

Effects of grain refining and modification on mechanical properties and microstructures of Al–7.5Si–4Cu cast alloy

Guang-lei LIU¹, Nai-chao SI¹, Shao-chun SUN¹, Qin-fang WU²

1. School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China;

2. Suzhou Mingzhi Technology Ltd., Suzhou 215217, China

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Abstract: Al–7.5Si–4Cu cast alloy melt modified by Al–5Ti–B, RE and Al–10Sr master alloys were poured in the chromite sand moulds, to investigate comparatively the effects of individual or combined additions of grain refiners and modifiers on the mechanical properties, microstructures, grain refining and modification, and intermetallic compounds of the alloy. The results show that the mechanical properties and the microstructures of Al–7.5Si–4Cu cast alloys are improved immensely by combining addition of 0.8%Al–5Ti–B, 0.1%RE and 0.1%Al–10Sr grain refiners and modifiers compared with the individual addition and cast conditions. For individual addition condition, addition of 0.8% Al–5Ti–B master alloy can obtain superior tensile strength, Brinell hardness and finer equiaxed α (Al) dendrites. The alloy with 0.1% RE master alloy shows the highest improvement in ductility because the rare earth can purify the molten metal and change the shape of intermetallic compounds. While the alloy with 0.1% Al–10Sr modifier shows only good improvement in yield strength, and the improvement of other performance is unsatisfactory. The Al–10Sr modifier has a significant metamorphism for the eutectic silicon, but will make the gas content in the aluminum alloy melt increase to form serious columnar grain structures. The effects of grain refining and modification on mean area and aspect ratio have the same conclusions obtained in the mechanical properties and the microstructures analyses.

Key words: Al–7.5Si–4Cu cast alloy; grain refinement; modification treatment; mechanical properties; microstructures

1 Introduction

With the rapid development of automotive industry, the requirement for engine performance has become increasingly higher and higher, such as power performance, environmental performance, fuel economy and so on. Obviously, using lighter all-aluminum engine has become the future of the automobile industry. At present, the domestic industrial production of engine with aluminum cylinder block and heads is still in its infancy. Apart from dealing with the problem of technology and equipment, the most important thing is to find suitable aluminum alloy material. The Al–Si cast alloy possesses outstanding properties, such as excellent casting performance, easy molding, good corrosion resistance and abrasion resistance. It has advantages of low casting manufacturing cost and higher specific strength. Hence, the Al–Si cast alloy has been widely

used for manufacture of engine components [1–4]. However, the silicon forms brittle needle-like particles and coarse primary aluminium forms which reduce impact strength in cast structures. The Al–Si alloys that are refined and modified, display a finer, less needle-like microstructure and exhibit excellent castability, mechanical and physical properties.

Traditionally, the grain refining and modification effect of Al–Si alloy can be achieved by three ways [5–10]: rapid cooling, chemical process by introducing certain elements, exogenic actions such as mechanical vibration and electromagnetic induction. Chemical process is usually used in the industrial field and combination modification has become a research hotspot. Several elements were used as the grain refiner and modifier, such as Na, Sr, Sb, Ti, Ba, Ca and rare earth elements. Strontium is the most widely used and a very effective element for modifying the morphology of eutectic silicon, while Al–5Ti–B and RE are commonly

present in the commercial grain refiners used for Al–Si alloys. It is agreed that these elements added either individually or in combination can improve the mechanical properties of Al–Si cast alloy. However, details on the morphology, size, and distribution of the RE containing intermetallic compounds were rarely reported. Besides, grain refining and modification of eutectic and hypereutectic Al–Si alloys were investigated a lot [11–15]. The influence of combination use of Al–10Sr, rare earth and Al–Ti–5B modifiers for hypoeutectic Al–Si alloy is not reported.

In this work, systematic studies on the effects of individual or combined additions of Al–5Ti–B, RE and Al–10Sr grain refiners and modifiers on the eutectic silicon and primary aluminium solidification of Al–7.5Si–4Cu cast alloys were performed. The relationship between mechanical properties and microstructures were also discussed, in order to improve mechanical properties, and microstructures of the alloy and help enterprises enhance the quality of the products.

2 Experimental

Table 1 illustrates the designed chemical composition of the multivariate Al–7.5Si–4Cu cast alloys. They were prepared by melting as-received commercial ingots in a silicon carbide crucible using a 12 kW electric resistance furnace. The as-received commercial ingots used in this work were primarily prepared from the same batch to avoid any undesired variations and effects from minor element contamination.

The silicon carbide crucible was preheated to 400 °C before charging the commercial ingots and was then heated up to 740 °C to melt. In order to study the effect of grain refining and modification on mechanical properties and microstructure of Al–7.5Si–4Cu cast alloy, the grain refiners (Al–5Ti–B and RE master alloys) and modifier (Al–10Sr master alloy) were later added to adjust the chemical compositions. Chemical compositions of the grain refiners and modifier are listed in Table 2. Degassing was done with argon supplied at a flow rate of 15 L/h for 20 min by porous plug method. Molten alloy was poured at 710 °C into the chromite sand moulds having 25 mm in diameter and 250 mm in length. Table 3 presents the number of alloys including how to adding the grain refiners and modifier.

For tensile test, the specimens were machined into ones having 5 mm in diameter and 25 mm in gauge according the Chinese tensile testing standard of GB/T 228.1–2010. Tensile properties at room temperature were performed using a computerized universal tensile testing machine (Instron 5581). Brinell hardness tester (HB–3000) was used for hardness test on multi-element Al–7.5Si–4Cu alloy before and after grain refinement and modification. For each alloy, four test specimens were used. Each value of properties was the average value of four specimens.

Standard metallographic techniques were used to prepare the samples for microstructural analysis. These prepared samples were etched using 0.5%HF+99.5% H₂O by volume. The polished specimens were taken for the scanning electron microscopy (Hitachi–3400N SEM) analysis.

Table 1 Chemical composition of Al–Si–Cu cast alloy (mass fraction, %)

| Si | Cu | Mg | Mn | Ni | Cr | Zn | Fe | Pb | Sn | Al |
|-----|---------|-----------|-----------|-----------|-------------|---------|-------|--------|-------|------|
| 7–8 | 3.5–4.5 | 0.30–0.45 | 0.30–0.45 | 0.02–0.03 | 0.025–0.035 | 0.5–0.7 | ≤0.35 | ≤0.003 | ≤0.02 | Bal. |

Table 2 Chemical composition of grain refiner and modifier (mass fraction, %)

| Refiner or modifier | w(Si)/% | w(Cu)/% | w(Mg)/% | w(Fe)/% | w(Ti)/% | w(B)/% | w(Sr)/% | w(Ce)/% | w(Nd)/% | Else | Al |
|---------------------|---------|---------|---------|---------|---------|--------|---------|---------|---------|------|------|
| Al–5Ti–B | 0.11 | – | – | 0.07 | 4.92 | 0.96 | – | – | – | – | Bal. |
| Al–10Sr | 0.12 | – | – | 0.05 | – | – | 10.0 | – | – | – | Bal. |
| RE | – | – | – | – | – | – | – | 49.5 | 50.1 | Bal. | – |

Table 3 Number of alloy including adding grain refiner and modifier

| Alloy No. | Refiner | | Modifier | w(Al–7.5Si–4Cu)/% |
|-----------|---------------|---------|--------------|-------------------|
| | w(Al–5Ti–B)/% | w(RE)/% | w(Al–10Sr)/% | |
| 1 | – | – | – | 100 |
| 2 | 0.8 | – | – | 99.2 |
| 3 | – | 0.1 | – | 99.9 |
| 4 | – | – | 0.1 | 99.9 |
| 5 | 0.8 | 0.1 | 0.1 | 99.0 |

3 Results and discussion

3.1 Mechanical properties

Table 4 shows the influence of the grain refiners and modifiers on the mechanical properties of Al–Si–Cu cast alloy. From Table 4, it is clearly observed that the improvement in the mechanical properties, such as yield strength, tensile strength, elongation and Brinell hardness, dramatically increases with the addition of Al–5Ti–B, RE and Al–10Sr due to change in the microstructure. It is also clear that the combined addition of grain refiner and modifier to Al–Si–Cu cast alloy results in more improvement in mechanical properties compared with the individual addition of grain refiner, modifier (Alloys 2–4) and untreated as-cast condition (Alloy 1). Addition of the grain refiner to Al–Si–Cu cast alloy predominantly converts columnar grain structure to fine equiaxed grain structure, thereby enhancing the mechanical properties. The modifier can change the shape of eutectic silicon. The mechanical properties depend on the size, shape and distribution of eutectic silicon and $\alpha(\text{Al})$ grains in the case of Al–Si alloy. It is also clear from the experimental results that the alloy without grain refiner and modifier shows yield strength σ_s of 178 MPa, tensile strength σ_b of 226 MPa, elongation δ of 2.3% and HB78.8, while with the combined addition of grain refiner and modifier, σ_s of 190 MPa, σ_b of 246 MPa, δ of 2.9% and HB86.4 are obtained.

Table 4 Mechanical property of multivariate Al–Si–Cu cast alloy

| Alloy No. | Yield strength/MPa | Tensile strength/MPa | Elongation/% | Brinell hardness, HB |
|-----------|--------------------|----------------------|--------------|----------------------|
| 1 | 178 | 226 | 2.3 | 78.8 |
| 2 | 184 | 238 | 2.6 | 84.0 |
| 3 | 181 | 233 | 3.2 | 81.6 |
| 4 | 187 | 231 | 2.5 | 80.5 |
| 5 | 190 | 246 | 2.9 | 86.4 |

Table 5 lists the improvement rates of the mechanical properties of Al–Si–Cu cast alloy compared with the cast condition (Alloy 1). It is observed that mechanical properties have been improved to a certain extent by grain refining and modification. It is worth mentioning that the alloy with 0.8% Al–5Ti–B master alloy exhibits superior tensile strength and Brinell hardness compared with the individual addition of grain refiner or modifier. Such materials record 5.310% improvement rate in the tensile strength and 6.599% improvement rate in the Brinell hardness compared with the untreated conditions. The alloy refined with 0.1% RE

master alloy shows the highest improvement rate of 39.130% in ductility, while the alloy treated with 0.1% Al–10Sr master alloy exhibits 5.056% improvement rate in yield strength. It is also clearly observed that the alloy treated with combined addition of 0.8% Al–5Ti–B, 0.1% RE and 0.1% Al–10Sr master alloy shows the best mechanical property. According to this result, if we want to improve the mechanical properties is obtained due to the addition of grain refiner and modifier to multivariate Al–Si–Cu cast alloy. If we want to improve the mechanical properties of the alloy, such as elongation, we can add RE master alloy properly.

Table 5 Improvement rate on mechanical properties of multivariate Al–Si–Cu cast alloy compared with cast condition (Alloy 1)

| Alloy No. | Improvement rate/% | | | |
|-----------|--------------------|------------------|------------|------------------|
| | Yield strength | Tensile strength | Elongation | Brinell hardness |
| 2 | 3.371 | 5.310 | 13.043 | 6.599 |
| 3 | 1.685 | 3.097 | 39.130 | 3.553 |
| 4 | 5.056 | 2.212 | 8.696 | 2.157 |
| 5 | 6.742 | 8.850 | 26.087 | 9.645 |

3.2 Microstructures

Figures 1 and 2 show the SEM images of multivariate Al–Si–Cu cast alloy in the absence or with addition of the grain refiner and modifier. From Figs. 1(a) and 2(a), it is clear that in the absence of grain refiner and modifier, the alloy shows coarse columnar $\alpha(\text{Al})$ dendritic structure and unmodified long needle/plate-like eutectic silicon is distributed arbitrarily in the $\alpha(\text{Al})$ matrix, which dissects the $\alpha(\text{Al})$ matrix seriously. As is well known, the mechanical properties of Al–Si alloy depend not only on their chemical composition but also on their microstructure such as the morphologies of the $\alpha(\text{Al})$ phase and the eutectic Si particles. The coarser eutectic Si phase which surrounds the $\alpha(\text{Al})$ has greatly deteriorated the strength and elongation of multivariate Al–Si–Cu cast alloy.

As is known, the grain refining could predominantly convert columnar grain structure to fine equiaxed grain structure and the modification could alter the growth of the eutectic silicon to produce an irregular fibrous form rather than the usual acicular structure. With the addition of 0.8% Al–5Ti–B master alloy, the structure of multivariate Al–Si–Cu cast alloy changes from columnar to finer equiaxed $\alpha(\text{Al})$ dendrites compared with the cast one as clearly observed in Fig. 1(b), while eutectic silicon shown in Fig. 2(b) remains unmodified as expected. This could be due to the presence of Al_3Ti and TiB_2 particles present in the Al–5Ti–B master alloy and these particles act as heterogeneous nucleating sites

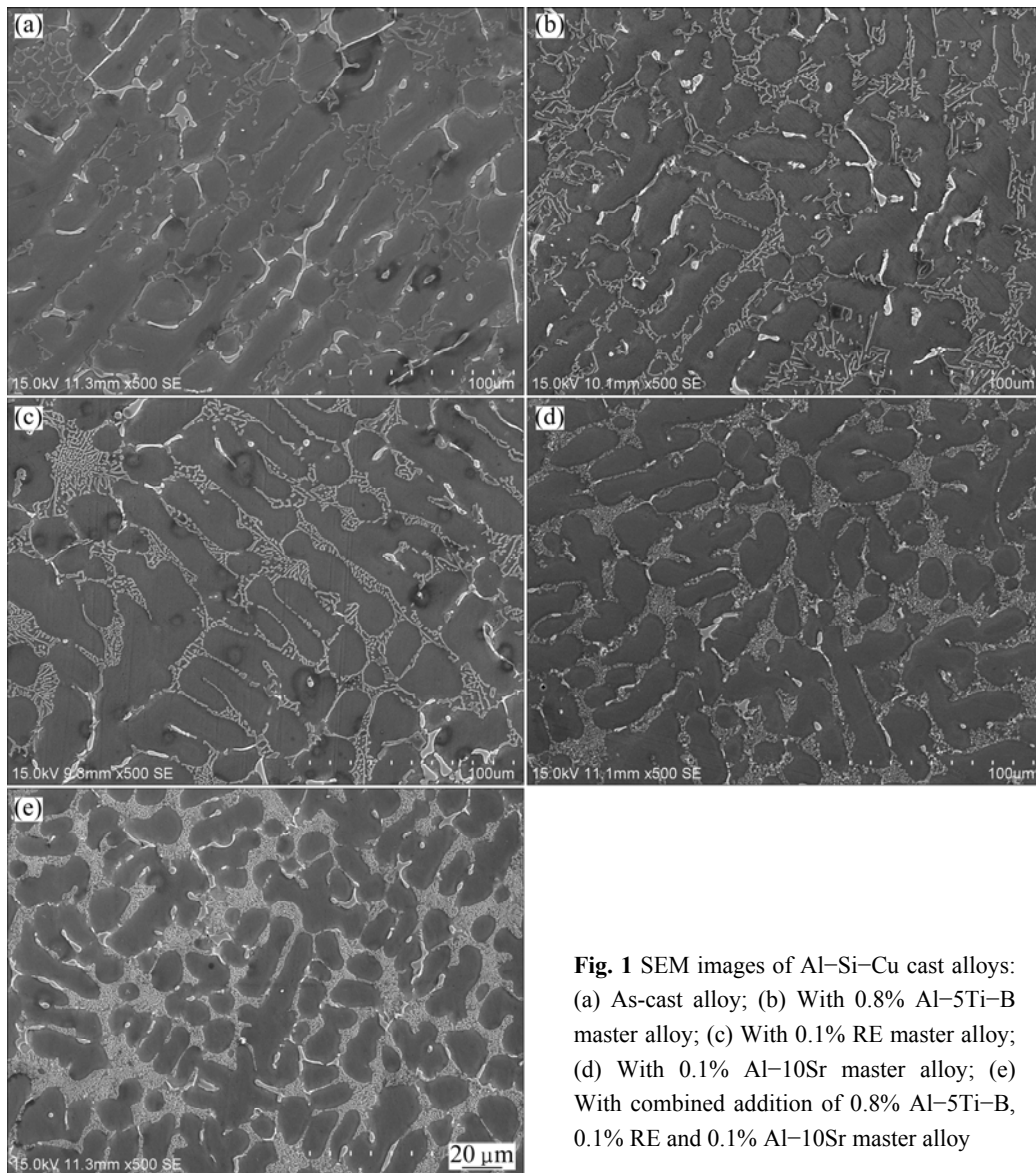


Fig. 1 SEM images of Al-Si-Cu cast alloys: (a) As-cast alloy; (b) With 0.8% Al-5Ti-B master alloy; (c) With 0.1% RE master alloy; (d) With 0.1% Al-10Sr master alloy; (e) With combined addition of 0.8% Al-5Ti-B, 0.1% RE and 0.1% Al-10Sr master alloy

during solidification of $\alpha(\text{Al})$ [7]. So, it can be found that the Al-5Ti-B master alloy has an important function as the grain refiner. With the addition of 0.1% RE master alloy, as shown in Figs. 1(c) and 2(c), the $\alpha(\text{Al})$ phase changes only a little, while the shape of eutectic silicon changes from long needle/plate-like to short rod/smaller plate-like one and has a more uniform distribution. Most researches [16,17] show that the rare earth can purify the molten metal and change the shape of intermetallic compounds. This distribution of eutectic silicon and other intermetallic compounds could play a role in the intercrystalline strengthening. That is why the alloy with adding RE master alloy has an excellent elongation. While with addition of 0.1% Al-10Sr master alloy, the long needle/plate-like eutectic silicon is converted into fine particles and $\alpha(\text{Al})$ dendrites remain as columnar dendritic structure only as clearly seen in Figs. 1(d) and 2(d). The Al-10Sr master alloy has a significant

metamorphism for the eutectic silicon except other intermetallic compounds. Some studies [18,19] show that Sr modification can make the gas content in the aluminum alloy melt increase and form serious columnar grain structures. That is why the mechanical properties of the alloy are not good enough.

Thus, Al-5Ti-B, RE and Al-10Sr master alloys have their own advantages. Optimum use of compound modification can play out their respective advantages uniformly and improve the mechanical properties of the aluminum alloy in the maximum degree. Figures 1(e) and 2(e) show the simultaneous refinement ($\alpha(\text{Al})$ dendrites) and modification (eutectic Si) of Al-Si-Cu cast alloy due to the combined action of Al-5Ti-B, RE and Al-10Sr modifier, respectively. The microstructures of alloy were significantly refined and became more compact after a complex grain refining and modification. The $\alpha(\text{Al})$ phase became very small and

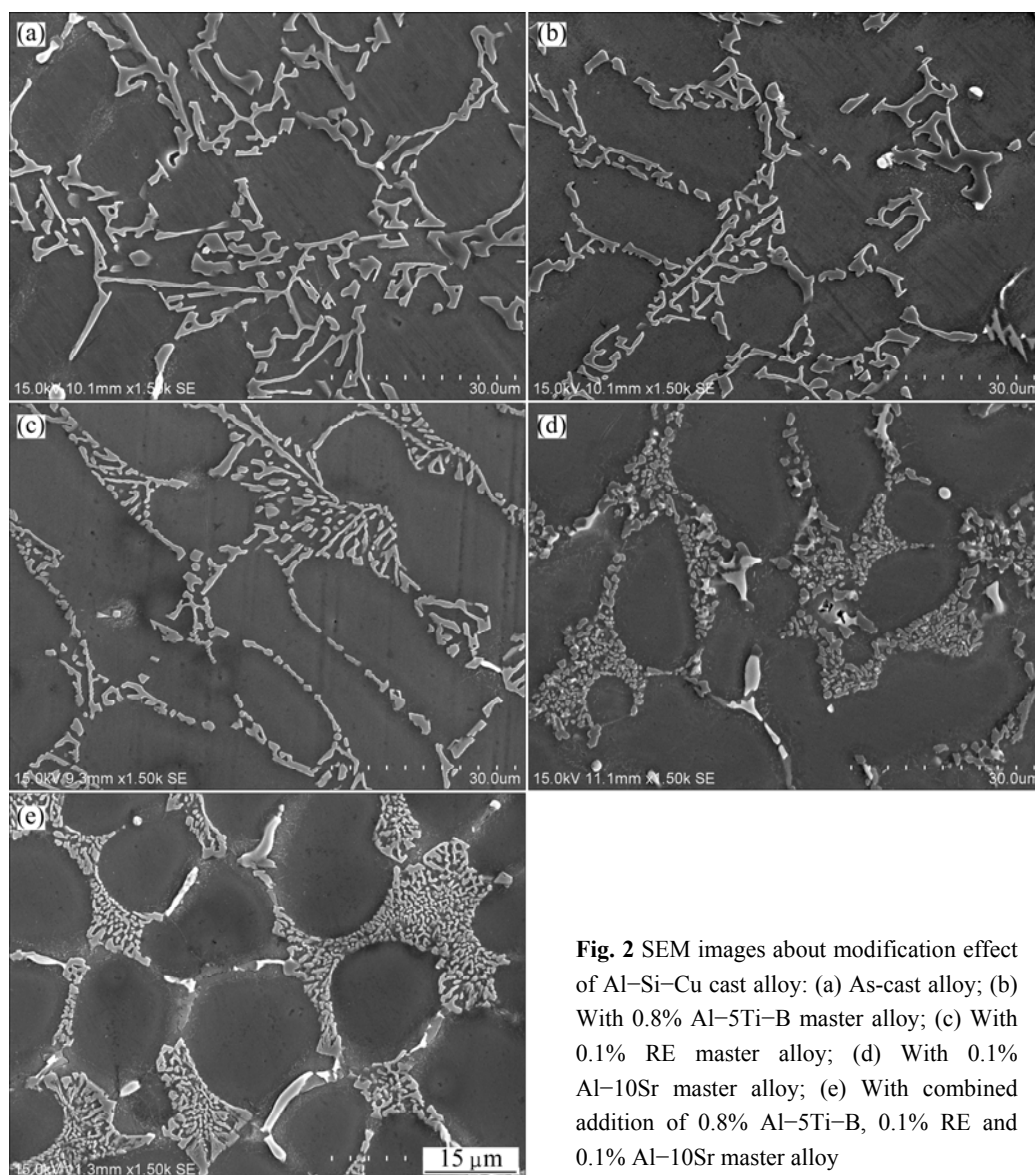


Fig. 2 SEM images about modification effect of Al-Si-Cu cast alloy: (a) As-cast alloy; (b) With 0.8% Al-5Ti-B master alloy; (c) With 0.1% RE master alloy; (d) With 0.1% Al-10Sr master alloy; (e) With combined addition of 0.8% Al-5Ti-B, 0.1% RE and 0.1% Al-10Sr master alloy

clear. The eutectic silicon phase and other intermetallic compounds become dot-like and distribute uniformly at the grain boundary. This indicates that the interaction between the grain refiners and modifiers is strengthened.

3.3 Grain refining and modification

In order to further evaluate the grain refining and modification rate with different grain refiner and modifier additions, two parameters (mean area and aspect ratio) were measured for the quantitative metallographic analysis using IMAQ Vision Builder 6 image analyzer [20,21]. Mean area and aspect ratio are calculated as follows:

$$\text{Mean area} = \frac{1}{m} \sum_{j=1}^m \left(\frac{1}{n} \sum_{i=1}^n A_i \right)_j \quad (1)$$

$$\text{Aspect ratio} = \frac{1}{m} \sum_{j=1}^m \left(\frac{1}{n} \sum_{i=1}^n \left(\frac{L_i}{L_s} \right)_i \right)_j \quad (2)$$

where A_i is the area of a single silicon particle; L_i/L_s is the ratio of the longest to the shortest dimensions of a single silicon particle; n is the number of particles in a single field (each $20553.5 \mu\text{m}^2$); m is the number of the fields. The pretest shows that the mean area and aspect ratio remain constant when the field number is greater than 16 ($m > 16$). Thus, the total 20 fields were measured on each sample in order to get convictive data. The mean area and aspect ratio values of a specimen were the average value for the 20 fields ($m=20$).

The mean area and aspect ratio of eutectic silicon particles of test alloys measured by image analyzer are listed in Table 6. The mean area and aspect ratio of grain refiner and modifier-containing alloy are better

Table 6 Image analysis results of Al–Si–Cu cast alloy with different additions of grain refiner and modifier

| Alloy No. | Mean area/ μm^2 | Aspect ratio |
|-----------|----------------------------|--------------|
| 1 | 38.4 | 8.3 |
| 2 | 34.8 | 7.7 |
| 3 | 24.0 | 6.8 |
| 4 | 5.8 | 1.5 |
| 5 | 2.3 | 1.4 |

compared with the alloy 1. It is also clear that the combined addition of grain refiners and modifier to Al–Si–Cu cast alloy has the best mean area and aspect ratio. For the individual addition of grain refiner or modifier, the mean area and aspect ratio of the alloy with

the addition of Al–10Sr master alloy are superior to others. In a word, the analysis results of mean area and aspect ratio have the same conclusions which have been obtained in the mechanical properties and the microstructures analysis.

3.4 Phase analysis

Figure 3 shows the SEM microphotographs of Al–Si–Cu cast alloy in the absence or with combined addition of the grain refiner and modifier. In the absence condition, as shown in Fig. 3(a), long needle/plate-like eutectic silicon and other intermetallic compounds (*A* phase, compounds of five elements Al(MnCuFe)Si and little Ni, Cr, Zn element) connect together. They distribute at the grain boundaries of α (Al) phase. In the

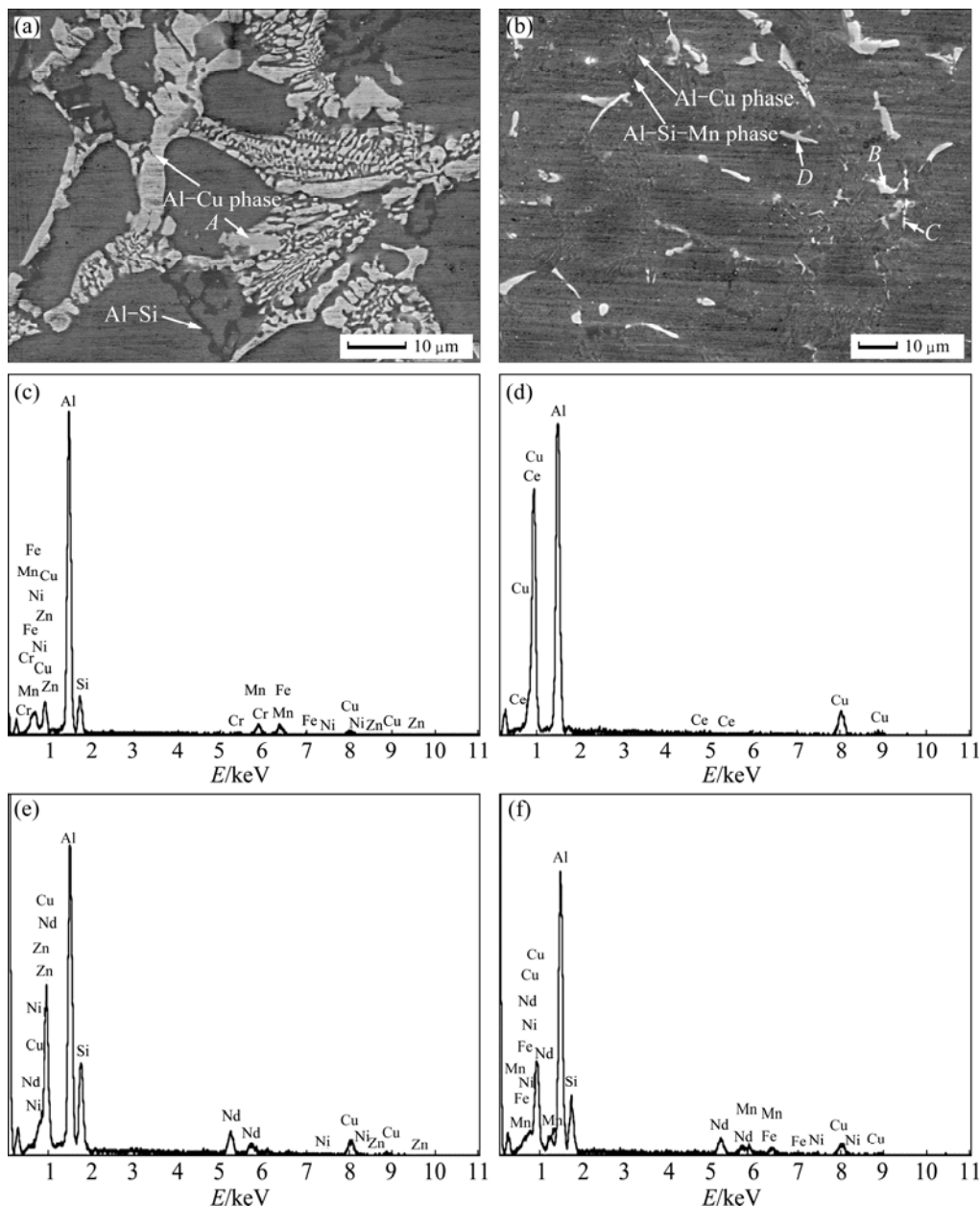


Fig. 3 SEM micrographs of alloy without grain refiner and modifier (a) and combined addition of grain refiner and modifier (b), EDAX spectra of *A* phase (c), *B* phase (d), *C* phase (e) and *D* phase (f)

tensile test, the size and shape of them, especially Fe-containing phase, can easily cause stress concentration, which is the main reason of the poor mechanical properties. Secondly, thick iron-rich phase in can hinder the flow of liquid metal the early solidification, likely to cause casting flaws.

After combining grain refining and modification, as shown in Fig. 3(b), the long needle/plate-like eutectic silicon is converted into fine particles. The addition of RE leads to form a new AlCuCe (*B*) phase and the shape of AlCu phase changes from a rod or a bar into a smaller leaf or a feather-like one. Other metal compounds, such as AlSiCuZnNiNd (*C*) phase, change from thick strip shape into band or bar-like shape. The Fe-containing phase changes into AlSiCuMnFeNiTi (*D*) phase, which is smaller and more round. In short, after combining grain refining and modification, the size and shape of eutectic silicon, α (Al) phase and other metal compounds change immensely and distribute uniformly like a network. In the tensile deformation, they can act as the intercrystalline strengthening phase, impeding dislocation movement and improving the comprehensive mechanical properties of the alloy.

4 Conclusions

1) The combined addition of grain refiners and modifiers (0.8% Al–5Ti–B, 0.1% RE and 0.1% Al–10Sr) to Al–7.5Si–4Cu cast alloy results in the maximum improvement in mechanical properties and microstructures compared with the individual addition and untreated as-cast condition.

2) Addition of 0.8% Al–5Ti–B master alloy can exhibit superior tensile strength and Brinell hardness. The alloy refined with 0.1% RE master alloy shows the highest improvement in ductility, while the alloy treated with 0.1% Al–10Sr master alloy exhibits the highest improvement in yield strength.

3) Compared with the cast condition, the Al–5Ti–B master alloy has an important function as the grain refiner because the structure of Al–Si–Cu cast alloy changes from columnar to finer equiaxed α (Al) dendrites. The RE can affect both the α (Al) phase and eutectic silicon, so it is the grain refiner and modifier. The Al–10Sr master alloy as the modifier has a significant metamorphism for the eutectic silicon.

4) The effects of grain refining and modification on mean area and aspect ratio have the same conclusions obtained in the mechanical properties and the microstructures analyses.

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细化变质处理对铸造 Al–7.5Si–4Cu 合金力学性能和组织的影响

刘光磊¹, 司乃潮¹, 孙少纯¹, 吴勤方²

1. 江苏大学 材料科学与工程学院, 镇江 212013;
2. 苏州明志科技有限公司, 苏州 215217

摘要: 研究了单一和复合 Al–5Ti–B、RE 和 Al–10Sr 细化变质剂对砂型铸造 Al–7.5Si–4Cu 合金力学性能、显微组织、细化变质效果及其金属间化合物变化的影响。结果表明: 与单一细化变质处理以及铸态相比, 经过添加质量分数为 0.8% 的 Al–5Ti–B、0.1% 的 RE 和 0.1% 的 Al–10Sr 细化变质剂复合细化变质处理后铸造 Al–7.5Si–4Cu 合金的力学性能和显微组织都得到了显著改善。对于单一细化变质处理, 加入 0.8% 的 Al–5Ti–B 中间合金后, 合金的抗拉强度和布氏硬度得到大幅度提高, 并且细化了 $\alpha(\text{Al})$ 相。加入 0.1% 的 RE 中间合金后, 合金的伸长率得到了最大程度的提高。这是因为 RE 的加入使铝合金熔液而得到净化, 同时改变了金属间化合物的形状。而加入 0.1% 的 Al–10Sr 变质剂后, 合金的屈服强度得到改善, 但其他性能的改善有限。Al–10Sr 变质剂对共晶硅具有较强的变质作用, 但使得铝合金熔体含气量增加并形成严重的柱状晶组织。利用硅相的平均面积和长宽比描述细化变质效果得到的结论与力学性能和组织分析的结果相同。

关键词: 铸造 Al–7.5Si–4Cu 合金; 晶粒细化; 变质处理; 力学性能; 显微组织

(Edited by Xiang-qun LI)