Complex modification effect by ZrAlSi intermetallic and element Sr on the microstructure and mechanical properties of hypereutectic Al–Si alloys

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In this study, the morphological evolution of ZrAlSi intermetallic in ternary Al–Si–Zr alloys was investigated. In hypereutectic Al–18Si alloy, the introduction of Zr results in the formation of flakey ZrAlSi particles. Besides, there form almost no primary Si, while replaced by ZrAlSi. Using ZrAlSi to modify primary Si and Sr to modify eutectic Si, complex modification effect can be realized in an Al–Si multicomponent piston alloy. Correspondingly, the mechanical properties were significantly improved.

1. Introduction

Al–Si alloys are well-known casting alloys and widely used in many fields, due to good corrosion resistance, low thermal-expansion coefficient, high wear resistance, low shrinkage in casting and improved mechanical properties [1–3].

Zr is an important element in Al–Si alloys, for its grain refining role and solution strengthening effect [4–6]. Since the solubility limit of Zr in α-Al is quite limited, commonly, there forms Zr-containing phase when the content of Zr is relatively high. However, rare information can be referred about the AlSi–Zr system in existed papers. For instance, experimental information is restricted to some partial isothermal sections [7,8], and is limited to the Al-rich part. Hirano et al. [9] have calculated the ternary system using first-principles method, but their results remain disagreement with the rare experiment data. In our previous work [10], we have conducted some investigation on the composition and crystal structure of Zr-containing phases in Al–Si–Zr alloys. Ternary Al–, Si– and Zr-containing phases were detected. Since the composition of the phases can vary over a wide range, due to the replacement effect of Al and Si in the phases, the intermetallics are simply written as ZrAlSi, just as the condition of TiAlSi [10–12].

According to the references [13], ZrAlSi phase is quite stable and may be a candidate for improving the properties of Al–Si alloys. However, almost all ZrAlSi phases reported in previous literatures are flake-like, which are quite harmful for the alloys. During our investigation process, we tried to control the morphology of ZrAlSi intermetallic and investigate its effect on the microstructure and mechanical properties of Al–Si alloys.

The purpose of the present work is to further report the control of ZrAlSi morphology. Due to its modification effect on primary Si, flakey ZrAlSi particles were introduced in an Al–Si multicomponent piston alloy. Complex modification using ZrAlSi intermetallic to modify primary Si and element Sr to modify eutectic Si has been tried. Accordingly, the mechanical properties were tested.

2. Experimental

The materials used in this paper are commercial pure Al (99.7%), commercial pure crystalline Si (99.9%), sponge Zr (99.9%), K2ZrF6 salt (99%) and other commercial pure elements. Al–18Si–5Zr alloy was prepared using different Zr-containing raw materials, i.e. sponge Zr or K2ZrF6 salt, to investigate the microstructure varieties. First, Al and Si were melting in a clean clay-bonded graphite crucible by medium frequency induction furnace, and then sponge Zr or K2ZrF6 salt was added in the melt. After the Zr-containing raw materials were totally melted, the melts were holding for 10 min and then poured into a cast iron chill. The alloy prepared by sponge Zr was marked as Sample-1, while the one by K2ZrF6 as Sample-2. Metallographic specimens were all cut from the same position of the as-cast samples, then mechanically ground and polished in standard routines.

Since flakey Zr-containing particles were obtained in Sample-2, the next experiment was conducted in order to introduce the blocky particles in an Al–Si– multi-component piston alloy. The alloy was prepared in a clay-bonded graphite crucible heated by medium frequency induction furnace at 800 °C, and Al–18Si–5Zr master alloy (the above Sample-2 alloy) was used to provide Zr. 0.4 wt.% of Al–10Sr master alloy was added in order to modify eutectic Si. The melts were carried out using 0.5% C2Cl6 for slag-removing and degassing, and then they were...
poured into a pre-heated (200 °C) mold at 780 °C to obtain tensile test bars. Another group of alloy without Zr was also prepared for comparison. The compositions of the alloys are listed in Table 1.

Test bars were then heat-treated in the process: solution treated at 505 °C for 4 h; water quenched; aging treated at 200 °C for 8 h and cooled in air. The test bars were machined to ‘dog-bone’ type specimens (Fig. 1). The ultimate tensile strength (UTS), elongation (δ) and yield strength (σ) were tested and shown in Table 1. Specimens for metallographic microstructure observation were cut from tensile bars after heat-treatment.

3. Results and discussion

Fig. 2a shows the microstructure of Al–18Si–5Zr alloy (Sample-1), which was prepared using sponge Zr. Except for primary Si particles, the main ZrAlSi intermetallic exhibits flake-like (Fig. 2a), while it performs dendrite in three-dimensional space (Fig. 2b). It can be seen that the dendrite is quite coarse, with the average size of about 100 μm. It has a main trunk, perpendicular to which the secondary dendrites form. Since the dendrites have sharp edges, they are quite easy to be the origin for crack forming. Fig. 2c shows the fracture image, from which the alloy breaks along the dendrites, thus resulting in poor mechanical properties. EDS result shows that the compositions are 13.28 at.% Al, 56.36 at.% Si and 30.36 at.% Zr, indicating that the phase can also be marked as $\text{Zr(Si}_{1-x}\text{Al}_x)_{2}$.

The microstructure of Sample-2 is shown in Fig. 3a. It can be found that, except for eutectic Si, the main phase ZrAlSi exhibits blocky, with average size of about 25 μm. The three-dimensional morphology of this phase is displayed in Fig. 3b. It can be seen that the particles form as polyhedral, quite different from the dendrite mentioned above. The compositions are 11.91 at.% Al, 57.74 at.% Si and 30.35 at.% Zr, indicating that the phase also belongs to the chemical formula $\text{Zr(Si}_{1-x}\text{Al}_x)_{2}$. Besides, it is necessary to note that there form almost no primary Si particles in the hypereutectic Al–18Si–5Zr alloy. Since the precipitation temperature of ZrAlSi phase is higher than that of primary Si [10], the precipitation of ZrAlSi promotes the replacement of primary Si by ZrAlSi particles. It is known that angular primary Si particles dissever the matrix, leading to a decrease of strength and elongation [14]. Since the blocky ZrAlSi particles have no sharp edges, it may lead to improvements of elongation and ductility of the alloy. What is more, the experimental results provide a method to modify primary Si particles in hypereutectic Al–Si alloy by forming blocky ZrAlSi particles.

For hypereutectic Al–Si alloys, coarse primary Si particles have to be refined before applying in industries [15]. Commonly, phosphorus-containing master alloys, e.g. Al–P, Si–P and Al–Zr–P, are used to refine primary Si [14,16,17]. However, the precipitation of flake-like eutectic Si is another problem restricting further improvement of hypereutectic Al–Si alloys. To change this harmful morphology, strontium-containing master alloys, for instance Al–10Sr, are added in the melt to modify eutectic Si. But, P and Sr can not be used together to refine and modify primary Si and

![Fig. 1.] Pattern dimensions of ‘dog-bon’ type specimen.

Table 1

<table>
<thead>
<tr>
<th>Alloy grades</th>
<th>Nominal compositions (wt.%)</th>
<th>UTS (MPa)</th>
<th>σ (MPa)</th>
<th>δ (%)</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>Cu</td>
<td>Mg</td>
<td>Sr</td>
<td>Zr</td>
</tr>
<tr>
<td>Group 1</td>
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<td>4.5</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Group 2</td>
<td>16.5</td>
<td>4.5</td>
<td>0.6</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Each value of UTS, σ and δ is an average of four measurements.

![Fig. 2.] Microstructure of Al–18Si–5Zr alloy (Sample-1) (a), three-dimensional morphology of ZrAlSi phase (b), and the fractograph (c).
eutectic Si, due to the poisoning effect between them [18]. Based on the above experimental result, complex modification effect may be realized by using blocky ZrAlSi intermetallic to modify primary Si and Al–10Sr master alloy to modify eutectic Si, since no poisoning reaction happens between Sr and ZrAlSi.

Fig. 4a and b shows the microstructures of the Al–Si multicomponent alloy before and after complex modification. Correspondingly, the morphologies of the eutectic structures are displayed in Fig. 4c and d. It can be found that, before the complex modification, the primary Si particles are quite coarse, with sharp edges (Fig. 4a). The eutectic Si exhibits flake-like, which is also harmful for the properties of the alloy (Fig. 4c). After applying the complex modification, the primary Si particles are replaced by blocky ZrAlSi particles, whose average size is about 35 μm, and the eutectic Si structures are coralliform (Fig. 4b and d). EDS result shows that the compositions of ZrAlSi are 13.06 at.% Al, 53.52 at.% Si and 33.42 at.% Zr, similar with those in Sample-2.

The mechanical properties of the two experimental alloys are displayed in Table 1. It can be found that, without complex modification, the values of UTS, δ and σ are 275.6 MPa, 247.5 MPa and 3.09%, while for the alloy after complex modification, the increase of 15.5%, 13.2% and 18.1% can be achieved, respectively. The enhancement is supposed to due to the modification of both primary and eutectic Si.

4. Conclusions

In this paper, the morphologies of ZrAlSi intermetallic in hypereutectic Al–Si alloys were investigated. Blocky ZrAlSi particles were obtained. Accordingly, there form almost no primary Si in Al–18Si–5Zr alloy, due to the precipitation of blocky ZrAlSi particles. Based on this experimental result, complex modification effect can be achieved using ZrAlSi to modify primary Si and
element Sr to modify eutectic Si in an Al–Si multicomponent piston alloy. Correspondingly, the mechanical properties were improved significantly.

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