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Grain refinement effects of Al based alloys with low titanium content produced by electrolysis①

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[Abstract] A series of Al based alloys with low titanium contents (mass fraction) from 0.178% to 0.526% were directly produced in ordinary industrial electrolyzer. The electrolyzing results show that producing Al based alloys with titanium contents of less than 0.30% without great loss of electrolysis efficiency is possible. The quantitative analysis shows that this method has a great refining effect on transiting the coarse columnar grains in pure Al to equiaxed grains. The grain sizes decrease with the increase of titanium content and tend to a low limit at about 130 μm. During the solidification, the non-equilibrium distribution of titanium leads to a great growth-restricting effect and a constitutional under-cooling zone in front of the growing liquid / solid interface.

[Key words] aluminum alloy; low titanium content; electrolysis; grain refinement

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1 INTRODUCTION

The grain refinement plays an important role in determining the ultimate properties of Al alloy products, it improves the tensile intensity and plasticity, increases feeding of complex castings, and reduces the tendency of hot tearing and porosity[1, 2]. The pure Al produced in industrial electrolyzer exists in coarse columnar grains. In order to refine the coarse grains into fine equiaxed grains, a common industrial application is to add inoculum as master alloys into the melts during the melting process even though ultrasonic vibrations and electromagnetic stirring are used some times[3~5]. These master alloys with high titanium contents are preliminarily produced by melting pure titanium either by thermal reduction of fluorides or chloride ($TiCl_4$) in molten aluminum in induction heating furnaces or electric arc furnaces[6]. Qiu et al[7~9] prepared the Al-Ti master alloys with titanium contents of less than 2% by electrolyzing titania in cryolite-alumina melts, and their method lowered the cost of producing Al-Ti master alloy. However, there are seldom reports about producing Al based alloys with low titanium contents by direct electrolysis, and the alloys can substitute for pure Al as the starting materials.

In the present work, a series of Al based alloys with low titanium contents have been directly produced in the industrial electrolyzer with common cryolite-alumina melts. The quantitative analyses on the grain sizes of these alloys have been carried out with image collection and treatment. It is shown that such a method can refine the grains. The mechanism of refinement has also been investigated. It is possible that this method will open a new refinement route of Al alloys in industrial application without great loss of electrolysis efficiency and may simplify processes.

2 EXPERIMENTAL

The industrial electrolyzing of Al based alloys with low titanium contents were carried out in one of series-wound electrolyzers in Tianyuan Aluminum Corporation (San Menxia City, Henan province, China). During the whole experiment the equipment and technological parameters were not changed, except of adding the preheated mixture of TiO_2(purity 98%) and Al_2O_3 powders into cryolite melts timely and the others electrolyzers were under the ordinary pure Al electrolyzing.

Samples for measuring macro-structures and grain sizes were taken from the same positions of ingots for pure Al and the Al based alloys. Image collections and quantitative analyses were carried out on Olypas microscope equipped with image analysis system. Grain areas and sizes of each alloy in 10 pieces of images were measured and were averaged as the mean values.

3 RESULTS AND DISCUSSIONS

3.1 Electrolyzing of Al based alloys

The parameters of electrolyzing the Al based alloys were : current intensity 42 kA; temperature 1218 ~ 1228 K; electrolyzer voltage 4.4 V; cryolite ratio 2.7~

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2.8; inter-polar distance 36~37 mm; height of aluminum melt 160~170 mm and height of cryolite melt 150~160 mm; extraction period of Al melts 3 d. Table 1 shows the compositions of pure Al and 5 kinds of Al based alloys.

The electrolyzing processes are successful, so producing Al based alloys by the addition of TiO_2 powders into cryolite-alumina melts are possible. From theoretical calculation and the practical test, titanium (L) depositions at the cathode are caused by electrolysis and thermal reduction.

On one hand, titania and alumina can be co-electrolyzed at the cathode under the electrolyzing condition of pure Al. Qiu et al[8] reported that the standard decomposition potentials for titania and alumina were 0.82 V and 1.15 V in 1 233 K respectively and the testing decomposition potentials for titania and alumina were in the range from 1.2 V to 1.5 V. The similar result can also be obtained from calculating the difference of standard decomposition potential between titania and alumina. With a carbon anode and with carbon dioxide as primary product, as well as with the reactions of $Al_2O_3 + 1.5C \rightarrow 2Al + 1.5CO_2$, $E_T^0(Al_2O_3) = 1.87 - 5.5\times10^{-4}T$ and $TiO_2 + C \rightarrow Ti + CO_2$, $E_T^0(TiO_2) = 1.43 - 4.78\times10^{-4}T$[9], the difference of standard decomposition potential between titania and alumina can be calcuated as $\Delta E_T^0(TiO_2) - \Delta E_T^0(Al_2O_3) = -0.44 + 0.72\times10^{-4}T$. If with a carbon anode and with carbon monoxide as primary product, as well as with the reactions of $Al_2O_3 + 3C \rightarrow 2Al + 3CO$, $E_T^0(Al_2O_3) = 2.32 - 1.01\times10^{-3}T$ and $TiO_2 + 2C \rightarrow Ti + 2CO$, $E_T^0(TiO_2) = 1.88 - 1.06\times10^{-3}T$[9], the difference of standard decomposition potential between titania and alumina can also be calculated as $\Delta E_T^0(TiO_2) - \Delta E_T^0(Al_2O_3) = -0.44 - 0.05\times10^{-3}T$. Regardless which one as the primary product, this difference value will always be negative within the electrolyzing temperature range from 1 218 K to 1 228 K. In other words, the standard decomposition potential of titania is less than that of alumina. So both titanium and aluminum can be co-electrolyzed at the cathode under the electrolyzing condition of pure Al.

On the other hand, as long as the thermal reduction $2Al(L) + 1.5TiO_2(\text{dissolved}) \rightarrow 1.5Ti(Al) + Al_2O_3(\text{dissolved})$ takes place in the liquid aluminum/electrolyte interface, dissolved titania can be deoxidized directly to titanium. At equilibrium stage, the relationship between the standard Gibbs energy for one mole titanium ΔG_T^0 and the temperature T (: 298 K~1 300 K) is supposed as $\Delta G_T^0 = -256.234 + 0.042T$ (kJ)[9]. Within the temperature range from 1 218 K to 1 228 K of this electrolysis process, the values of ΔG_T^0 are calculated to remain in large negative values from −205.078 kJ to −204.658 kJ, and the equilibrium constant K of this thermal reduction is also very large, for example[7], $K_{1\,233\,K} = 4.61\times10^8$. In both criteria of $\Delta G_T^0 < 0$ and large K value, it can be concluded that this thermal reduction can automatically proceed, so dissolved titania can directly be deoxidized to titanium in the electrolysis process.

The experimental results also show that when titanium content was less than 0.30%, the electrolysis efficiency of electrolyzing the Al based alloy decreases less compared with that of electrolyzing pure Al. However, the experimental results also show that the electrolysis efficiency still has a certain degree of loss when titanium content exceeds 0.30%. The efficiency loss may be due to the secondary oxidation reaction of titanium as $Ti - 4e \rightarrow Ti^{4+}$ and the above thermal reaction. The higher content of titanium not only induces the secondary oxidation of titanium react severely, but also promotes the thermal reaction, which will lower the production of aluminum. In the electrolysis process, there should not exist secondary solid particles such as Al_3Ti in the aluminum liquids, because these solid particles certainly will deposit at the cathode, and make the shape of bottom of the cathode changing from a convex to a concave. Considering such phenomenon would harm electrolyzing process severely, Qiu et al[7, 8] determined that the maximum titanium content in electrolysis should be less than 1.5% or 2%. However, our results show that when taking the electrolysis efficiency into account further more, titanium content should not exceed 0.30%.

3.2 Macro-structure analysis

Fig. 1 shows the ingots macro-structures of Al

Table 1 Compositions of pure Al and Al based alloys (mass fraction, %)

Sample	Cu	Mg	Fe	Ti	Si	Ni	Mn
Pure Al	0.02	0.006	0.087	0.006	0.047	< 0.002	< 0.003
Alloy 1	0.02	0.008	0.087	0.178	0.045	< 0.002	< 0.003
Alloy 2	0.025	0.008	0.082	0.214	0.040	< 0.002	< 0.003
Alloy 3	0.034	0.008	0.074	0.294	0.046	< 0.002	< 0.003
Alloy 4	0.038	0.008	0.086	0.477	0.060	< 0.002	< 0.003
Alloy 5	0.055	0.008	0.08	0.526	0.050	0.004	< 0.003

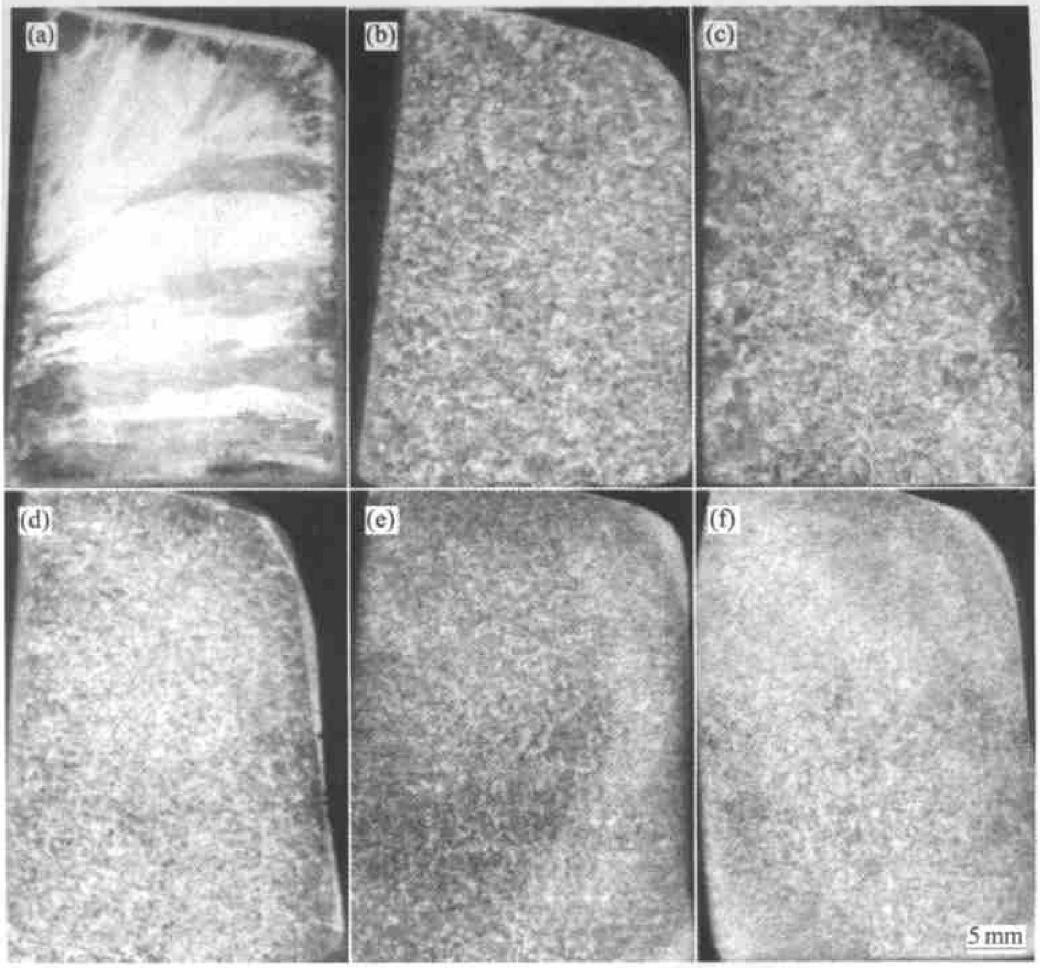

Fig. 1 Macro-structures of pure Al and Al based alloys with different contents of Ti
(a) — Pure Al; (b) —Ti: 0.178%; (c) —Ti: 0.214%;
(d) —Ti: 0.294%; (e) —Ti: 0.477%; (f) —Ti: 0.526%

(Ti: 0.006%) and the Al based alloys containing titanium of 0.178%, 0.214%, 0.294%, 0.477%, 0.526% respectively. It can be seen clearly that the coarse columnar grains appears in pure Al, while fine equi-axed grains appear in the Al based alloys, and the grain size decreases as the titanium content increases. So adding low titanium content by electrolyzing into alloy can promote the transition from columnar grains to fine equi-axed grains. This direct electrolysis reduces the producing and adding processes of Al-Ti master alloy, so we think this new method could be another efficient way for grain refinement. During the electrolysis, the Al melts can be obtained free from the contamination of oxygen, hydrogen and azote of the air, so the Al based alloys may get better quality. Furthermore, plentiful CO_2 gas will be produced from the anode[7], which plus the effect of electromagnetic field will make a uniform distribution of the solute titanium in the liquid of aluminum, and in turn be helpful to form even distribution of Al_3Ti particles in the following solidification.

3.3 Quantitative analysis of grain sizes

The mean grain areas and mean grain sizes of the pure Al and the Al based alloys are plotted against titanium contents as shown in Fig. 2 and Fig. 3. Low Ti content can make grain sizes have a sudden decrease and the sizes approach to a low limit about 130 μm, which is equivalent to the grain size of pure Al refined by solid or molten Al-5Ti-B master alloy[5, 10, 11], the mean area of pure Al refined by Al-5Ti-B master alloy[5, 10] is 0.018 mm^2, and the grain size should be about 134.2 μm. Mark et al[12, 13] have studied in detail the effect of

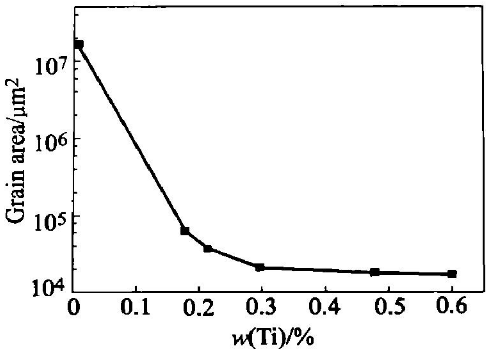

Fig. 2 Grain areas against Ti content

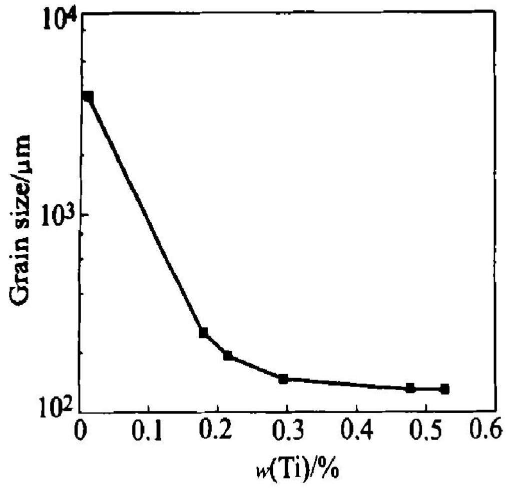

Fig. 3 Grain sizes against Ti content

solute titanium contents on grain sizes of pure Al, and found that the refined grain sizes approach to the low limit at about 200 μm.

During solidification process of ingots, under cooling is required for both homogeneous nucleation and heterogeneous nucleation. At the beginning of solidification, the driving force for nucleation is usually thermal under cooling in the melts at the mold wall. Thermal under cooling is quickly dissipated by latent-heat evolution, and there will be no further nucleation in absence of solute, as a result, the grains will continue growing until solidification is complete to form columnar grains. Such case can be found in Fig. 1 where the grains of pure Al exhibit coarse columnar grains. It has been reported that solute elements such as titanium, silicon or ferrum elements in Al melts are very important for grain refinement[12, 14, 15]. During the non-equilibrium solidification, the solubility of solute element is different in solid α phase and liquid aluminum, and solute element will be redistributed by diffusion at the solidification front. This non-uniform distribution will cause segregation and constitutional under-cooling zone in front of the growing interface. The necessary condition for the presence of constitutional under-cooling in the Al-based alloy whose dominating structure being α solid-solution is

$$G/R \leqslant mc_0(1-K_0)/(DK_0)$$

where G is the temperature gradient of the melts, R the solidification rate, c_0 the solute content in the melts, m the liquidus slope, $K_0 = c_s/c_l$ the partition coefficient between the equilibrium concentrations of solid and liquid at the growing interface, and D the solute diffusion coefficient in the melts. As the rise of R, c_0 and $|m|$ or the fall of G, D and $|1-1/K_0|$, the under-cooling degree tends to increase. Considering the effect of solute element on the grain refinement is directly ascribed to constitutional under-cooling[3, 14], Spittle and Sadli[15] used a super-cooling parameter P defined as $mc_0(K_0-1)/K_0$ to describe the solute effect, they found that with the increase of P the grain size decreases to a minimum limit at P value of about 15~ 20 K. If the effect of solute element is supposed as segregation and growth restricting on the solid-liquid interface of new grains[3, 12, 14, 16], the G_{RF} defined as $mc_0(K_0-1)$ was used to describe the solute effect. The grain size decreases as the G_{RF} increases. For titanium, m is 30.7 K/%, K_0 is about 9, $m(K_0-1)$ is 245.6 K/%[12], (or m is 35 K/%, K_0 is about 7, $m(K_0-1)$ is 210 K/%)[3]. For the Al based alloy by electrolyzing, providing that titanium element has approached its maximum solubility in Al melts, i. e. $c_0 = 0.15\%$[12], then the value of G_{RF} and P can be calculated. And when taking titanium into account only, the values of G_{RF} and P are 36.84 K (or 31.5 K) and 4.09 K (or 4.5 K) respectively; when considering all the solute elements including Ti and impurity elements of Fe, Si, Cu and Mg into account, the values of ΣG_{RF} and ΣP are respectively 37.483 K (or 32.019 K) and 19.299 K (or 16.525 K). The G_{RF} of titanium accounts for 98.3% (98.39%) of total ΣG_{RF}. So titanium has a large G_{RF} factor, and may have a great growth-restricting effect. Although P of titanium is smaller than the required value for the presence of limit grain size, ΣP has been already in the required range of 15~ 20 K, and our results show that the grain size of the Al based alloy has achieved the minimum limit.

3.4 Secondary particle and effect on grain sizes

During the solidification of the Al based alloys, secondary particles Al_3Ti will precipitate from the melts. The solute titanium has a great growth-restricting effect and provides the necessary under-cooling for activating heterogeneously nucleating of the potential nuclei of Al_3Ti phase or facilitates the nucleation by the peritectic reaction[2, 12]: $Al_3Ti + Al\ (L) \rightarrow \alpha\text{-}Al\ (S)$. The α-Al has the face-centered cubic lattice structure[11] and it favorites matching with particles of the body-centered tetrahedron lattice structure, so α-Al grains can be easily nucleate on the Al_3Ti particles[13]. The secondary particle of about 5 μm in diameter is found in the center of α-Al grain under SEM (shown in Fig. 4), and it is determined to be Al_3Ti phase structure from the energy spectrum analysis (shown in Fig. 5). Around the Al_3Ti particles there are few etched holes, however a little far away, there is a uniform distribution of the etched holes in similar shapes extending outward along radius orientation centered and around the Al_3Ti phase particle. This behavior indicates that the initial nucleating rate is rapid, and the dendrites grow at equal rates towards the radius orientations. This growth behavior can be considered as the free dendrite growth, and growing of grains will be completed until being

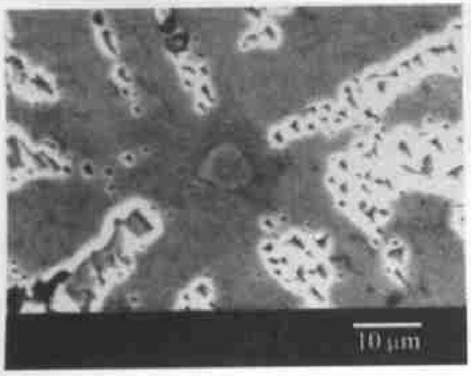

Fig. 4 Secondary particles in center of α-Al

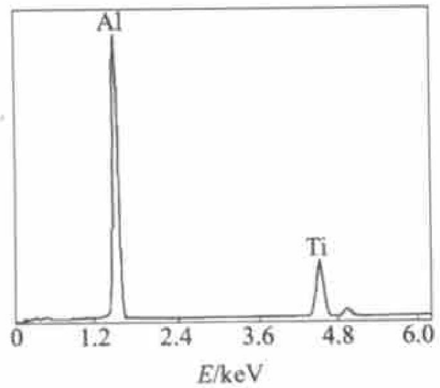

Fig. 5 Analysis of energy spectrum

contacted with the nearby growing grains. So, the equi-axed grains are formed.

The refinement mechanism of the Al based alloy by electrolysis has not been very clear until now. For example, whether the solute or the potency of nucleating particle plays main role in grain refining? And which parameter, such as G_{RE}, P or others, should be used to describe the solute effect? Many researchers think that both the solute effect and the potency of nucleating particles are important to grain refining[3, 12, 15, 16]. In our opinion, the solute titanium element is essential to promote the columnar to equi-axed transition for the Al based alloys produced by electrolysis. Compared with that of the addition of master alloy, the Al based alloys produced by electrolysis may contain higher solute content of titanium in the melts, which may have higher values of both G_{RF} and P. The higher of growth-restricting, the under-cooling may activate more nuclei in front of interface and more heterogeneous nucleation can occur fully at the same time. So the equi-axed grains may form in the Al-based alloys instead of columnar grains.

The industrial electrolyzing of Al based alloys was carried out in one month. The Al melts quantities in the extraction period for the 5 kinds of alloys with different contents of titanium were obtained. The results showed that the electrolysis efficiency had a certain degree of loss when the titanium contents were over 0.30% whereas the electrolysis efficiency decreased less when titanium contents were less than 0.30%. The project of electrolyzing the Al based alloy with titanium content less than 0.30% for several months is being carried out in order to determine the effect of titanium on the electrolysis efficiency. As the refinement effect by addition of Al-Ti-B master alloy is proved better than that by only addition of Al-Ti master alloy, the project of directly electrolyzing the Al based alloy with low contents of titanium and boron is also being studied.

4 CONCLUSION

The experiment shows that it is possible to produce Al based alloy with titanium content less than 0.30% in the industry electrolyzer for producing pure Al without great loss of efficiency. Adding titanium by electrolysis promotes the grain transition from coarse columnar to fine equi-axed. The grain sizes approach to the low limit at about 130 μm as the titanium contents increase. During the solidification, the non-equilibrium distribution of titanium leads to a great growth-restricting effect and a constitutional under-cooling zone in front of the growing liquid/solid interface.

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