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Variation of microstructure of RE-containing $AlSi_{20}Cu_2Ni_1RE_{0.6}$ alloy with different cobalt contents

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ABSTRACT

Cobalt is generally considered as the element that can promote the high-temperature mechanical properties of Al–Si alloys. In order to develop new hypereutectic Al–Si alloys that can be used at high temperature, the changes of microstructure of Al–20Si–2Cu–1Ni–0.6RE–*x*Co alloy with different contents of Co were studied in this paper. The results show that, under P–RE complex modification of the alloy melt, the content of Co varying from 0 to 1.5% had little influence on the refining effect of primary Si and modification effect of eutectic Si, but the amount of acicular RE-bearing Al–RE–Ni–Co–Si compounds gradually increased with the increase of Co content. In addition, Co could also modify the morphology of Fe-bearing phases, which solidified as particles instead of long needles. The addition of Co even has an adverse effect on the tensile strength of this RE-containing hypereutectic Al–Si alloy.

1. Introduction

Hypereutectic Al–Si alloy, which has low thermal expansion coefficient, small density, high wear resistance, corrosion resistance, high temperature strength and good castability, is especially good for production of high heat-load pistons and other friction and wear resistant parts [1,2]. However, the microstructure of hypereutectic Al–Si alloy is composed of coarse polygonal primary Si particles and coarse acicular shape eutectic Si, which make the mechanical and cutting performance worse. Hence, the use of this alloy is limited if it is not modified or refined, particularly for the alloy with Si content over 18% [3,4]. Generally P is added to this alloy melt to refine the primary Si particles.

The prophase research results of the authors [5] showed that the use of rare earth (RE) as a modifier could not only get refinement of eutectic Si, but also effectively promote the room-temperature strength of Al–20Si–2Cu–1Ni–0.6RE alloy. But when it works at high temperature, the strength of the matrix is still not high enough and the mobility of dislocations leads to the low strength. At the same time, the solid solubility of the matrix increases at high temperature. The solid solution strengthening capability, the resistance from dispersion particles to dislocation motion and the strengthening effect of dislocation network are all reduced considerably [6]. Therefore, the promotion of high-temperature properties of Al–Si alloys waits to further researches. It is reported that Co is one of the elements what is good for high temperature properties of Al alloys [1]. There are a few standards of aluminum alloys which contain Co in some countries (mostly in Russia, German and French) [1], but the effect of Co with different contents on the microstructure and properties of hypereutectic Al–Si alloy containing more than 20% Si is rarely reported, especially the effect on high Si aluminum alloy modified by RE. This paper aims to study the effect of different Co contents on microstructure and properties of Al–20Si alloys with P–RE complex modification.

2. Experimental procedure

In this experiment, the hypereutectic Al–20Si alloys were produced with raw materials of pure aluminum (99.8% Al, in mass%, same below), pure copper (99.99% Cu), nickel (99.9% Ni), magnesium (99.9% Mg), cobalt (99.9% Co), Al–25.8% Si and Al–10% Mn master alloys. The Cu–14% P and Al–15% RE master alloys were used to modify complexly the primary silicon and eutectic silicon respectively, in which the RE was composed of 63% Ce and 36% La. High purity argon gas was used as degassing agent to minimize the hydrogen content in the melt. The chemical compositions of the Al–20Si alloys are shown in Table 1. In order to investigate the effect of Co on the microstructure of the alloy, various amounts of cobalt were added to the base alloy to obtain alloys containing 0, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, and 1.5% Co.

After the melting of the main raw materials, the temperature of the melt was raised to 850 °C and hold for 20 min. Then the Al–15% RE modifier was added at 800 °C and the RE content added to the melt was 0.6%. The Cu–14% P refiner was added at 830 °C and the added amount of P was 0.08%. The melt was then poured into cast iron mold preheated at 180 °C to get standard tensile samples with diameter of 8 mm. In order to test tensile strength, six samples of every composition were heat treated with T6 process (solutionized at 510 °C for 8 h, followed by quenching in hot water (80 °C) and artificial aging at 190 °C for 10 h). The room-temperature tensile strength and elevated-temperature tensile strength (300 °C) are average values of three samples at every composition respectively.

The as-cast samples were analyzed using optical microscopy after grinding, polishing and corroding by 0.5% HF aqueous solution. Phase compositions and elements

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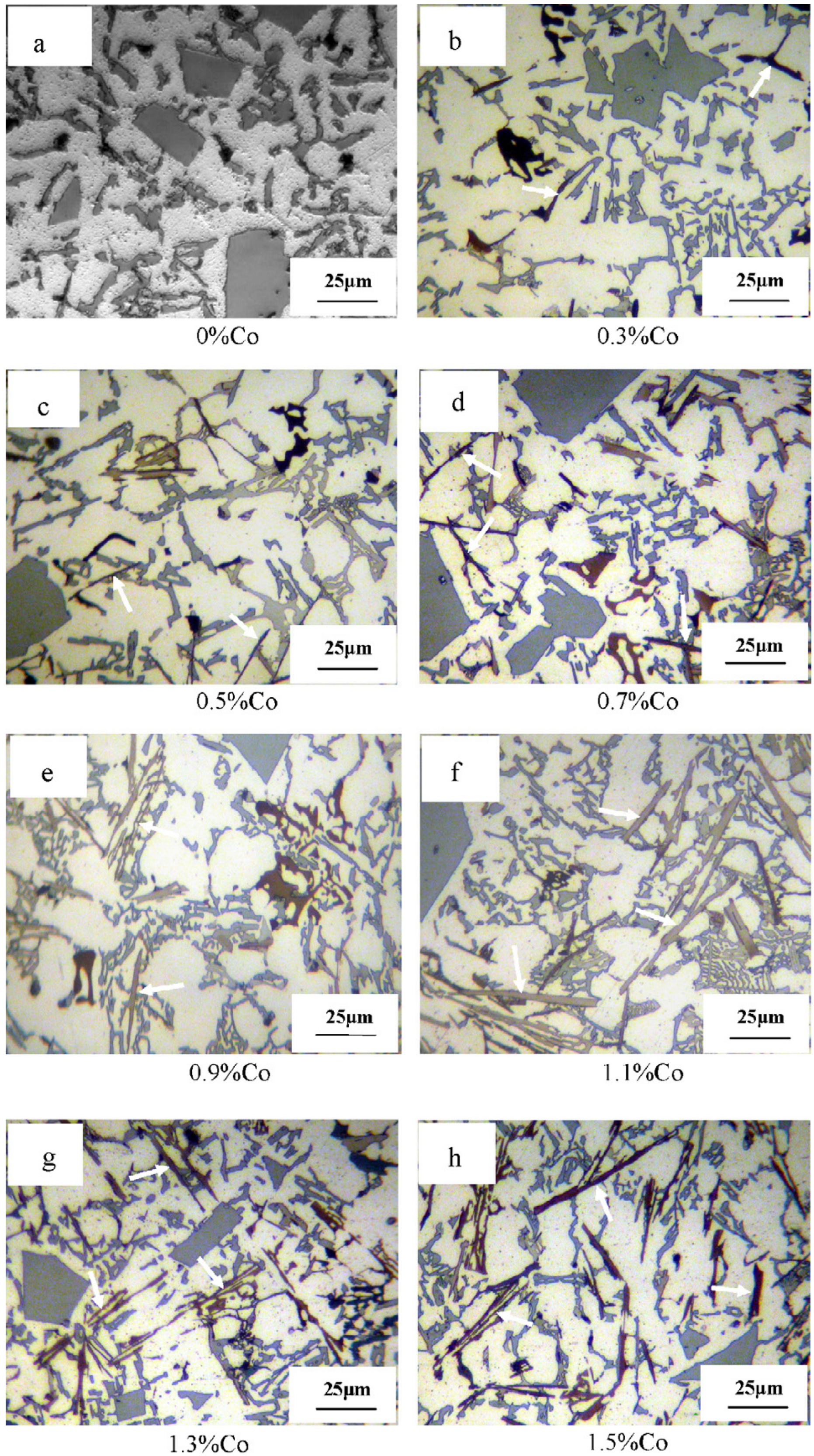


Fig. 1. Optical photos of high-silicon aluminum alloys with different cobalt concentrations. The compounds indicated by arrows increased with Co content: (a) 0% Co; (b) 0.3% Co; (c) 0.5% Co; (d) 0.7% Co; (e) 0.9% Co; (f) 1.1% Co; (g) 1.3% Co; (h) 1.5% Co.

Table 1
Composition of high Si content aluminum alloy (mass%).

	Element								
	Si	Cu	Ni	RE	Mg	Co	Mn	Fe	Al
Mass%	20	2.0	1.0	0.6	0.4	*x*	0.5	<0.23	Balance

were identified by using a Scanning Electron Microscope. The X-ray diffractometer of X'Pert Pro type was used to make phase analysis of the alloy powder. The room tensile tests were conducted on a WDW3200 tester while the elevated tests were made on a MTS810 tester.

3. Results and discussion

3.1. The effect of cobalt content on microstructure of the alloy

Fig. 1 shows optical photos of as-cast high-silicon aluminum alloys with different concentrations of cobalt (from 0% Co to 1.5% Co). The massive primary Si particles were evidently refined by the P refiner and had a mean size about 25 μm (Fig. 1a–h). The eutectic Si was also modified by RE from plates or needles to short rots or granulose, that was beneficial to promote the mechanical properties. Obviously the addition of Co has little effects on primary and eutectic Si, but long acicular compounds formed as pointed by arrows in Fig. 1b–h gradually increased with the increase of cobalt content. As a result, the properties of the alloy would be severely decreased. A discussion in detail will be made later, combed with SEM, EDX and other detection means.

Fig. 2a and b shows respectively for photos of SEM and XRD of Al–20Si–2Cu–1Ni–0.6RE–1.5Co alloy. Fig. 2a shows the as-cast microstructure of sample formed in permanent mold, which is composed of primary Si (A), eutectic Si (B), long acicular compounds (white C), block-shape compounds (gray D). According to Fig. 2b, the compounds that could be detected were including not only Al matrix, Si phase and AlP, which was formed because of addition of P refiner, but also Co–RE compounds like $Co_{13}La$, Ce_5Co_{19} and Co–Fe compounds, such as CoFe and Co_3Fe_7.

3.2. The effect of cobalt content on intermetallic compounds

Fig. 3 shows the SEM image of an alloy with no addition of Co, i.e., Al–20Si–2Cu–1Ni–0.6RE–0Co alloy. The white acicular compounds

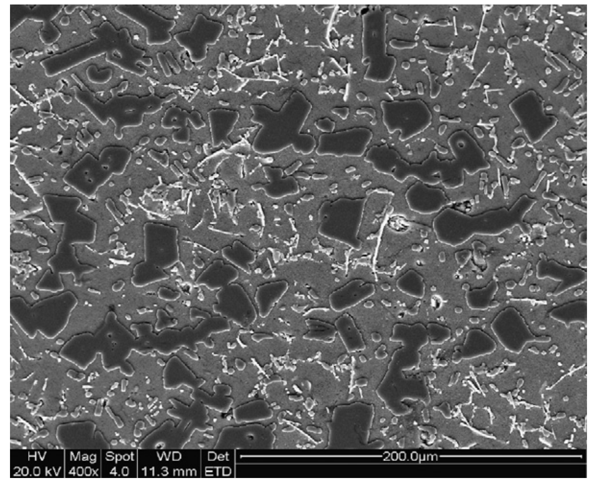


Fig. 3. SEM of aluminum alloy Al–20Si–2Cu–1Ni–0.6RE–0Co. The white short acicular compounds are RE-containing Al–RE–Cu–Ni–Si alloy.

already existed before cobalt was added. Comparing with Fig. 2a, the white acicular compounds in Fig. 3 remained a low content until the addition of cobalt; meanwhile, the length was also shorter. Former research about the compounds in Fig. 3 [5] showed that these acicular compounds were RE-bearing Al–RE–Cu–Ni–Si compound. Fig. 4 represents the SEM photos of alloys of 0% Co, 0.9% Co and 1.5% Co. Results of energy spectrum analyses of Points 1–4 are shown in Table 2, and in Fig. 5 the EDX results of Points 3 and 4 are illustrated.

Fig. 4 shows the acicular compounds in microstructure of the alloy. As listed in Table 2, the compound in Fig. 4a is a kind of five elements compounds, which is Al–RE–Cu–Ni–Si. Some of the cobalt added in alloy appears in the acicular compounds shown in Fig. 4b and c, i.e., Al–RE–Co–Ni–Si compound was formed, as indicated in Table 2. The block-shape compound with a small size of Point 4

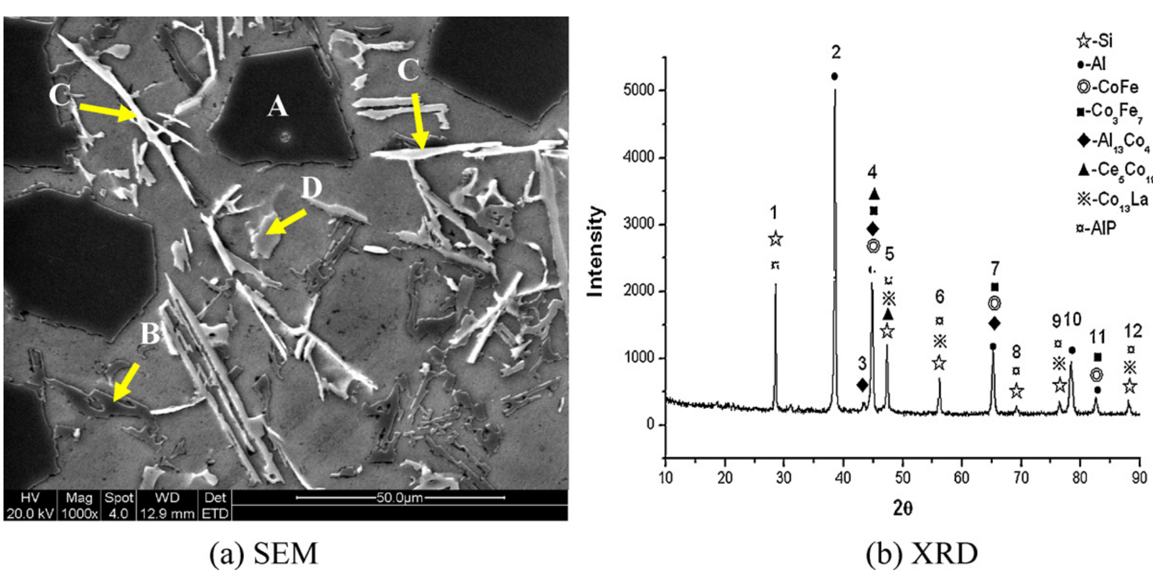
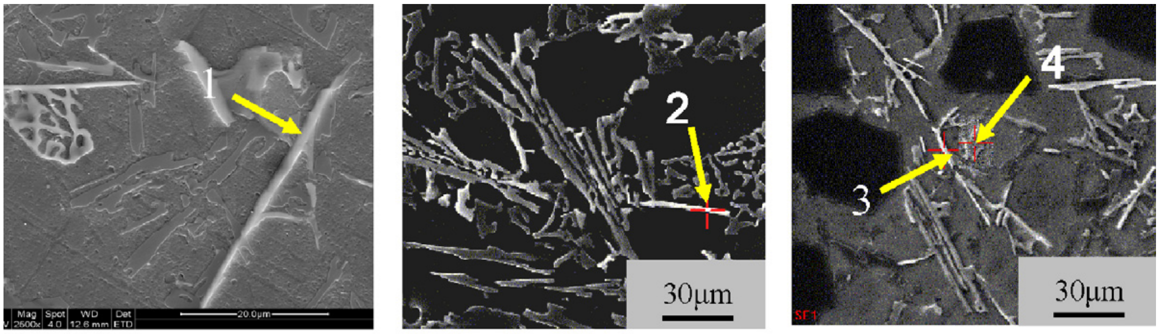


Fig. 2. SEM and XRD of aluminum alloy Al–20Si–2Cu–1Ni–0.4Mg–1.5Co: (a) SEM; (b) XRD.



(a) 0%Co (b) 0.9%Co (c) 1.5%Co

Fig. 4. SEM of hypereutectic Al–Si alloy with different contents of Co: (a) 0% Co; (b) 0.9% Co; (c) 1.5% Co.

Table 2
EDX results of points in Fig. 4 (mass%).

Detected spots	Element (mass%)							
	Al	Si	Cu	Ni	Co	Mn	Fe	La	Ce
1	59.36	8.91	6.59	7.17	–	–	–	7.62	10.35
2	57.19	13.64	–	7.26	1.93	–	–	8.53	11.45
3	45.98	11.58	–	7.47	4.49	–	–	18.02	12.46
4	48.89	26.66	–	3.02	13.29	8.08	4.06	–	–

in Fig. 4c is confirmed to be Al–Co–Mn–Fe–Ni–Si by EDX, as also indicated in Fig. 5b.

Rare earth (RE) metals are active elements and usually relied on the adsorption to grain boundary or phase boundary to refine and modify eutectic Si by changing interfacial energy, lowing surface activity and preventing growth of Si phases. Besides, RE can also enter into a certain phase and change the thermodynamic characteristics to enhance or prevent the formation and growth [7]. Elements in solution that have weak interaction with RE would be promoted to enter into solid solution with addition of RE. Oppositely, the addition of RE would enhance formation of compounds with the elements. Excessive RE easily forms compounds with other elements. Taking A390 alloy as an example, it was easy to observe one type of long straight intermetallic compound in the microstructure of 3% La-added A390 alloy [8]. The EDX results shown in Table 2 illustrate that those acicular compounds all contain a large amount of rare earth elements as Ce and La. Meanwhile, as shown by the optical metallographic pictures shown in Fig. 1, the quantity of acicular compounds is increased with increasing Co content.

Both Co and RE all have active chemical properties. The atomic radius of Co and Ce is 1.67 Å and 2.74 Å respectively, with a relative difference of 61.7%. The electro negativity of Co and RE is 1.88 and 1.12 respectively, with a difference of 0.76. The differences of atomic size parameter and electronic affinity make it much easier for RE to form compounds with Co than other elements. On the one hand, the enriched RE on interfaces can enter into phases enriched with Co to form new compounds to change the composition. On the other hand, it might also adsorb on the surface of Co enriched phases. As a result, RE, which has active chemical property, could enter into grain boundary to form new compounds with Co.

What is more, the active RE is very easy to adsorb on surroundings of phases enriched with Co, and then prevent the migration of cobalt atoms to the periphery. The probability of Co entering into α-Al is decreased, and Co concentration gradient in liquid phase at interface front increased, which leads to bigger constitutional undercooling, accelerating growth of dendrites of eutectic α-Al phase. For example, in the Ce–Co and La–Co binary alloy systems,

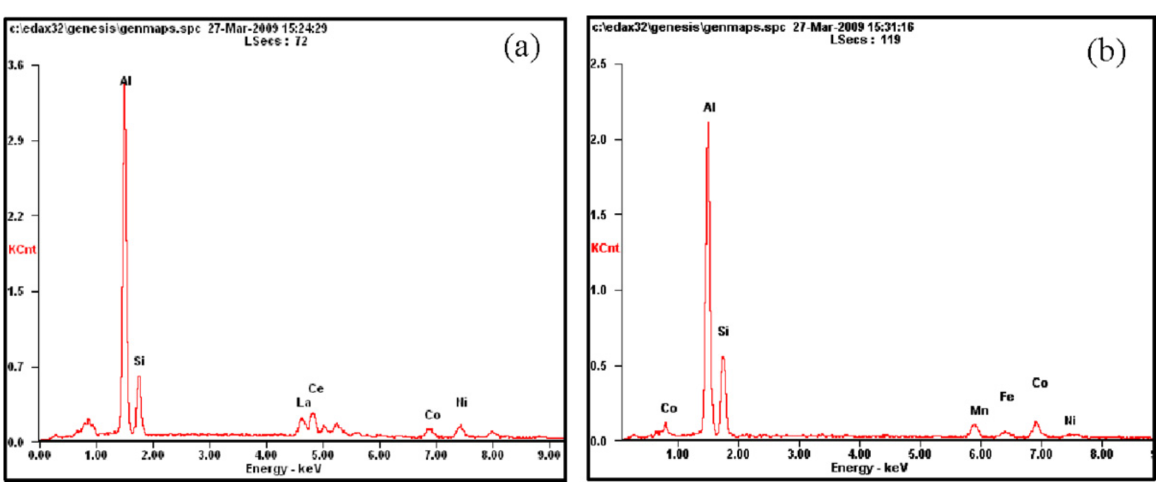


Fig. 5. EDX of compounds of arrows 3 and 4 indicated shown in Fig. 4: (a) arrow 3; (b) arrow 4.

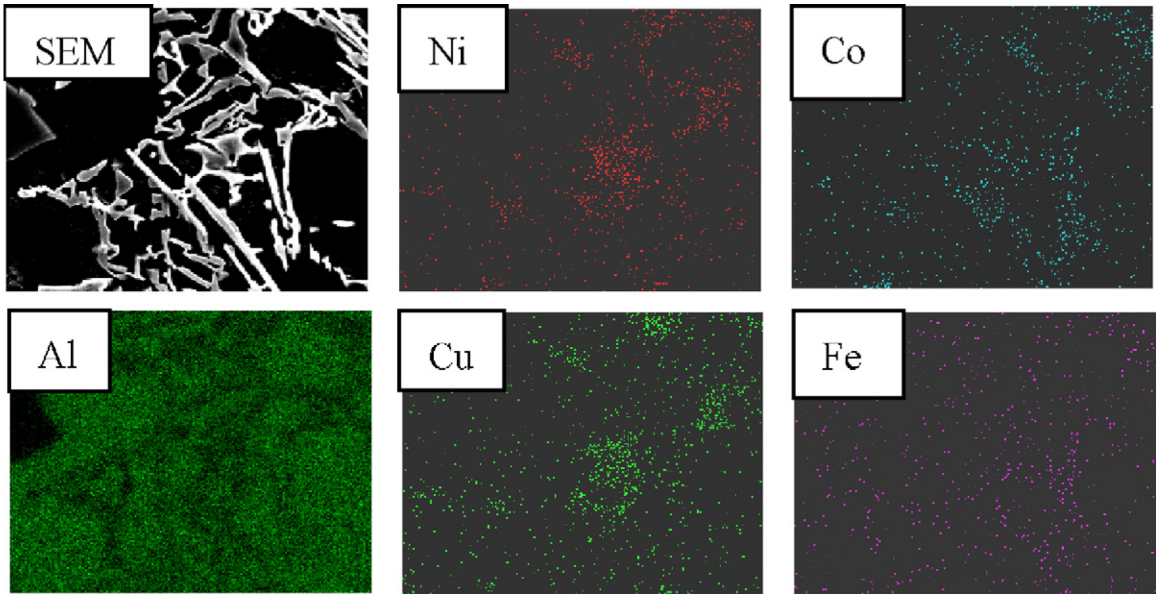


Fig. 6. Surface scanning of Al–20Si–2Cu–1Ni–0.6RE–0.9Co alloys.

compounds Ce_5Co_{19} and $Co_{13}La$ are formed respectively:

$$5Ce + 19Co = Ce_5Co_{19} \quad (1)$$

$$La + 13Co = Co_{13}La \quad (2)$$

For the Al–20Si–2Cu–1Ni–0.6RE–xCo alloy in this study, the most reactive elements are Al, Ce and Co, and they form three elements compounds such as Al_8CeCo_2 and Al_4CeCo in the Al–Ce–Co alloy. The acicular Al–RE–Co–Ni–Si compounds shown in Figs. 1 and 4 are formed based on these compounds. These acicular compounds dissever matrix of the alloy and lower the mechanical properties.

Fig. 6 shows the surface scanning films of elements distribution of 0.9% Co alloy. Cobalt not only exists everywhere in the matrix but also aggregates in the distribution area of Ni and Cu. The accumulation of Co and Fe can be seen at lower right region of the picture, but common phases of long acicular β-Al_5FeSi in cast aluminum alloy has not been observed. Fe-containing phase as indicated by the arrow in Point 4 in Fig. 4 displays as particle or short stick in the matrix. The EDX results indicated that the Fe-containing phases are enriched with Co (Table 2).

The reasons that β-Al_5FeSi phases in cast aluminum alloy are harmful to mechanical properties are that the difference of deformation performance between Fe-bearing phase and the matrix, and the stress concentration produced at the tip of acicular phases in deformation process. As illustrated in Fig. 4, the addition of Co can effectively improve the morphology of Fe-containing compounds and change them from long acicular to particle or spheroid, which could produce pinning effect in certain extent on matrix and make a hindering effect on the dislocation of elastic strain field, so that the particle compound would be sheared by dislocation and the latter can also bound the former, therefore the alloy can be strengthened. But it is worthy to point out that in this Al–20Si–2Cu–1Ni–0.6RE–xCo alloy, Fe was an impurity element introduced from iron crucible and the content was less than 0.23%. Consequently, the elevation of mechanical properties caused by the morphology improvement of Fe-containing compounds was not obvious, even though the addition of Co could indeed change them.

The research of Jiang and Liu [9] showed that the addition of Co can promote the stability of intermetallic compound θ-AlFe (Si) thus properties improved. Crepeau concluded that [10] like the common neutralizer Mn for β-Al_5FeSi phases, the addition of Co could change the Fe-containing phases to spheroid. Because of the smaller solidification segregation of Co, the properties of Co-containing alloy are better than those of Mn-containing alloy. Mondolfo [11] argued that the best neutralizer is Co, for it does not combine with Si, and fewer additional phases can be formed.

3.3. The effect of cobalt content on mechanical property of the RE-containing alloys

Fig. 7 shows the effect of Co content on mechanical property at room and elevated temperature of the Al–20Si–2Cu–1Ni–0.6RE–xCo alloys. The tensile strength at both room temperature and elevated temperature was increased a little when Co content was increased from 0.3% to 0.9%. The ultimate tensile strength σ_b was around 250 MPa and 127 MPa respectively when Co ≤ 0.9% after T6 treatment. But, the tensile strength was decreased about 10% when Co content was equal or greater than 1.1%. The main reason is that, when the Co content was high, the acicular RE-containing Al–RE–Co–Ni–Si compounds

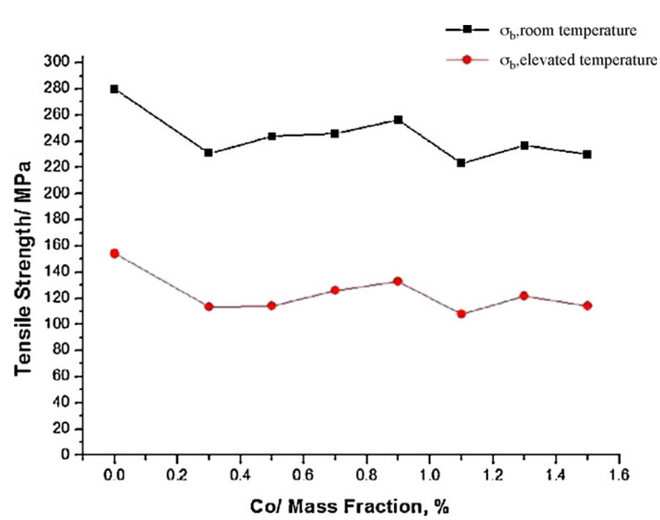


Fig. 7. Effect of Co content on tensile strength at room temperature and elevated temperature (300 °C) of hypereutectic Al–Si alloys containing RE, after T6 treatment.

became coarse and longer, and the amount of these compounds was also increased, as indicated in Fig. 1f–h. This leads to reduction of mechanical property. From Fig. 7, it is known that when Co was added, the tensile strength at room temperature was reduced from 279 MPa (0% Co) to about 250 MPa (xCo, $0.3\% \le x \le 1.5\%$) while the tensile strength at elevated temperature reduced from 154 MPa (0% Co) to about 127 MPa (xCo, $0.3\% \le x \le 1.5\%$). In addition, the elongation values of the Al–20Si–2Cu–1Ni–0.6RE–0Co alloy were 3.33% at room temperature and 8.63% at elevated temperature. While these values of the Al–20Si–2Cu–1Ni–0.6RE–xCo alloys ($0.3\% \le x \le 1.5\%$) fluctuated in a narrow range, from 2.62% to 3.09% at room temperature, and the elevated-temperature elongation values were around 7%. For all that, the elongation values were better than the research results of Xu et al. [12,13]. The above strength result means that the addition of Co even has an adverse effect on the mechanical properties not only at room temperature but also at elevated temperature of this RE-containing Al–Si alloy. This result is in agreement with the change of microstructure when Co added into the RE-containing alloy as discussed beforehand. This result is also in accord with the research results of Holecek in Germany [14,15] although in his research there was no RE: the addition of Co makes no obvious effect of promoting the tensile properties of the Al–Si alloy and even has a counteraction.

4. Conclusions

1. When added 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, 1.3%, 1.5% Co respectively into Al–20Si–2.0Cu–1.0Ni–0.6RE alloys with P–RE complex modification, the RE-containing acicular compounds were increased with the increasing of Co content. There was little effect of Co on microstructure of primary Si and eutectic Si.
2. The RE-containing acicular compounds enriched with Co. After the addition of Co, long acicular intermetallic compounds Al–RE–Co–Ni–Si were formed.
3. The Fe-containing phases in the alloy also contained Co, and cobalt could neutralize the harmful effect of Fe and make Fe-bearing phases to precipitate as particles instead of acicular compounds.
4. Because the RE-containing Al–RE–Co–Ni–Si needle-like compounds became coarse and more amount when Co was added into the alloy, the addition of Co has an adverse effect on tensile strength of the Al–20Si–2Cu–1Ni–0.6RE–xCo alloys.

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