The in-situ Ti alloying of aluminum alloys and its application in A356 alloys

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Abstract: This research has investigated the in-situ Ti alloying of aluminum alloys and its application to A356 alloys and wheels through the evaluation of microstructure and mechanical properties. The results showed that stable titanium content can be obtained by adding a small quantity of TiO$_2$ into electrolyte of pure aluminum. Under this approach, a greater than 95% absorptivity of titanium was achieved, and the microstructure of the specimens was changed to fine equiaxed grains from coarse columnar grains in the pure aluminum. In comparison with the tradition A356 alloys and wheels, the corresponding microstructure in the testing A356 alloys and wheels was finer. Although the tensile strength was similar between the testing and the tradition A356 alloys and wheels, the ductility of the former (testing) is superior to that of the later (tradition), leading to an excellent combination of strength and ductility from the testing alloys and wheels.

Keywords: aluminum alloy; in-situ Ti alloying; A356 alloy; wheels; grain refinement; mechanical property

1. Introduction

Titanium is one of the most effective grain refinement elements of aluminum alloys. The grain of aluminum alloys can be effectively refined if containing up to 0.2% titanium, which results in improvement of mechanical properties and performance [1-8]. Titanium is usually added into aluminum melt by melting Al-Ti or Al-Ti-B (Ti/B=5:1) master alloy. This requires strict control in melting temperature and holding time, resulting in the complicity to control the quality of alloys such as the effect of grain refinement and chemical composition as well as the microstructure and mechanical properties of the alloys.

Zhuxian QIU et al tentatively carried out the in-situ titanium alloying of Al alloys [9-10]. Their results showed that it is possible to produce the Al-2%Ti alloys by adding some TiO$_2$ into electrolyte. The distribution of titanium in alloy produced is homogeneous. At about 60%, however, the current efficiency of the process is low. This is because some Ti in melt may settle down on the cell bottom in the form of TiAl$_3$ during the electrolytic production. Ruyao WANG et al conducted the electrolytic production of the Al-Si-Ti alloys containing 6.5%-13%Si, 0.08%-0.6Ti% and 0.07%-0.7% Fe, respectively, by adding alumyte powder containing some alumina, titania and silica into electrolyte [11-13]. They found that the electrolytic Al-Si-Ti alloy possesses the ability to refine α-Aluminum dendrite. But, in this case, the chemical composition of alumyte needs to be strictly controlled.

Al-Si alloys, especially the A356 alloys containing nominally 7%Si, 0.25%-0.7% Mg and 0.1%-0.2%Ti have broad applications in the automotive to meet the growing demand for components and structures with high strength and low weight [14]. It has been found that the melt quality has an important effect on the mechanical properties of the A356 alloys [15-17]. Optimizing the chemical composition and refining the grain of billet can result in effective improvement in the microstructure and the mechanical properties of the alloys. This is usually attributed to the heredity of the microstructure of billets. Therefore, some suppliers of wheels begin to have a requirement to both the chemical composition and the grain size of the billet.

The authors and their colleagues have been developing the in-situ titanium alloying method to directly and electrolytically produce low-titanium aluminum alloy containing 0.1%-0.3%Ti since the recent years. The pilot production test has been conducted. The variation in titanium content and the grain refinement of the alloys have been analyzed. The alloy produced has been tentatively used in the A356 alloys (testing A356 alloys) and wheels (testing wheels, including car and motorcycle wheels). The microstructure and mechanical properties of the testing A356 alloys and wheels were investigated and compared with those of tradition A356 alloys and wheels.
produced by melting Al-Ti master alloys.

2. Materials and experimental procedure

The experiment of in-situ titanium alloying to aluminum was carried out in an 85 kA prebaked cell for aluminum-reduction. Except for adding 0.02% ~ 0.03% TiO$_2$ into electrolyte, all other ingredients of electrolyte used in the experiment have the same composition/proportion as that of pure aluminum electrolysis. The absorbility of titanium, $Ab$ is defined as $Ab = \frac{\Sigma q_{Ti}}{\Sigma Q_{Ti}}$, where $\Sigma q_{Ti}$ is the actual titanium production calculated based on the measuring results of titanium in alloys, $Q_{Ti}$ is the theoretic titanium production calculated based on the quantity of TiO$_2$ added into electrolyte.

In order to investigate the difference in the microstructure and the mechanical properties of testing alloys, two kinds of A356 alloys were produced using two different titanium alloying methods. One is alloyed with titanium by remelting Al-5Ti master alloys into aluminum melt, named tradition A356 alloys. The other is directly produced by remelting the Al-0.15% Ti low-titanium alloys made from electrolysis without adding any pure aluminum and Al-5Ti master alloy, which is referred to as testing alloys. The application of the testing A356 alloys in wheels (including car wheels and motorcycle wheels) was investigated. Two groups of wheels were produced using the same production methods as those for the tradition A356 alloys and testing A356 alloys, named the tradition wheels and testing wheels correspondingly. All A356 alloys were heat treated by T5 and T6 processes, while car wheels and motorcycle wheels were treated by T6 and T5 processes, respectively. The chemical composition of the testing alloys was analyzed with a Metalscan 2500 spectrometer. The results are shown in Table 1. The mechanical properties (strength and plasticity) were measured with a MTS810 tester at the loading rate of 1.5 mm/min using smooth rod samples from two different sources.

One is the casting tensile samples directly produced by A356 melt in laboratory with 10 mm diameter and 80 mm gauge length. The other is directly cut from the wheel rib with 5 mm diameter and 25 mm gauge length. The macrostructure and microstructure of the alloys were examined using a Nikon MBA-21000 optical microscope with a Prix image collect system. The fracture surface of tensile samples was observed with a JSM-5600 scanning electronic microscope (SEM).

| Table 1 The composition of A356 alloys and wheels (%)
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<tbody>
<tr>
<td>Testing A356 alloys</td>
<td>Si</td>
<td>Fe</td>
<td>Mg</td>
<td>Ti</td>
<td>Sr</td>
<td>Cu</td>
<td>Al</td>
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<tr>
<td>Tradition A356 alloy</td>
<td>6.79</td>
<td>0.119</td>
<td>0.323</td>
<td>0.118</td>
<td>0.008</td>
<td>0.008</td>
<td>Bal.</td>
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<tr>
<td>Testing car wheels</td>
<td>6.76</td>
<td>0.116</td>
<td>0.316</td>
<td>0.113</td>
<td>0.017</td>
<td>0.008</td>
<td>Bal.</td>
</tr>
<tr>
<td>Tradition car wheels</td>
<td>6.57</td>
<td>0.109</td>
<td>0.316</td>
<td>0.109</td>
<td>0.008</td>
<td>0.009</td>
<td>Bal.</td>
</tr>
<tr>
<td>Testing motorcycle wheels</td>
<td>6.85</td>
<td>0.155</td>
<td>0.362</td>
<td>0.125</td>
<td>0.028</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
<tr>
<td>Tradition motorcycle wheels</td>
<td>6.83</td>
<td>0.175</td>
<td>0.375</td>
<td>0.105</td>
<td>0.008</td>
<td>0.008</td>
<td>Bal.</td>
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3. Results and discussion

3.1 Production of low-titanium alloys and grain refinement of A356 alloys

Fig. 1 shows the absorptivity of titanium, the actual titanium content and the required titanium content of experimental aluminum alloys. The titanium content of the aluminum alloys could be easily controlled, and the measured values of titanium content were rather close to the required content. The absorptivity of titanium was kept above 95% after the titanium content became stable.

According to the thermodynamic and the electrochemical calculation results, the Gibbs free energy of the thermal reduction reaction of TiO$_2$ with aluminum melt at 1 213−1 233 K is between -204 470.66 and -203 630.66 J·mol$^{-1}$. The value of chemical equilibrium constant is $6.45 \times 10^7$ to $4.28 \times 10^8$. The theoretic decomposition voltage of TiO$_2$ is about 0.73 v and 0.85 v when the decomposition
product in anode is CO and CO$_2$, respectively, which is lower than that of Al$_2$O$_3$ (about 1.08 v and 1.16 v, respectively). The titanium can be preferentially precipitated in cathode by the thermal reduction and the electrochemical deposition of TiO$_2$ in cathode. Both the absorptivity of titanium during electrolytic process and the titanium content of alloys produced are affected by the loss of the TiO$_2$ and its solubility in electrolyte, especially, the loss of TiO$_2$. About five percent of titanium was lost in the present test, which was mainly attributed to that some TiO$_2$ powder was drafted out by the circulating air fan. Since almost all of the TiO$_2$ added into electrolyte can be decomposed into titanium after the solubility of TiO$_2$ in electrolyte approaches to saturation, the fluctuation of titanium content of the alloys is relatively insignificant, and it can be easily eased by controlling the quantity of TiO$_2$ added into electrolyte.

Fig.2 shows the macrostructure of the direct electrolytic low-titanium aluminum alloy and pure aluminum. It can be seen that the direct electrolytic low-titanium aluminum alloy contains fine equiaxed grains, while the pure aluminum reveals the typical coarse columnar structure. The macrostructure and microstructure of both testing and tradition A356 alloys are shown in Fig.3. The grain of testing A356 alloys is, to some extent, finer than that of the tradition A356 alloys. The dendrite cell size of the former is smaller than that of the latter.

For both the testing A356 alloys and the tradition A356 alloys, the grain refinement mechanism can be explained by the combination effect of the compositional undercooling from alloying elements (e.g. Si, Ti and Mg) and the heterogeneous nucleation of TiAl$_3$ or Ti (Al, Si)$_3$[7,8]. Because the content of alloy elements, the casting processes and heat treatment processes are similar to each other, the difference of the microstructure and the mechanical properties between two kinds of A356 alloys must be related to the titanium alloying method.
Xiangfa LIU et al suggested that the effect of grain refinement in aluminum can be affected by the microstructure of the Al-Ti, Al-Ti-B or Al-Ti-C master alloys\cite{16-17}. The grain refining efficiency of master alloys largely depends on the surface characteristics, the morphologies, the size and the distribution of the TiAl$_3$, TiB$_2$, or carbides particles. They found that the smaller the size of the compounds, the better the effect of the grain refinement. Homogeneous distribution of the compounds in the melt is beneficial to the grain refinement, due to the effect of microstructure heredity of TiAl$_3$, TiB$_2$, or carbides particles in the master alloys. For the direct electrolytic aluminum alloys, the distribution of titanium in alloys is homogeneous under the stirring of the anode magnetic field during electrolytic process. A vast number of TiAl$_3$ particles can be in situ precipitated from melt during the billet solidification, letting the grains of low-titanium alloys billets be self-refined into the fine equiaxed structure. When the low-titanium aluminum alloy billets are remelted to produce the testing A356 alloys, a high number of the intrinsic TiAl$_3$ particles existing in the billets are transmitted to the A356 melt, remaining either as TiAl$_3$ particles or in the form of the Al-Ti atom clusters. Because the melting temperature is lower than that required for the disordering melt structure, the Al-Ti atom clusters can exist in melt for a long time. These TiAl$_3$ particles or Al-Ti atom clusters can serve as the effective heterogeneous nuclei of $\alpha$-Al grains, effectively reducing the grain size of the alloys. On the other hand, in the tradition A356 alloys, the heterogeneous nuclei for the $\alpha$-Al grains are the extrinsic TiAl$_3$ particles supplied by melting the Al-5Ti master alloys. The number and size of the heterogeneous nuclei of the $\alpha$-Al grains depend on the melting and fragmentation of TiAl$_3$ particles existing in master alloys. Although it is difficult to identify the TiAl$_3$ particles in the microstructure, it can be deduced that the number of the TiAl$_3$ particles is smaller, the size of the TiAl$_3$ particles is larger and the distribution of titanium is inhomogeneous, compared to those of the testing A356 alloys. It is obvious that the melt quality of testing A356 alloys is superior to that of the tradition A356 alloys, leading to better effect of the grain refinement in the testing A356 alloys.

3.2 Tensile Properties of the A356 alloys and the wheels

Fig.4 exhibits the tensile properties of the tradition and testing A356 alloys treated by T5 and T6 processes. It can be found that about 250 MPa and 300 MPa of the tensile strength for testing A356 alloys are obtained after treated by T5 and T6 processes respectively, which is corresponding to that of the tradition A356 alloys. But, obviously, the ductility of the testing A356 alloy is significantly improved over that of the tradition A356 alloys. About 13.5% and 10.5% of elongation were achieved in the testing A356 alloy respectively under T5 and T6 treatment, while only about 8.4% and 6.5% in the tradition A356 alloys.

Fig.5 shows the testing car wheels and testing motorcycle wheels. Six tensile samples were cut from two kinds of wheel ribs respectively to measure the tensile properties (shown in Fig.6). The quality index $Q$, which can be used to properly evaluate the combination of strength and plasticity, is shown in Fig.7 for both A356 alloys and wheels. It can be seen that both the tensile strength and the elongation of testing wheels are higher than those of the tradition wheels. Although both the testing and the tradition wheels have about the same tensile strengths (approximately 250 MPa for motorcycle wheels and 270 MPa for car wheels), the testing wheels
present superior ductility (6.5% for testing motorcycle wheels and 8.5% for car wheels), to the tradition wheels (5.9% and 6.2% respectively). The testing A356 alloys and testing wheels have an excellent combination of strength and ductility/plasticity. Fig.8 shows the fracture surface of tensile samples of testing A356 alloys. Both tradition and testing alloys have a similar fracture surface that is mainly composed with dimples. It seems that the size of dimples of the testing alloys is larger than that of tradition alloys, which is corresponding to the results of tensile tests.

Fig.4 Mechanical properties of the testing A356 alloy and tradition A356 alloy

Fig.5 The wheels produced by testing A356 alloy and tradition A356 alloy

Fig.6 Mechanical properties of the testing wheels produced by testing A356 alloy and tradition A356 alloy
The mechanical properties of A356 alloys mainly depend on the morphology, size and spacing of eutectic silicon and Mg\textsubscript{2}Si particles as well as the dendrite cell size\textsuperscript{18-20}. In the present experiment, both the testing and the tradition A356 alloys have almost the same Si and Mg content and are treated by the same heat treatment process. The difference in mechanical properties between the two kinds of alloys must be related to the titanium alloying methods. The fracture of A356 alloys usually occurs in a ductile manner by initiation of voids at the eutectic silicon particles and the inclusions for their brittle fracture, debonding from the α-phase matrix, and then propagating through the α-phase matrix and along interdendritic channels. The testing A356 alloys have the fine grain and small size of the dendrite cell, which can increase the strain hardenability of α-phase matrix because of the increase in the resistance to dislocation motion. The uniformity and compatibility of deformation of the testing A356 alloys must be superior to that of tradition A356 alloys. Otherwise, decreasing the size of dendrite cells of α-phase would increase the total dendrite boundary area, and the crack growth resistance must be also increased because the crack may be branched and meandered at the boundary of dendrites. It is difficult to form voids by the accumulation and coarsening of micro-cracks, which would lead to improved strength and elongation of the alloys. Especially, the elongation of the testing A356 alloys is evidently better than that of the tradition A356 alloys.

4. Conclusions

1. The low titanium Aluminum alloys containing up to 0.2% Ti can be produced by adding a small quantity of TiO\textsubscript{2} into electrolyte. In this process, about 92% of current efficiency can be maintained, which is corresponding to that of pure Al production.

2. Above 95% of the absorptivity of titanium has been achieved during electrolysis. The titanium content of the alloy is stable and can be easily controlled by adjusting the addition of TiO\textsubscript{2} according to the requirement of commercial aluminum alloys.

3. The grains of low-titanium aluminum alloys can be effectively refined to equiaxed structure from the typical coarse columnar grain structure in the pure aluminum. The grain size of the testing A356 alloys and testing wheels produced by low-titanium aluminum alloys is smaller than that of tradition A356 alloys and tradition wheels produced using pure aluminum and Al-Ti master alloys.

4. The yield strength and tensile strength of testing A356 alloys and wheels are about the same as those of the tradition A356 alloys and wheels. But the ductility of the
former is superior to that of the latter. Comparing to the tradition alloys and wheels, the testing alloys and wheels have an excellent combination of strength and ductility.

References


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