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Effect of combined RE−Ba−Sb addition on microstructure and mechanical properties of 4004 aluminum alloy

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Abstract: As a brazing foil, 4004 Al alloy has good welding performance. However, the high Si content decreases the plasticity of the alloy. In order to improve the plasticity of 4004 Al alloy and subsequently improve the productivity of 4004 Al foil, 4004 Al alloy was modified by RE−Ba−Sb. As a comparison, the 4004 Al alloy was also modified by RE with different addition. The tensile properties of the alloy reach the best when the addition of RE was 0.2%, in which the tensile strength and elongation were 194 MPa and 5%, respectively. For RE−Ba−Sb modification, the addition of three elements was optimized by orthogonal analysis. The results showed that the greatest impact parameter of RE−Ba−Sb modification was RE addition, followed by addition of Ba and Sb. The optimum addition amounts of RE, Ba and Sb obtained by orthogonal analyses were 0.01%, 0.3%, and 0.05%, respectively. The tensile strength and the elongation of 4004 Al alloy modified by the optimal modification process were 224 MPa and 6%, respectively. The amount of RE addition in RE−Ba−Sb modification is lower than that in RE modification.

Key words: aluminum alloy; rare earth; Ba; Sb; compound modification

1 Introduction

4004 Al alloy has been widely used as brazing foil and coating layer of 434 composite brazing foils due to its good welding performance. These brazing foils have been widely used as heat dissipater in air conditioner, automobile, and oxygen maker [1]. However, the Si content in 4004 Al alloy is as high as 11%. As a brittle phase, Si undermines the mechanical properties, especially the plasticity of 4004 Al alloy. Since the thickness of 4004 Al foil product is 0.04−0.1 mm, the low plasticity will severely decrease the rate of finished products [1−5].

In order to improve mechanical properties, Al−Si alloys are generally subjected to modification melt treatment, which transforms the acicular Si to fibrous one, resulting in a noticeable improvement in elongation and strength [6]. Since it was found that Na and its salts could refine the microstructure of Al−Si alloy, many refinement agents have been investigated, such as RE, K, Na, Ca, Sr, Ba, Sb, Bi, P [2,7−14]. To overcome the drawbacks of single refinement agent, researchers have made a great deal of efforts to investigate compound modifications [14]. KANG et al [15] obtained good modification effect by using Al−Sr master alloy and NaF. LIANG and CAI [16] modified the microstructure and improved the mechanical properties of ZL102 by using 0.1%−0.05% RE and 0.1%−0.15% Sb. The addition amounts of RE and Sb are only 1/10 and 1/6 of the addition amounts of RE and Sb as single refinement, respectively. LIU and ZENG [17] found that Sb−RE compound modification could decrease eutectic transformation temperature of Si. And the modification effect of the compound modification was better than that of single modification. RE, Ba and Sb have good modification effect on Al−Si alloy, and have been investigated [16−20]. The mechanism of compound modification of these elements together is not clear. To use RE−Ba−Sb as a practical and effective Si refinement of 4004 Al alloy, it is crucial to understand the modification parameters and effects of RE−Ba−Sb on

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castability and mechanical properties of the alloy. Improper melt treatment procedures, fading and poisoning of modifiers often result in the microstructure far from the desired one. Hence, it is essential to assess the effect of melt treatment before pouring [6].

In this work, modification effect of RE−Ba−Sb on 4004 Al alloy was investigated. The optimum process was obtained by orthogonal design. As a comparison, the alloy was also modificated by RE. Moreover, the effect of different modification processes was studied.

2 Experimental

Around 6 kg 4004 Al alloy was melted at 750 °C in an electric resistance furnace with a power of 7.5 kW. The melt was degassed by a rotary impeller refining machine (XD−J−100BP) using high pure argon (99.999%) under a pressure of 0.5 MPa, with rotating speed of 400 r/min for 15 min. After degassing, the melt was heated to 760 °C, and then modified by adding RE or RE−Ba−Sb. The modification agents were Al−10RE master alloy, $BaSO_4$ and Sb powders.

For RE modification processes, the addition amounts of RE were 0.04%, 0.06%, 0.1%, 0.2%, and 0.4%. The optimal modification parameters of RE−Ba−Sb on 4004 alloy were acquired through an orthogonal experiment. An orthogonal test design $L9(3^3)$ was used for optimization of the modification conditions. Three factors and three levels were determined as shown in Table 1. Nine modification tests were carried out at the modification temperature 760 °C, and holding time of 60 min. The modified Al melt was poured into a metal mold which was preheated to 400 °C.

Table 1 Factors and levels of orthogonal experiments

Level	Factor		
	Ba addition (A)/%	Sb addition (B)/%	RE addition (C)/%
1	0.1	0.05	0.01
2	0.2	0.1	0.02
3	0.3	0.2	0.03

The microstructure of as-cast 4004 Al alloy was observed by an optical microscope. The average aspect ratio and the average length of Si phase were determined by taking the average of 50 Si particles in each metallograph. The elemental distribution of the alloy was investigated on a scanning electron microscope (FEI Siron) equipped with an energy dispersive spectrometer. The microstructure of 4004 Al alloy was observed on a transmission electron microscope (JEM 2100).

Tensile properties of as-cast 4004 Al alloy were measured. The optimized parameters were obtained by orthogonal analysis.

3 Results and discussion

3.1 4004 alloy without modification

The microstructure of the 4004 alloy without modification is shown in Fig. 1. It can be seen that the α(Al) is coarse. And the morphology of Si in 4004 Al alloy without modification is acicular with large aspect ratio, which greatly undermine the mechanical properties of the alloy. The aspect ratio and the length of Si in the 4004 Al alloy without modification are 19.4 and 27.2 μm, respectively.

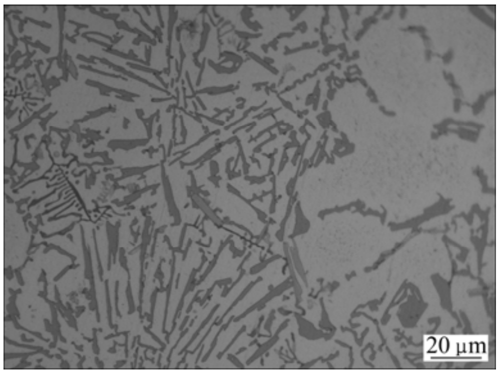

Fig. 1 Metallograph of 4004 Al alloy without modification

3. 2 RE modification

The metallographs of 4004 Al alloy modified by different RE addition amounts are shown in Fig. 2. According to Fig. 2, the average aspect ratio and the average length of Si in 4004 Al alloy with different RE addition amounts were calculated, and are shown in Fig. 3. The microstructure of 4004 Al alloy modified by RE is effectively refined compared with that without modification (Fig. 1). The average length of Si decreases to less than 5 μm from 27.2 μm in 4004Al alloy without modification. Meanwhile, the average aspect ratio decreases to one quarter of that in 4004Al alloy without modification. When the addition of RE is lower than 0.4%, the size and the aspect ratio of Si decrease with increasing RE addition. The shape of Si changes from acicular to fibrous ones. This can effectively improve the mechanical properties of the alloy. Although the aspect ratio of Si in the alloy with RE addition of 0.4% is the smallest, the length of Si increases, and the microstructure of the alloy gets coarse.

Compared with Si in 4004 alloy without modification, Si in 4004 alloy modified by RE gets smaller and has more branches. The solid solubility of RE in Al alloy is low (usually less than 0.05%), and RE elements are surfactants, so RE will be absorbed in the surface or the lattice of Si. Meanwhile, the atomic radius of RE is larger than that of Si, so RE can trigger reflection twins of Si. The twinning plane is {111}, and

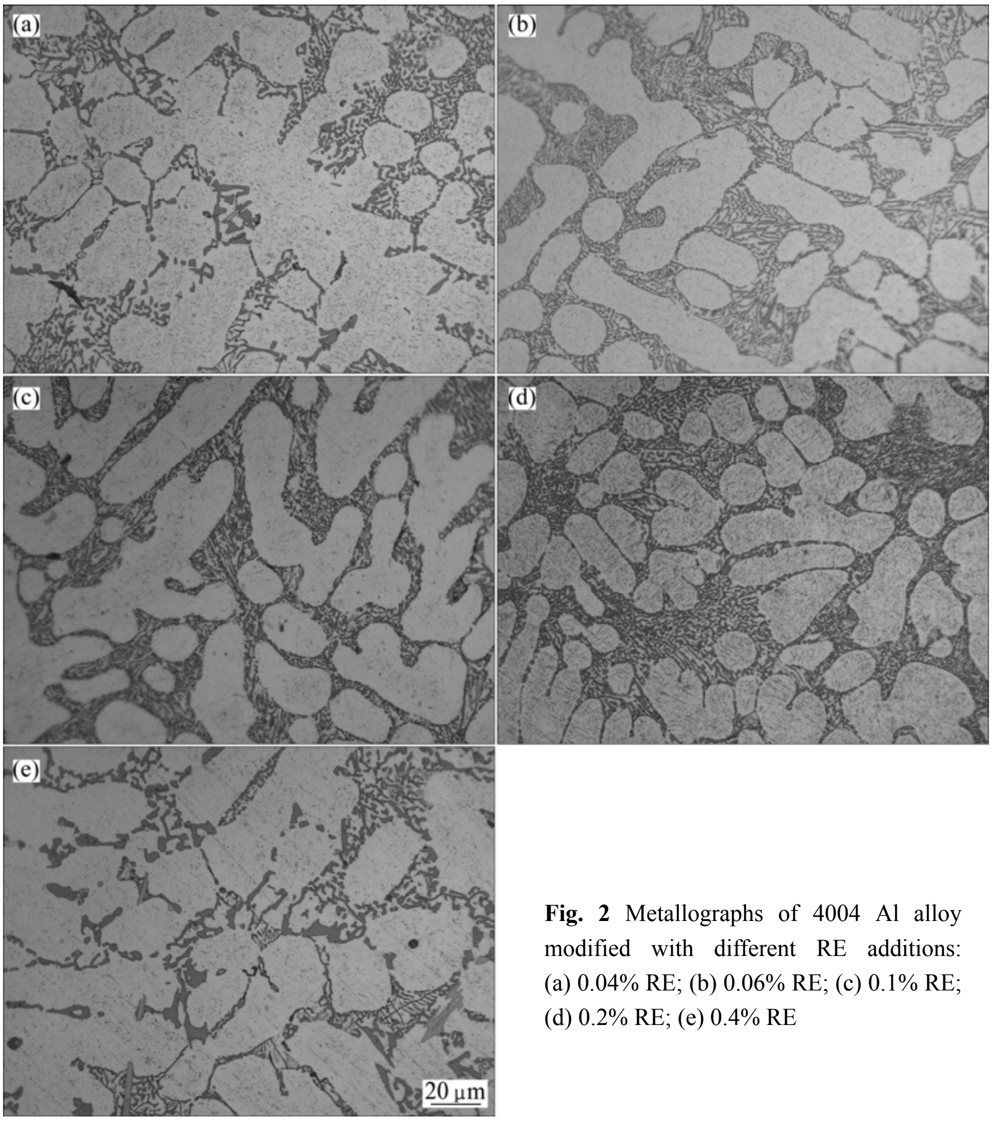

Fig. 2 Metallographs of 4004 Al alloy modified with different RE additions: (a) 0.04% RE; (b) 0.06% RE; (c) 0.1% RE; (d) 0.2% RE; (e) 0.4% RE

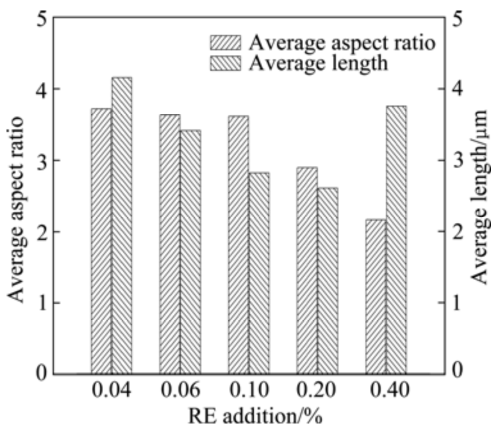

Fig. 3 Average aspect ratio and length of Si in 4004 Al alloy with different addition of RE

the growth direction is ⟨112⟩. The reflection twin can change the growth direction of Si.

When the addition of RE is small, the aggregation of RE in the front of Si growth direction is small. As a result, the influence of RE on Si growth is weak. With increasing RE addition, RE will trigger more twining of Si. These twins interweave together and make Si become fibrous. Meanwhile, the RE absorbed in growth steps locating in twinning grooves inhibits the growth of Si in easy-growing direction [21]. As a result, the Si gets refined and the shape is changed.

However, when the RE addition is over high, the content of RE in the growth front of Si is too much high. The Si atom that the growth needs reaches the growth front through transverse diffusion. As a result, Si grows up as the non-faceted material, and gets coarse [22].

The tensile properties changing with RE additions are shown in Fig. 4. The tensile properties of 4004 Al alloy improved by RE a lot than that without modification (corresponding no addition of RE). The tensile strength and the elongation increase at first and then decrease with increasing RE addition. When RE addition amount is 0.2%, the tensile strength and the elongation reach the highest values, which are 194 MPa and 5%, respectively.

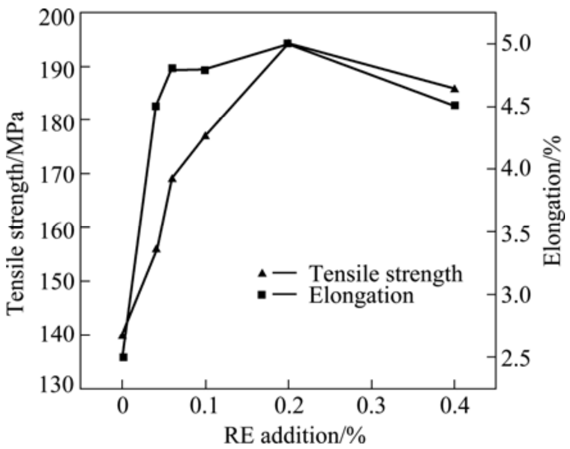

Fig. 4 Influence of RE addition on tensile properties of 4004 Al alloy

3.3 RE−Ba−Sb modification

An orthogonal test $L9(3^3)$ was designed to optimize the modification conditions and shorten experimental periods. Although various parameters including the modification temperature and holding time potentially affect the modification effect, the addition of master alloy is generally considered the most important factors. Optimization of suitable modification conditions can be carried out by using an orthogonal test design.

Tensile properties of 4004 Al alloy modified by RE−Ba−Sb are given in Table 2. From the table, the differences between tensile strengths of 4004 Al alloy under different modification processes were not great. Meanwhile, the production of 4004 Al alloy foils greatly depends on the plasticity of the alloy. Thus the modification effect was evaluated by elongation analysis. Extreme difference analysis of elongation, as shown in Table 3, indicates that RE addition is the most important factor, followed by the addition of Ba and Sb. The best modification parameter obtained by orthogonal analysis method is $C_1A_3B_1$, which is RE addition amount of 0.01%, Ba addition amount of 0.3%, and Sb addition amount of 0.05%. Compared with the data in Table 3, it can be seen that the elongation of 4004 alloy decreases with increasing the addition amount of RE and Sb. The change of elongation along Ba addition is otherwise.

Table 2 Results of orthogonal experiment

No.	Factor			Tensile strength/MPa	Elongation/%
	A	B	C		
1	1(0.1)	1(0.05)	1(0.01)	168	4
2	1(0.1)	2(0.1)	2(0.02)	182	4.1
3	1(0.1)	3(0.2)	3(0.03)	164	3
4	2(0.2)	1(0.05)	2(0.02)	189	4.5
5	2(0.2)	2(0.1)	3(0.03)	162	3.2
6	2(0.2)	3(0.2)	1(0.01)	219	5.5
7	3(0.3)	1(0.05)	3(0.03)	182	4.3
8	3(0.3)	2(0.1)	1(0.01)	206	5
9	3(0.3)	3(0.2)	2(0.02)	181	4.2

Table 3 Extreme difference analysis of elongation

Factor	Average			R	Degree of freedom
	Level 1	Level 2	Level 3		
A	3.7	4.4	4.5	0.8	2
B	4.27	4.1	4.1	0.17	3
C	4.83	4.27	3.17	1.66	1

The microstructures of the 4004 Al alloy after RE−Ba−Sb modification are shown in Fig. 5. Compared with that without modification (Fig. 1), the microstructure of the alloy modified by RE−Ba−Sb is much finer, which means that RE−Ba−Sb can effectively refine the microstructure of 4004 Al alloy. The size of α(Al) decreases with increasing the amount of RE and Ba, while the size of Si decreases at first and then increases.

Figure 6 shows the microstructure of 4004 Al alloy modified by optimized RE−Ba−Sb addition. The addition amount of RE, Ba and Sb are 0.01%, 0.3% and 0.05%, respectively. The average aspect ratio and length of Si in 4004 Al alloy with combined RE−Ba−Sb addition were calculated based on Fig. 5 and Fig. 6. The results are shown in Fig. 7. The microstructure of 4004 Al alloy gets further refined. And the aspect ratio of Si is smaller than that in 4004 Al alloy with RE addition, which means the shape of Si is further modified. The 4004 Al alloy with optimized RE−Ba−Sb addition has the best microstructure. The tensile strength and the elongation of 4004 Al alloy modified by optimized process are 223 MPa and 6%, respectively.

To clarify the combined effect of RE−Ba−Sb, the elemental distribution in 4004 Al alloy with optimized RE−Ba−Sb addition was observed. The test points are shown in Fig 8, and the results are shown in Table 4. It can be seen that Ba distributes mainly in Al, and RE elements in Si, while Sb distributes evenly. Figure 9 shows HRTEM image of Si. AlSb coherent precipitates in Si. During the solidification process, Ba deposited on interface between α(Al) and the melt. The diameter of Ba atom is too large to dissolve into Al lattice, so Ba enriches at interface, which leads to constitutional supercooling. As a result, the size of α(Al) decreases [16].

Due to the difference between RE and Sb, the absorption of RE and Sb to Si is different, and they maybe absorb on different planes of Si, which can reinforce the modification effect. The absorption of RE on the surface of Si may trigger reflection twins of Si

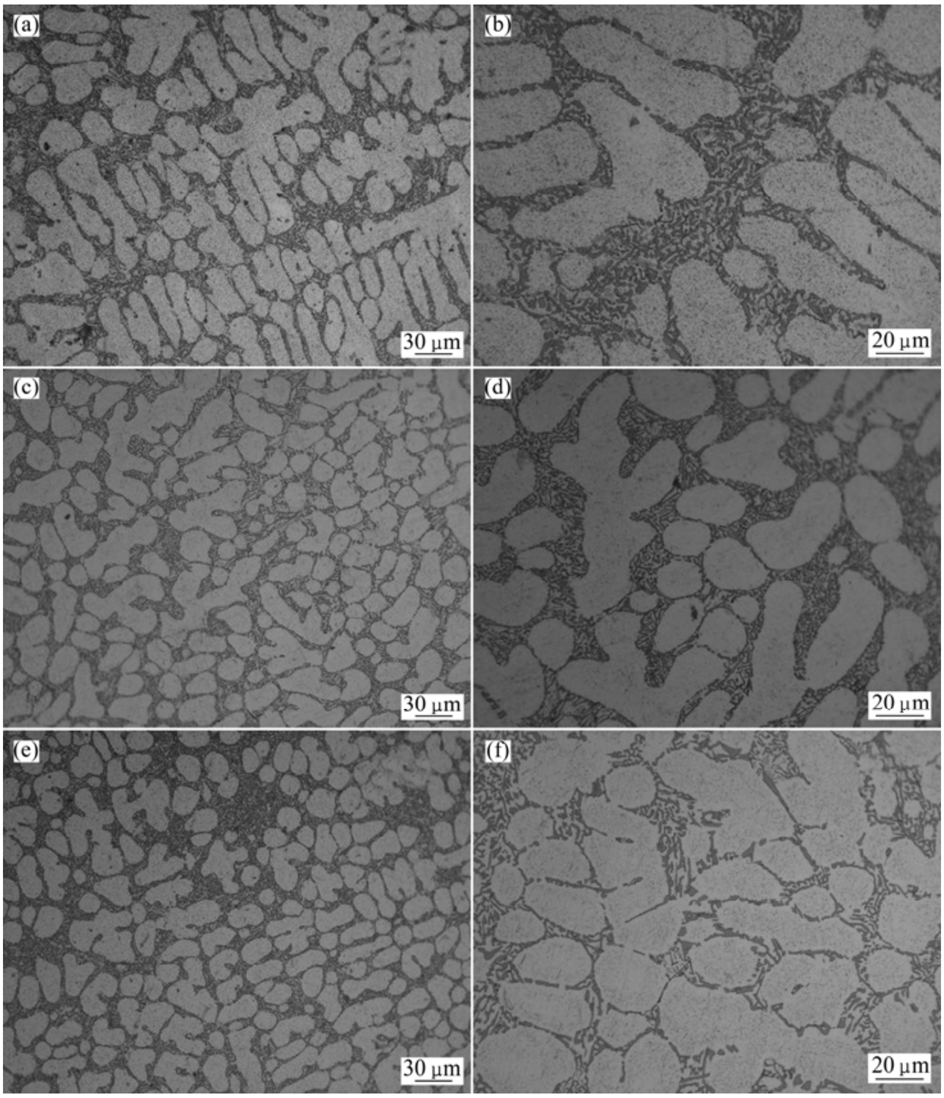

Fig. 5 Microstructures of 4004 alloy modified with RE−Ba−Sb with different magnifications: (a), (b) 0.01%RE−0.1%Ba−0.05%Sb; (c), (d) 0.02%RE−0.2%Ba−0.05%Sb; (e), (f) 0.03%RE−0.3%Ba−0.05%Sb

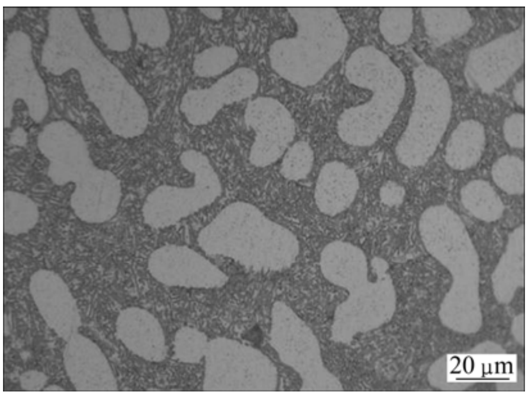

Fig. 6 Microstructure of 4004 alloy modified with 0.01%RE−0.3%Ba−0.05%Sb

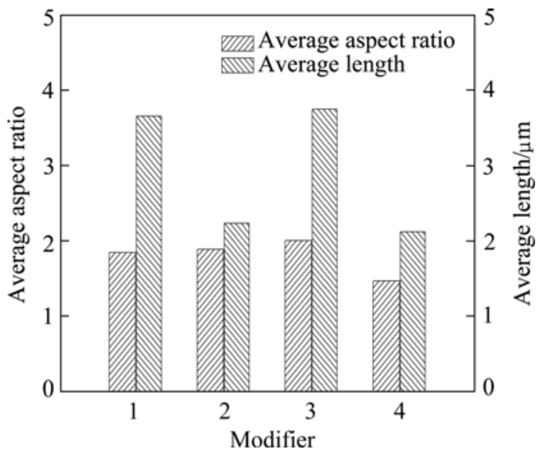

Fig. 7 Average aspect ratio and length of Si in 4004 Al alloy with combined RE−Ba−Sb addition: 1—0.01%RE−0.1%Ba−0.05%Sb; 2—0.02%RE−0.20%Ba−0.05%Sb; 3—0.03%RE−0.30%Ba−0.05%Sb; 4—0.30%RE−0.01%Ba−0.05%Sb

and change growth direction, which can decrease the aspect ratio of Si. This can be observed in Figs. 2, 5 and 8. In Fig. 8, a Si piece grows into several branches.

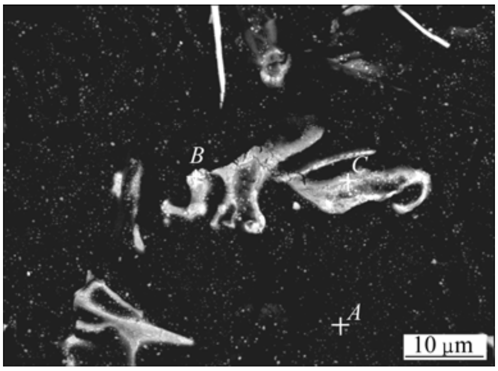

Fig. 8 SEM image of Si in 4004 Al alloy with optimized RE−Ba−Sb addition

Table 4 Elemental composition of 4004 Al alloy modified with optimized RE−Ba−Sb addition in Fig. 8 (mass fraction, %)

Position	Al	Si	Sb	Ba	La	Ce
A	92.81	1.61	1.36	1.12	1.24	0.47
B	52.61	17.58	0.99	0.00	8.48	17.64
C	47.66	18.06	1.85	0.58	10.9	18.03

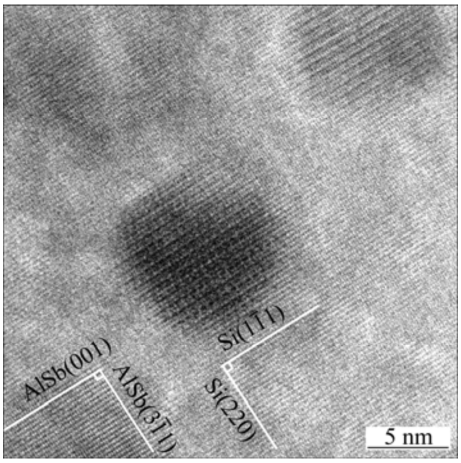

Fig. 9 HRTEM image of Si

The coherent precipitation, AlSb, may introduce stress in Si with little defects, which hinders the growth of Si. As a result, the effect of combined modification is better than that of RE modification.

4 Conclusions

1) The modification effect of RE on 4004 Al alloy was investigated. And the modification effect of RE−Ba−Sb on 4004 Al alloy is investigated by orthogonal design.

2) For RE modification, the tensile properties increase at first and then decrease with increasing RE addition. The microstructure of 4004 Al alloy can be effectively refined by RE addition. And the microstructure changes in a sequence of coarse to refined to coarse with increasing RE addition.

3) For RE−Ba−Sb modification, the best additions optimized by orthogonal design are RE addition amount of 0.01%, Ba addition amount of 0.3%, and Sb addition amount of 0.05%. The microstructure of 4004 Al alloy modified by the optimal process is the finest. Under this modification process, the tensile strength and the elongation of 4004 Al alloy are 224 MPa and 6%, respectively.

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RE−Ba−Sb 复合变质对 4004 铝合金组织与性能的影响

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摘　要：4004 铝合金具有良好的可焊性。然而，由于其 Si 含量较高，在凝固过程中会形成粗大的 Si 相而降低该合金的塑性，从而降低箔材的成品率。为了提高该合金的塑性和成品率，采用 RE−Ba−Sb 对 4004 铝合金进行复合变质处理。作为对比，对该合金亦采用不同含量稀土进行变质处理。对于单一稀土变质处理，当稀土加入量为 0.2%时，材料的组织和性能达到最佳，此时材料的的抗拉强度为 194 MPa，伸长率为 5%。对于 RE−Ba−Sb 复合变质处理，变质剂的最佳加入量采用正交设计的方法而进行优化。结果表明，RE 的加入量影响最大，其次是 Ba 的加入量，Sb 的加入量影响最小。三种元素的最佳加入量分别为 RE 0.01%，Ba 0.3%，Sb 0.05%，此时材料的抗拉强度为 224 MPa，伸长率为 6%。且复合变质中 RE 的加入量约为单一 RE 变质加入量的 1/20。

关键词：铝合金；稀土；Ba；Sb；复合变质

(Edited by Hua YANG)