Study on the Preparation of Al$_2$O$_3$/Al-15Si-4Mg composite material

Yingfan Zhao$^{1,a}$, Zelin Yan$^{1,b}$, Tieshuai Li$^{1,c}$, Jing Gao$^{1,d}$, Weiping Tong$^{1,e}$

$^1$Key Laboratory of Electromagnetic Processing of Materials, Northeastern University, Shenyang, 110819, China

$^a$mail: 2166898454@qq.com, $^b$mail: yanzelin1998@163.com, $^c$mail: litieshuai1234@163.com, $^d$mail: 467014557@qq.com

*Corresponding author: $^e$mail: wptong@mail.neu.edu.cn

Abstract: In this research, microstructure refinement treatment was carried out by adding different content of lanthanum to Al-15Si-4Mg alloy. The effect of heat treatment process on the alloy after metamorphism was studied, and the optimal performance matrix was selected for Al$_2$O$_3$/Al composite research. The results show that La has good metamorphism effect on Al-15Si-4Mg alloy. With the increase of La metamorphic agent content, the eutectic silicon structure was obviously refined. When the La content reached 1wt.%, the refining effect was the best. The hardness of the alloy was 111HBS. When the optimum amount of La was 1wt.%, the XRD phase and EDS spectrum analysis show that the alloy without modification was mainly composed of Al, Si and Mg$_2$Si, and the metamorphic alloy also forms a rich La phase. The mechanical properties can be significant improved by the heat treatment process. After the heat treatment, the acicular structure of the eutectic silicon structure became smooth and smooth, which reduced the splitting effect on the aluminum matrix. The hardness was 113HBS. The toughness of the material can be significantly improved by the heat treatment process. The sample with 1wt.% La was selected as the matrix of the Al$_2$O$_3$/Al composite. Al$_2$O$_3$/Al was prepared by liquid sintering method and no rich La phase but Mg$_2$Al$_2$O$_4$ was found near the interface which is well reactivate wetted.

1. Introduction

High silicon aluminum alloys are widely used in automotive engine components, aerospace industry, electronic parts and other aspects of social production due to their high strength, high wear resistance, good conductivity and other advantages$^{[1,2]}$. However, due to the increase of silicon content, the presence of acicular eutectic silicon in high Si aluminum alloy will split the aluminum matrix, resulting in brittle alloy, which is not conducive to the cutting performance of the alloy$^{[3-6]}$. Therefore, the addition of rare earth is considered to modify the alloy, followed by heat treatment process to improve the mechanical properties of the matrix alloy. At the same time, if ceramic particles are added to high Si aluminum alloy to make aluminum matrix composite material, the wear resistance and specific strength of the alloy can be significantly improved, and the composite material with excellent performance can be obtained.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
2. Materials and Methods

2.1. Materials
In the research we used Al powders 99.9% Grade, Si particles 99.9% Grade, Mg particles 99.9% Grade, La powders 99.9% Grade purchased from Top metal material Co. Ltd. The mixtures were shaken for 1 hour in the three-dimensional mixing equipment to homogenize the powders. The mixed powders and particles are placed into alumina crucibles. The crucibles with the powders and particles were sintered at 650℃ for 0.5h and then 1050℃ for 0.5h in vacuum. Finally, the composites of the alloys should be Al-15Si-4Mg-xLa (wt.%, x=0, 0.05, 0.1, 0.2, 0.4, 1, 3).

2.2. Microstructural Analysis
Samples sintered as 2.1 were cut into 10mm×10mm×10mm and followed by wet-grinding on a series of grinder papers 800-4000#, polished with 1μm diamond polishing paste and without etching. The microstructure of the samples was investigated with scanning electron microscopy (SEM) on an MIRA3 XMH instrument and EDS energy spectrum analysis was performed for different component points. The phase of the samples was analyzed by the X-ray diffraction (XRD, X’ Pert Pro PW3040/60). In addition the heat treatment detail is 540℃×6h+175℃×8h.

2.3. Hardness
The hardness was measured with a Brinell hardness tester with the load of 250kN, the time of holding pressure was 30s and the indenter was a milling-ball with the diameter of 5mm. The average value of 5 different measurements is reported.

2.4. Microstructure
As is shown in Fig.1, Si was 15wt.%, Mg was 4 wt.%, La was different in different figures. Fig.1(a) was Al-15Si-4Mg without La, from Fig.1(b) to Fig.1(g), the additive amount of La was 0.05wt.%, 0.1 wt.%, 0.2 wt.%, 0.4 wt.%, 1 wt.%, 3 wt.% respectively. The pictures show that, without La, the eutectic Si was needle-like or lath-shaped in Al-15Si-4Mg. The existence of needle-like eutectic Si in α-Al will dissever the unmetamorphosed Al-15Si-4Mg alloy. When the additive amount was 0.05wt.%, 0.1wt.%, 0.2wt.%, 0.4wt.% respectively, the microstructure of eutectic Si was improved, but the effect of La was limited. Until the addition of La reaches 1wt.% and 3wt.%, the microstructure was improved significantly.

In comparison with the results given in Fig.1, When La reaches 1wt.% and 3wt.%, the microstructure of eutectic Si was refined significantly; Si phase particles become smaller and presents as fine granular and short rod-like. With modifier, the la-riched phase appears white in the SEM micrographs. It is shown that the la-riched phase has diffuse arrangement, appears lath-shaped or small shape. Black porosities can be observed clearly in Fig.1, that is because of the addition of Mg. Although the sintering temperature didn’t reach the boiling point of Mg, the vapor pressure still exists, which impel vaporization of Mg and then porosities left. Porosities are defects, which decrease the properties of the alloys, but our final purpose is to make aluminum matrix composite, the existence of Mg helps wetting the interface of ceramic particles and aluminum matrix phase.

As a kind of modifier, La helps to refine the microstructure of eutectic Si and the reasons are as below: (1) La becomes basement while the Si phase nucleating, impelling the heterogeneous nucleation of Si phase. (2) The generation of the reaction of La and Si precipitated decrease the precipitation temperature of Si, which makes the Si phase supercooled and then reaches modification effects. (3) La preferred stacked at the groove of the twin crystal nucleation of Si, which hindered the gather of Si, thus make the Si isotropic growth. (4) The addition of La at metamorphic temperature strengthens the Al-Al radicals, which helps the α-Al spontaneous nucleation and makes Si phase supercooled.

The existing form of La, whether in simple substance or in compounds can not be observed in the X-ray diffraction spectrogram, but some la-riched phase can be observed in the SEM micrographs. Because of the content of La is just 1wt.% and can not be observed in the X-ray diffraction
spectrogram, EDS analysis is used in this research to study the microstructures in different color and different shapes.

![Fig.1 SEM micrographs of different La addition alloys](image)

3. Results and discussion

3.1. Hardness

The average hardness results are shown in Fig.2. It is shown that the hardness of the unmetamorphosed alloy is 101.2HBS. With the increase of the content of La, the hardness increases obviously. The hardness of sample 2 is 5% higher than Sample 1; when the content of La reaches 0.1wt.%, the hardness decrease and the reason might be experimental error; when the content of La reaches 1wt.%, the hardness of the alloy reach its maximum value 111HBS, 10% higher than unmetamorphosed alloy.

![Fig.2 Hardness of the alloys with different content of La](image)

As was shown in Fig.2, with the increase of La, the hardness of the alloy rises, but the rising rate decreases, which proved that La can help to improve the hardness of the alloy. That is because the existence of modifier makes eutectic Si slightly-rounded to reduce the dissevering to the matrix and improve the mechanical properties of the alloy.
3.2. Heat treatment
As shown in Fig.3, figure (b) is Al-15Si-4Mg-1La after heat treatment and figure (a) is the alloy without treatment. Compare the figures, it is clearly observed that after the heat treatment, the edges of the eutectic silicon phase become more smooth, acicular structure decreases, moderate fragmentation effect on matrix weakens and the properties of the alloy improves. The reason is that supersaturated solid solution can be generated during the solution treatment process and promote the homogenization of alloying elements; At the same time, the aging treatment at lower temperature can make the supersaturated solid solution and vacancy obtain enough diffusion time and energy, so that the strength and hardness of the material can be improved. Table 1 shows the contrast of each alloy. From the table, it can be seen that, after heat treatment, both hardness. The hardness of the alloy after heat treatment is 113HBS, which is 4% higher than that of the alloy without heat treatment, and 10% higher than that of the unmetamorphosed alloy.

As shown in Fig. 3, figure (a) is the Al-15Si-4Mg-1La without treatment and figure (b) is the alloy after heat treatment. As can be seen from the comparison in the figure, both of the two alloys have dimples and no brittle fracture platform, and both are ductile fracture. For the alloy after heat treatment, the dimples are relatively larger and the fluctuation is more obvious, indicating the properties of the alloy can be significantly improved by the heat treatment. That is because the eutectic silicon structure can be refined by the heat treatment process, which changed the shape of the eutectic silicon structure from a needle to a smooth one and reduced the splitting effect on the matrix and increased the plasticity index of the alloy.

3.3. Analysis on the microstructure of Al2O3/Al-15Si-4Mg-1La
With the rapid development of discontinuous reinforced composite materials, Al2O3 / Al composites are widely used in Aerospace, automobile and other structural industries due to their low cost, high strength and high wear resistance. If ceramic particles are added to high silicon aluminum alloy to make aluminum matrix composites, the wear resistance and specific strength of the alloy can be improved obviously, and the composite with excellent performance can be obtained. In this paper, Al-15Si-4Mg-1La was selected as the matrix to study the Al2O3/Al composite material.

For the enhancement phase of large particles, the problem of interface combination, which is wetting, should be considered firstly. According to the young-Dupre formula:

$$\sigma_{LS} = \sigma_{SV} - \sigma_{LV}\cos\theta$$  \hspace{1cm} (1)

Where $\sigma_{LS}$, $\sigma_{SV}$ and $\sigma_{LV}$ are the tension of liquid-solid, solid-gas and liquid-gas, $\theta$ is the wetting angle.
Due to the poor chemical compatibility and poor wettability between Al₂O₃ and Al, which wetting angle is more than 90°, the wetting effect cannot be achieved under normal conditions. The addition of magnesium plays a certain role in wetting, and the wetting temperature of the alloy matrix and ceramic particles decreases with the increase of magnesium content. The main reasons are as below:

1. Magnesium is a kind of surface active element, which can reduce the surface tension of the aluminum solution and improve the wettability of alumina particles and aluminum solution.

2. The addition of magnesium makes the oxidation state at the interface change to some extent, which makes the expansion of the aluminum liquid easier. When aluminum melts, magnesium under high vapor pressure and will volatilize. When the magnesium volatilizes, it will cause the flow of the alloy and destroy the oxide film. Moreover, the affinity between magnesium and oxygen is greater than that between aluminum and oxygen, and the magnesium in the alloy liquid will react with the surface of alumina as follows:

\[
\begin{align*}
3\text{Mg} + \text{Al}_2\text{O}_3 & \rightarrow 3\text{MgO} + 2\text{Al} \\
4\text{MgO} + 2\text{Al} & \rightarrow \text{MgAl}_2\text{O}_4 + 3\text{Mg}
\end{align*}
\]

The reaction equation above results in the porosity and rupture of the oxide film.

3. The concentration of magnesium at the interface reduces the solid-liquid interface, reduces the surface tension of the alloy and the liquid, and reduces the free energy of the interface, thus improving the wettability.

In summary, magnesium was used as an activator in this experiment to improve wettability at the Al₂O₃/Al interface.

3.4. Analysis of macroscopic surface and microscopic phase of the composite material

The macro surface of the composite material is shown in FIG.4. It can be seen from FIG. 4 (a) that when the alumina ceramics are combined well with the aluminum matrix, and some dendrites still exist on the matrix surface and the surface gap is small. After successful sintered, the sample was taken out and tested with hammer. The sample did not break or shatter, showing excellent toughness.

The purpose of this experiment is to analyze the wetting layer between alumina ceramics and Al-Si matrix, as shown in figures. As shown in the Fig.5, the scanning image analysis for the composite interface of Al₂O₃/Al composite material. The presence of the composite layer can be clearly seen from the figure, and the linear scanning analysis is carried out to determine the components.

As can be seen from the figure, the content of oxygen elements in A is extremely rich, and gradually decreases to B and C regions. According to the microstructure, it can be concluded that A is Al₂O₃ ceramics, B is the wetting layer, and C is the Al-Si matrix. There are almost no aluminum elements in
zone A, and the content of aluminum elements in phase B increases gradually. The content of aluminum elements in zone C is the highest in the matrix. The content of silicon element is high in zone A and low in zone B, with the highest content in zone C. Zone A is Al₂O₃ ceramics, which theoretically does not contain silicon element. The porous property of ceramics and good mobility of silicon may exist at 0-280μm, so that the first precipitated silicon in the cooling process will be enriched here. Magnesium element is almost absent in zone A, while there is an abrupt increase in 840-940μm at the junction of zone B and zone C. Meanwhile, aluminum element is observed to decrease abruptly there. It is speculated that it is due to a certain chemical reaction, and the combination of other elements and formula (2) and (3) may lead to the formation of compound MgAl₂O₄. At 280-840μm, Al₂O₃ can be observed. At the same time, La could not be detected at the line scanning. Compared with the previous research results, the addition of Si did not affect the wetting effect.

The wetting process is reactive wetting and its mechanism is described in section 3.5. During reactive wetting, the wetting process depends more on the interfacial reaction than on the surface tension of the liquid metal because of the interfacial chemical reactions, shown as formula (2) and formula (3). The wettability of liquid metal and ceramic surfaces can be improved by MgAl₂O₄, which is formed as new interface products. Because the interfacial products are obtained in the process of physical chemical reaction, they are more pure. The production of interface products enables the wetting process to be carried out in the middle layer with better wettability, so that the wetting effect can be greatly improved.

4. Conclusions
In this paper, different content of lanthanum modifier was added to Al-15Si-4Mg alloy for modification, and the influence of heat treatment process on the modified alloy was studied, and the optimal performance matrix was selected for the study of Al₂O₃/Al-15Si-4Mg composite. The results are as follows:

1) La has good metamorphic effect on Al-15Si-4Mg alloy. With the increase of the content of La, the microstructure of eutectic silicon has been obviously refined, and get best when the content of La content reaches 1 wt.%. The hardness of the alloy reaches 111 HBS XRD and EDS spectrum analysis showed that unmodified alloy is mainly composed of Al, Si and Mg₂Si, while modified alloy also contents rich lanthanum phase.

2) The alloy with 1wt.% lanthanum modifier which has optimum performance has been selected for the heat treatment process, it is found that the heat treatment process can significantly improve the mechanical properties of the alloy. After heat treatment, the edge of eutectic silicon changes from needle tissue to smooth and the fracture to the aluminum matrix reduces, the hardness reaches 113 HBS.

3) The Al-15Si-4Mg alloy with 1wt.% La was selected as the matrix of Al₂O₃/Al-15Si-4Mg composite. The Al₂O₃/Al-15Si-4Mg composite was prepared by liquid phase sintering and the wetting effect of the bonding interface was combined excellent. The ceramic particles were closely combined with the matrix with fewer pores. La enrichment can not be observed at the interface according to EDS analysis, and the compound MgAl₂O₄ was generated by chemical reaction at the wetting interface. The wetting process belongs to reactive wetting.

Reference
[1] Zhang L Y, Jiang Y H, Ma Z, et al. Effect of cooling rate on solidified microstructure and mechanical properties of aluminium-A356 alloy[J]. Journal of Materials Processing Technology, 2008, 207(1-3): 107-111.
[2] Samuel A M, Samuel F H. Modification of iron intermetallics by magnesium and strontium in Al-Si alloys[J]. International Journal of Cast Metals Research, 1997, 10(3): 147-157.
[3] Zhu Man, Jian Zengyun, Yao Lijuan, Liu Cuixia, Yang Gencang, Zhou Yaohe[J]. Journal of Materials Science, 2011, 46(8): 2685-2694.
[4] Jenkinson D C, Hogan L M. The modification of aluminum-silicon alloys with strontium[J]. Journal of Crystal Growth, 1975, 28(2): 171-187.

[5] Kobayashi K F, Hogan L M. The crystal growth of silicon in Al-Si alloys[J]. Journal of Materials Science, 1985, 20(6): 1961-1975.

[6] Elsebaie O., Samuel, A., Samuel F. Effects of Sr-modification, iron-based intermetallics and aging treatment on the impact toughness of 356 Al-Si-Mg alloy [J]. Journal of Materials Science, 2011, 46(9): 3027-3045.