Ca-Sb systems supported with first-principles calculations. Calphad 2015, 48, 35–42, doi:10.1016/j.calphad.2014.10.008.
39. Zhang, M.-X.; Kelly, P.; Easton, M.; Taylor, J. Crystallographic study of grain refinement in aluminum alloys using the edge-to-edge matching model. Acta Mater. 2005, 53, 1427–1438, doi:10.1016/j.actamat.2004.11.037.
40. Qiu, D.; Zhang, M.-X. The nucleation crystallography and wettability of Mg grains on active AlY inclusions in an Mg–10 wt.% Y Alloy. J. Alloy. Compd. 2014, 586, 39–44, doi:10.1016/j.jallcom.2013.10.042.
41. Petch N.J. The cleavage strength of polycrystals. J. Iron Steel Inst. 1953, 174, 25–28.
42. Isfahani, M.J.N.; Payami, F.; Asadabad, M.A.; Shokri, A.A. Investigation of the effect of boron carbide nanoparticles on the structural, electrical and mechanical properties of Al-B4C nanocomposites. J. Alloy. Compd. 2019, 797, 1348–1358, doi:10.1016/j.jallcom.2019.05.188.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).