

## A NEW KIND OF Al-5Ti-0.3C MASTER ALLOY AND ITS REFINING PERFORMANCE ON 6063 ALLOY

Enzhao Wang, Sida Liu, Jinfeng Nie, Tong Gao, Tao Wang, Xiangfa Liu\*

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, 17923 Jingshi Road, Jinan 250061, PR China

\*Corresponding author. Tel.: +86 531 88392006; fax: +86 531 88392006.

Keywords: Al-Ti-C master alloy; 6063 aluminum alloy; Heterogeneous nucleation; Grain refinement limit; Mechanical properties; Corrosion resistance

### Abstract

A kind of Al-5Ti-0.3C master alloy with uniform microstructure has been prepared using a new technology. The pre-nucleating TiC particles with an average size of about 0.3 $\mu$ m are dispersed homogeneously in the  $\alpha$ -Al matrix.

This new Al-5Ti-0.3C master alloy has great refining performance on aluminum alloys. It is found that the average grain size of 6063 alloy can be reduced from 3000 $\mu$ m to 40 $\mu$ m by the addition of the prepared Al-5Ti-0.3C master alloy and the refining efficiency does not fade obviously within 60 min. Furthermore, the mechanical properties and corrosion resistance of 6063 alloy are also improved. The ultimate tensile strength and hardness of the 6063 alloy can be largely improved from 170MPa, 35 to 271MPa, 81.7, respectively. In addition, the corrosion resistance is also enhanced largely. Finally, the possible mechanisms are also discussed.

### Introduction

Due to light weight and high strength, aluminum alloys obtain widespread applications in industries [1]. 6063 alloy is a kind of Al-Mg-Si series alloys which can be strengthened by heat treatment, and it is always known as architectural and decorative alloy because of its light weight, good corrosion resistance, easy coloring and hot extrudability [2, 3]. According to statistics, the usage of aluminum profiles in the world accounts for about half of the total aluminum alloys, among which more than 60% are 6xxx series alloy. In addition, it becomes a potential corrosion resistant aluminum alloy as a widespread application on shipbuilding industry in recent years [4].

Nowadays, with increasing demand on aluminum alloys with high quality, how to significantly improve the comprehensive mechanical properties and corrosion resistance becomes an urgent problem. Grain refinement of aluminum and its alloy castings through additions of grain refiners has been a common industrial practice [5, 6]. It is an effective way to achieve a fine equiaxed grain structure and improve the comprehensive mechanical properties and corrosion resistance of aluminum products [7]. At present, Al-5Ti-0.3C and Al-5Ti-1B master alloys are the most widely used grain refiners for aluminum alloys in industries [8, 9], thus it is necessary to take further detail research to study their

grain refining performance on 6063 alloy [10-13]. The present study aims to research the grain refining performance of Al-5Ti-0.3C master alloy on the alloy and reveal the variation of the comprehensive mechanical properties and corrosion resistance of 6063 alloy under the addition of Al-5Ti-0.3C.

### Experimental procedures

The chemical composition of 6063 alloy used in the experiments is presented in Table 1. Al-5Ti-0.3C master alloy was prepared by pure Ti (99.8%, all compositions quoted in this work are in wt. % unless otherwise stated), Al-5C master alloy and commercial pure Al (99.7%) using a melt reaction method in a high frequency induction furnace. The used Al-5Ti-1B master alloy is rod-like and provided by Shandong Al & Mg Melt technology Co. Ltd.

Table 1 Chemical composition of 6063 alloy used in the experiments

Element	Mg	Si	Fe	Cu	Mn	Ti	Al
Content (wt. %)	0.7	0.58	$\leq 0.25$	$\leq 0.1$	$\leq 0.1$	$\leq 0.1$	balance

A series of grain refining tests for Al-5Ti-0.3C and Al-5Ti-1B master alloys on 6063 alloy with different additions, *i.e.* 0.2%, 0.5%, 1.0%, 1.5% and 2.0%, were carried out. At first, the 6063 alloy was melted in an electrical resistance furnace at 720 $^{\circ}$ C  $\pm$  10 $^{\circ}$ C. After 10 minutes holding, the grain refiners were added into the melt and stirred thoroughly. Then it was poured into a pre-heated KBI cylindrical steel mold with size of  $\varnothing 40$ mm  $\times$  25mm on a fireclay brick, which has an approximate cooling rate of about 6 $^{\circ}$ C/s, at regular intervals from 5 to 60 minutes [14]. After solidification, the bottom surface of the refined sample in contact with the brick was etched by a reagent (60%HCl + 30%HNO<sub>3</sub> + 5%HF + 5%H<sub>2</sub>O, the compositions here are in volume fraction). At last, the pictures of macrostructure were taken for each sample by a high scope video microscope (HSVM, KH-2200), and the average grain size was determined using the linear intercept method.

Specimens obtained at the same position from the above samples were heat-treated in the following process: solution treated at 415 $^{\circ}$ C for 2.5h and 520 $^{\circ}$ C for 1h, respectively, water quenched, aging treated at 175 $^{\circ}$ C for 8h and cooled in air, and then measured the

hardness (HB) by HB-3000C Brinell hardness tester with parameters of 10/1000. Each value is an average of at least five separate measurements taken at random places on the surface of specimens.

Furthermore, 6063 alloy was melted as the method mentioned above and used 0.5%  $C_2Cl_6$  for slag-removing and degassing, then added one of the master alloys and poured into a pre-heated (about 200 °C) mold to obtain tensile test bar. It was carried out by the same heat treatment procedure as the hardness testing and machined to tensile test specimens according to the GB/T228-2002 standard [15], and then tested by electronic all-purpose test machine at ambient temperature. In each case, the tensile strength data given below are an average value of four specimens.

In addition, Electrochemical measurements on the samples obtained from the above two groups of grain refinement tests in a 3.5% NaCl electrolytes solution were carried out using a typical three-electrode system: working electrode, platinum counter electrode and a saturated calomel electrode (SCE) and every sample was repeated in triplicate at a minimum. CHI660E advanced electrochemical workstation was used to measure the potentiodynamic polarization curves with a scanning rate of 5mV/s at room temperature, and the  $J_{corr}$ ,  $E_{corr}$ ,  $J_{pass}$  and the  $E_{pit}$  were measured via polarization curves. In addition, the surface morphologies of the samples after polarization experiments were examined using scanning electron microscopy (SEM).

## Results and discussion

### Microstructures of the Al-5Ti-0.3C and master alloy

Fig. 1 shows the microstructures of Al-5Ti-0.3C master alloy used in the experiments. It can be seen that second phase particles are dispersed in the Al matrix homogeneously. Fig. 1a shows the uniform microstructure of Al-5Ti-0.3C master alloy, and it shows that the alloy mainly contains two kinds of phases: needle-like  $TiAl_3$  and fine  $TiC$  particles. As illustrated in the magnified microstructure (Fig. 1b),  $TiC$  particles with sizes of about 0.3 $\mu m$  are disconnected with each other and dispersed in the  $\alpha$ -Al matrix homogeneously.

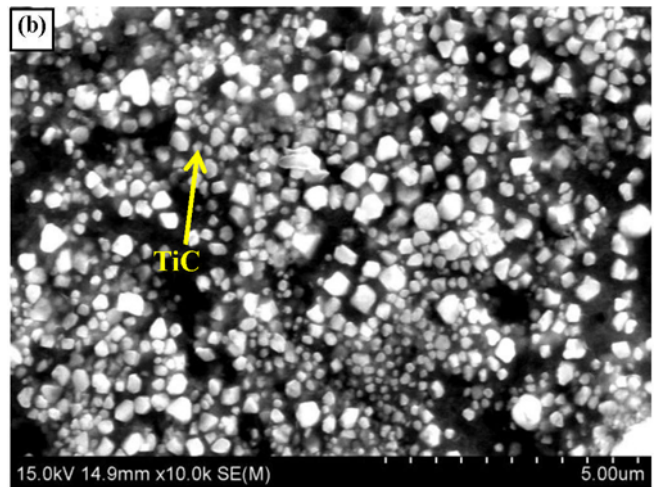
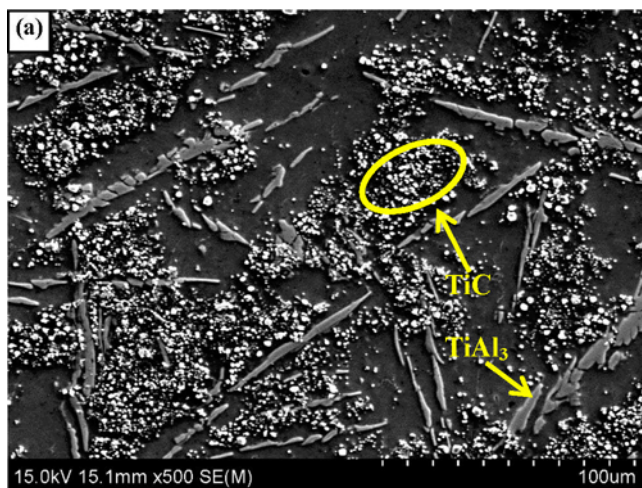


Fig. 1 Microstructures of (a, b) Al-5Ti-0.3C master alloy.

### Influence of grain refinement on mechanical properties of 6063 alloy

The Al-5Ti-0.3C master alloy has great refining performance on 6063 alloys. It is found that as adding level of Al-5Ti-0.3C master alloy were 0.2%, 0.5%, 1.0%, 1.5% and 2.0%, the average grain size of  $\alpha$ -Al grain can be reduced from several millimeters to about 220 $\mu m$ , 150 $\mu m$ , 95 $\mu m$ , 70 $\mu m$ , 40 $\mu m$ , respectively, and the refining efficiency does not fade obviously within 60 min.

In addition, the mechanical properties of 6063 alloy after refined by Al-5Ti-0.3C master alloy were also studied in this work. The ultimate tensile strength (UTS), elongation and hardness (HB) of the alloy before and after grain refinement are shown in Fig. 2 and Fig. 3, which indicates that both the values of UTS, elongation and hardness are obviously improved by adding grain refiner. It can be seen that the highest UTS of the alloy is about 271MPa and improved 59% than 170MPa of the blank samples without adding any grain refiner, and the highest elongation of it is about 13% and improved 225% than 4% of the blank samples, in addition, the highest hardness of the alloy is about 81.7 and improved 133% than 35 of the blank samples.

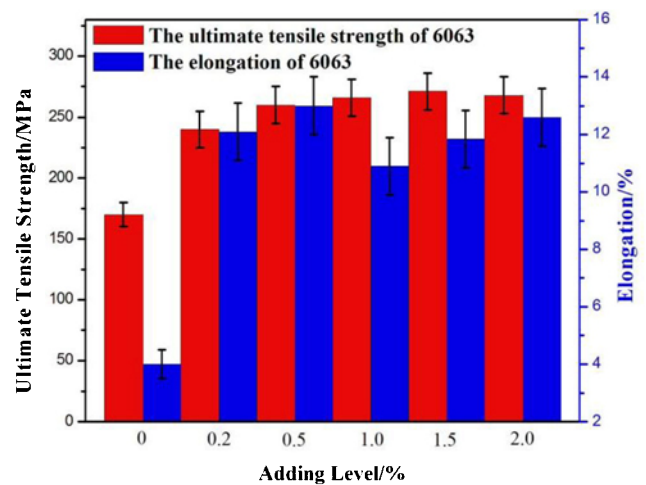


Fig. 2 Ultimate tensile strength (UTS) and elongation of 6063 alloy refined by Al-5Ti-0.3C master alloy.

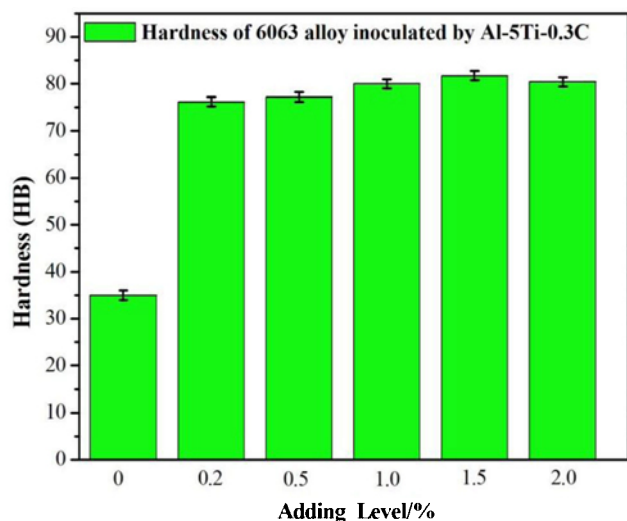


Fig. 3 Hardness (HB) of 6063 alloy refined by Al-5Ti-0.3C master alloy.

#### Effect of grain size on the corrosion resistance of 6063 alloy

The corrosion behavior of 6063 alloy inoculated by the above Al-5Ti-0.3C master alloy was also measured using a typical three-electrode system in 3.5% NaCl solution. Fig. 4 displays the polarization curves of the above 6063 alloy samples with different grain sizes and it shows the variation of corrosion current with increasing the corrosion voltage. Table 2 lists the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $J_{\text{corr}}$ ) fitted from Fig. 4 by Tafel extrapolation procedure. It can be seen that the  $E_{\text{corr}}$  improved and the  $J_{\text{corr}}$  decreased with decreasing of grain sizes, and the partial enlarged view of polarization curves indicates that the  $J_{\text{pass}}$  is also much lower when the grains are refined while the  $E_{\text{pit}}$  has no apparent variation, which can be seen that grain refinement can improve the corrosion resistance of 6063 alloy to some extent.

Table 2 The corrosion current density ( $J_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) of the 6063 alloy samples with different adding levels of Al-5Ti-0.3C master alloy.

Adding level (%)	0.2	0.5	1.0	1.5	2.0
$J_{\text{corr}}$ (A/m <sup>2</sup> )	1.298e-5	1.658e-5	1.251e-5	1.196e-5	0.973e-5
$E_{\text{corr}}$ (V)	-1.312	-1.264	-1.259	-1.272	-1.180

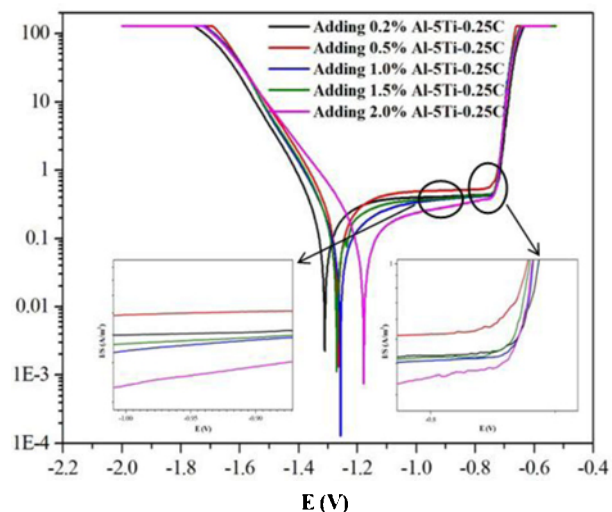


Fig. 4 Polarization curves and its partial enlarged view of 6063 alloy samples inoculated by Al-5Ti-0.3C master alloy.

#### Mechanism analysis

According to the literatures [16, 17], the morphology, dimension and distribution of TiC particles have major impacts on the grain refining efficiency. With smaller dimension and better dispersion of inoculating particles, the grain refining efficiency can be improved. It can be seen that TiC particles in Al-5Ti-0.3C master alloy with sizes of about 0.3 $\mu\text{m}$  are disconnected with each other and dispersed in the Al matrix homogeneously, thus, it is considered that the Al-5Ti-0.3C master alloy has great refining performance on 6063 alloy.

It is well known that due to the distribution of irregular arrangement of atoms and lots of crystal defects, grain boundary plays an important role as barrier for the transmission of the dislocations, *i.e.* grain boundary can obstruct plastic deformation [18]. The smaller grain size, the more grain boundary, the higher strength metals obtain in theory. The influence of grain size on the mechanical properties of a metal can commonly be described by the Hall-Petch formula:

$$\sigma_s = \sigma_0 + kd^{-1/2}$$

where  $\sigma_s$  is the yield strength,  $d$  is the grain size,  $\sigma_0$  and  $k$  are the constant. The formula indicates that a smaller grain size of the matrix leads to a higher yield strength. In addition, the research of Ref. [19] shows that the hardness of a metal is directly proportional to the inverse root of the grain size. On the other hand, 6063 alloy can be strengthened after solution and aging heat treatment by precipitating  $\text{Mg}_2\text{Si}$  phase. According to literatures, smaller grain size and broader area of grain boundary could promote the solution and precipitation of  $\text{Mg}_2\text{Si}$  phase [20, 21]. Therefore, the ultimate tensile strength, elongation and hardness of the alloy were largely improved after grain refinement.

Grain boundaries have special properties in terms of atomic coordination, reactivity and diffusion rates. Consequently, it is reasonable to expect fine grain surface with relatively high grain boundary densities to exhibit different electrochemical behavior (namely corrosion rates) than coarser grain surface with lower grain boundary densities. Grain refinement increases the areas of grain boundary which causes dispersion of crystal defects, and then lightens the electrochemical corrosion. According to the literatures [22, 23], the increasing of grain boundary makes a contribution to the forming of oxide film on the surface and

preventing the pitting corrosion. As a result, grain refinement can improve the corrosion resistance of 6063 alloy.

## Conclusions

- (1) The Al-5Ti-0.3C master alloy has great refining performance on 6063 alloy. The ultimate tensile strength (UTS), elongation and hardness (HB) of the alloy were largely improved after inoculated by Al-5Ti-0.3C. The highest UTS, elongation and hardness are about 271MPa, 13% and 81.7, and improved 59%, 225% and 133%, respectively, than the blank samples without adding any grain refiner.
- (2) Grain refinement can both increase the corrosion potential ( $E_{\text{corr}}$ ) and decrease the corrosion current density ( $I_{\text{corr}}$ ) and passive current density ( $I_{\text{pass}}$ ) of 6063 alloy, and then improve the overall corrosion resistance of the alloy.

## Acknowledgments

The authors wish to thank the financial support of the National Natural Science Foundation of China (No. 51071097) and the National Basic Research Program of China (973 Program, No. 2012CB825702).

## References

- [1] Y. Meng et al., "Effect of Vanadium on The Microstructures and Mechanical Properties of An Al-Mg-Si-Cu-Cr-Ti Alloy of 6XXX Series," *J. Alloys Compd.*, 573 (2013), 102–111.
- [2] A. Verma et al., "Influence of Cooling Rate on The Fe Intermetallic Formation in An AA6063 Al Alloy," *J. Alloys Compd.*, 555 (2013), 274–282.
- [3] F. Eckermann et al., "The Influence of Mg<sub>2</sub>Si Particle Reactivity And Dissolution Processes on Corrosion in Al-Mg-Si Alloys," *Electrochim Acta*, 54 (2008), 844–855.
- [4] T.D. Burleigh, A. Paris and K.H. Chan, "Technical Note: Photoelectrochemical Study of Inorganic Inhibitor Films Formed on Mild Steel in Aerated Municipal Water," *Corrosion*, 54 (1998), 237–240.
- [5] B. Yücel, "Production of Al-Ti-B Master Alloys From Ti Sponge And KBF<sub>4</sub>," *J. Alloys Compd.*, 440 (2007), 108–112.
- [6] K. Jiang and X.F. Liu, "The Effect of Melting Temperature And Time on The Tic Particles," *J. Alloys Compd.*, 484 (2009), 95–101.
- [7] M.A. Easton and D.H. Stjohn, "A Model of Grain Refinement Incorporating Alloy Constitution And Potency of Heterogeneous Nucleant Particles," *Acta Mater*, 49 (2001), 1867–1878.
- [8] S. Camero, E.S. Puchi and G. Gonzalez, "Effect Of 0.1% Vanadium Addition on Precipitation Behavior And Mechanical Properties of Al-6063 Commercial Alloy," *J. Mater Sci.*, 41 (2006), 7361–7373.
- [9] D.H. Lee, J.H. Park and S.W. Nam, "Enhancement of Mechanical Properties of Al-Mg-Si Alloys By Means of Manganese Dispersoids," *Mater. Sci. Technol.*, 15 (1999), 450–455.
- [10] V.H. López, A. Scoles and A.R. Kennedy, "The Thermal Stability of Tic Particles in An Al7wt.%Si Alloy," *Mater. Sci. Eng. A*, 356 (2003), 316–325.
- [11] A.L. Greer et al., "Grain Refinement of Aluminium Alloys by Inoculation," *Adv. Eng. Mater*, 1–2 (2003), 81–91.
- [12] M. Vandyoussefi, J. Eorth and A.L. Greer, "Effect of Instability of Tic Particles on Grain Refinement of Al And Al-Mg Alloys by Addition of Al-Ti-C Inoculants," *Mater. Sci. Technol.*, 16 (2000), 1121–1128.
- [13] G.S. Kumar, B.S. Murty and M. Chakraborty, "Development of Al-Ti-C Grain Refiners And Study of Their Grain Refining Efficiency on Al And Al-7Si Alloy," *J. Alloys Compd.*, 396 (2005), 143–150.
- [14] H.M. Ding, X.F. Liu and L.N. Yu, "Influence of Zirconium on Grain Refining Efficiency of Al-Ti-C Master Alloys," *J Mater Sci.*, 42 (2007), 9817–9821.
- [15] GB/T228–2002. *Metallic Materials–Tensile Testing at Ambient Temperature*. China Standard Press, 2002.
- [16] T.E. Quested and A.L. Greer, "The Effect of The Size Distribution of Inoculant Particles on As-Cast Grain Size in Aluminium Alloys," *Acta Mater.*, 52 (2004), 3859–3868.
- [17] P.L. Schaffer and A.K. Dahle, "Settling Behaviour of Different Grain Refiners in Aluminium," *Mater. Sci. Eng. A*, 413–414 (2005), 373–378.
- [18] M. Easton and D. StJohn, "Grain Refinement of Aluminum Alloys: Part II. Confirmation of, And A Mechanism For, The Solute Paradigm," *Metall. Mater. Trans. A*, 30 (1999), 1625–1633.
- [19] M. Abd El Aal et al., "Wear Properties of ECAP-Processed Ultrafine Grained Al-Cu Alloys," *Mater. Sci. Eng. A*, 527 (2010), 3726–3732.
- [20] X.L. Feng, H.J. Liu and S.S. Babu, "Effect of Grain Size Refinement And Precipitation Reactions on Strengthening in Friction Stir Processed Al-Cu Alloys," *Scripta. Mater*, 65 (2011), 1057–1060.
- [21] T. Wang et al., "Influence of A New Kind of Al-Ti-C Master Alloy on The Microstructure And Mechanical Properties of Al-5Cu Alloy," *J. Alloys Compd.*, 589 (2014), 19–24.
- [22] Z. Szklarska-Smialowska, "Fitting Corrosion of Aluminum," *Corros. Sci.*, 41 (1999), 1743–1767.
- [23] D. Song et al., "Corrosion Behavior of Ultra-Fine Grained Industrial Pure Al Fabricated by ECAP," *Trans. Nonferrous Met. Soc. China*, 19 (2009), 1065–1070.