

Article

Effect of Al-5Ti-0.62C-0.2Ce Master Alloy on the Microstructure and Tensile Properties of Commercial Pure Al and Hypoeutectic Al-8Si Alloy

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Abstract: Al-5Ti-0.62C-0.2Ce master alloy was synthesized by a method of thermal explosion reaction in pure molten aluminum and used to modify commercial pure Al and hypoeutectic Al-8Si alloy. The microstructure and tensile properties of commercial pure Al and hypoeutectic Al-8Si alloy with different additions of Al-5Ti-0.62C-0.2Ce master alloy were investigated. The results show that the Al-5Ti-0.62C-0.2Ce alloy was composed of α -Al, granular TiC, lump-like TiAl₃ and block-like Ti₂Al₂₀Ce. Al-5Ti-0.62C-0.2Ce master alloy (0.3 wt %, 5 min) can significantly refine macro grains of commercial pure Al into tiny equiaxed grains. The Al-5Ti-0.62C-0.2Ce master alloy (0.3 wt %, 30 min) still has a good refinement effect. The tensile strength and elongation of commercial pure Al modified by the Al-5Ti-0.62C-0.2Ce master alloy (0.3 wt %, 5 min) increased by roughly 19.26% and 61.83%, respectively. Al-5Ti-0.62C-0.2Ce master alloy (1.5 wt %, 10 min) can significantly refine both α -Al grains and eutectic Si of hypoeutectic Al-8Si alloy. The dendritic α -Al grains were significantly refined to tiny equiaxed grains. The morphology of the eutectic Si crystals was significantly refined from coarse needle-shape or lath-shape to short rod-like or grain-like eutectic Si. The tensile strength and elongation of hypoeutectic Al-8Si alloy modified by the Al-5Ti-0.62C-0.2Ce master alloy (1.5 wt %, 10 min) increased by roughly 20.53% and 50%, respectively. The change in mechanical properties corresponds to evolution of the microstructure.

Keywords: Al-Ti-C-Ce master alloy; preparation; microstructure; mechanical properties; commercial pure Al; hypoeutectic Al-8Si alloy

1. Introduction

It is well known that the structure modifying processes (morphology and fineness) strongly influence the mechanical properties and are commonly used in foundry practice of the non-ferrous metals and their alloys. The grain refinement of aluminum and aluminum alloy can significantly improve the mechanical properties, casting performance, deformation processing performance and surface quality of materials [1,2]. Thus, the grain refinement of aluminum and aluminum alloy is an important research subject in the modern aluminum processing industry.

The addition of Al-Ti, Al-B, Al-Ti-B and Al-Ti-C, as well as recently developed master alloys with other third elements, e.g., Zn, Si or rare earth (RE), has become a good way to decrease the mean grain size of the inoculated metals and alloys, particularly Al and Al-based alloys [3–7].

Because an Al-Ti-C master alloy has TiC particles and relatively few defects and faults related to Al-Ti-B refiner, it is considered as the most promising aluminum grain refiner [8]. It has the strengths

of containing TiC particles, small size, high dispersion in molten aluminum, and immunity to the poisoning of Zr and Cr atoms [9]. Thus, it has become important at home and abroad in recent years, and has good application prospects in the aluminum processing industry, especially in the aluminum sheet strip and foil processing industry. The key problems in the preparation of the Al-Ti-C alloy are the low wettability between the carbon source and molten aluminum and the difficulty in forming TiC [9–11]. It has been reported [12,13] that rare earth has a catalytic effect. Adding rare earth in the preparation of the Al-Ti-C alloy can promote the formation of the tiny particle TiC. Thus, Al-Ti-C-RE master alloy, whose refinement effect is better than Al-Ti-C master alloy, was developed [14].

There were many reports on rare-earth oxide as a reaction promoter in the preparation of composites [15,16], but there were a few reports on the application of rare-earth oxide in a direct melt reaction method to prepare Al-Ti-C alloy. The team headed by Wang Liandeng [17], in the preparation of the Al-Ti-C master alloy, with the addition of Ce₂O₃ to the fluoride salt method, discovered that it could not only lower the temperature of preparing alloy but also improve the wettability of C and molten aluminum and promote the formation of TiC particles [18]. The introduction of the titanium element by titanium fluoride resulted in the production of plenty of fluoride gas polluting the environment in the preparation, relatively long preheating and holding time and high energy consumption [13]. In this study, the Al-5Ti-0.62C-0.2Ce master alloy was prepared and adopted to modify commercial pure Al and hypoeutectic Al-8Si alloy with the aim of investigating the effect of the Al-5Ti-0.62C-0.2Ce master alloy on the microstructure of commercial pure Al and hypoeutectic Al-8Si alloy. At the same time, the tensile properties were also studied.

2. Experimental Procedures

The main materials used in the experiments included: Al powder (99.6%), Ti powder (99.3%), C powder (99.8%), CeO₂ powder (99.9%) and commercially pure Al (99.7%). The supplier, particle size of the powders, and purity are given in Table 1. First, the main raw materials were made through ball mixing and cold pressing into prefabricated blocks (Φ 25 mm \times 50 mm). The molar ratio of the composition of prefabricated blocks containing Al, Ti, and C powders was 5:2:1, and the amount of CeO₂ addition was 2 wt %. Second, the pure aluminum ingot was melted in a resistance furnace at 800 °C, and then the prefabricated blocks were added. About 3–5 min later, the melt was stirred by a graphite rod, and the melt temperature was again kept at 800 °C for 5 min. After purified and deslagged with C₂Cl₆, the melt was finally cast into a steel mould (Φ 50 mm \times 30 mm). After rough grinding, fine grinding, and electrolytic polishing (10% HClO₃ + 90% absolute alcohol, the composition of the electrolyte is in volume fraction, and the voltage is 20 V), the microstructure characterization of the samples was carried out by the JSM-7500 scanning electron microscope (SEM, SSX-550 fitted with Energy Dispersive Spectroscopy (EDS) equipment, Shimadzu Corporation, Kyoto, Japan) operated at 20 kV. Phase identification was performed by RigakuD/max-A X-ray diffract meter (XRD, PW 3040/60, PANalytical, Rotterdam, the Netherlands) with Cu K α radiation and an image plate detector over the 2 θ range of 20–90° at 0.02° step size.

Table 1. Characteristics of materials.

Materials	Supplier	Grain Size/ μ m	Purity/%
Al powder	The Northwest Aluminum Company	61–74	99.6
Ti powder	Shangxi Baoji state Construction Pioneer Metals Corporation	38–44	99.3
C powder	Qingdao Huatai Lubricate Pressurize Science & Technology	11–30	99.8
CeO ₂ powder	Tianjin Guanfu Fine Chemical Research Institute	1–2	99.5
Commercially pure Al	The Northwest Aluminum Company	-	99.7

Commercial pure aluminum (99.7%) was melted in a resistance furnace and heated to 730 °C. Al-5Ti-0.62C-0.2Ce master alloy (0.2 wt %, 0.3 wt %, 0.5 wt %, and 0.7 wt %) was added to molten aluminum, stirred and held for 5 min. It was purified and deslagged with C₂Cl₆ and cast into a steel mould (Φ 50 mm × 30 mm) with a preheated temperature of 200 °C. An experiment of the resistance to fading of the master alloy was conducted with the master alloy (0.3%) and the holding time (30 min, 60 min, 90 min). Pure aluminum samples were etched by a reagent (60% HCl + 30% HNO₃ + 5% HF + 5% H₂O, the compositions here are in volume fraction). Lastly, images were taken for each sample to analyze their macrostructures. The grain sizes were measured with the linear intercept method.

Hypoeutectic Al-8Si alloy was modified with Al-5Ti-0.62C-0.2Ce master alloy. A fixed amount of Al-8Si alloy was melted in graphite crucible and the temperature was risen to 730 °C with the addition of Al-5Ti-0.62C-0.2Ce master alloy (0.8 wt %, 1.0 wt %, 1.5 wt %, 2.0 wt %). It was stirred and held for 10 min. It was purified and degassed with C₂Cl₆ and cast into a steel mould. After the rough grinding, fine grinding, electrolytic polishing of samples, large optical microscope (OM, MEF3, Leica Inc., Wien, Austria) and SEM (SSX-550 fitted with EDS equipment, Shimadzu Corporation, Kyoto, Japan) were employed to observe the microstructure.

The room-temperature tensile test was carried out by an MST810 machine (MTS Systems Corporation, Eden Prairie, MN, USA). For tensile testing, all of the samples were cut and polished into dog-bone-shaped specimens with a gauge length of 100 mm and a cross nummular section of $d = 8.0$ mm. The operation of the testing machine was computer controlled and the digital data of load and displacement from the gage section were recorded. Tensile specimens were tested at a quasi-static strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

3. Results and Discussion

3.1. Microstructure of Al-5Ti-0.62C-0.2Ce Master Alloy

Figure 1 shows the XRD (X-ray diffraction) pattern of the Al-5Ti-0.62C-0.2Ce master alloy. As can be seen from Figure 1, except α -Al, there are many primary phases in Al-5Ti-0.62C-0.2Ce master alloy, such as TiAl₃, TiC and Ti₂Al₂₀Ce. Figure 2 shows the backscattering SEM image of the Al-5Ti-0.62C-0.2Ce master alloy. It can be seen from Figure 2a that there is a large amount of blocky particles is distributed with a size of roughly 5–7 μm in length and 4–6 μm in width on the Al matrix in Al-5Ti-0.62C-0.2Ce master alloy, among which the vast majority of blocky particles are gray, some are bright-white and there are plenty of granules with the size of 0.5–2 μm . Figure 2b shows the SEM image of blocky particles and granules.

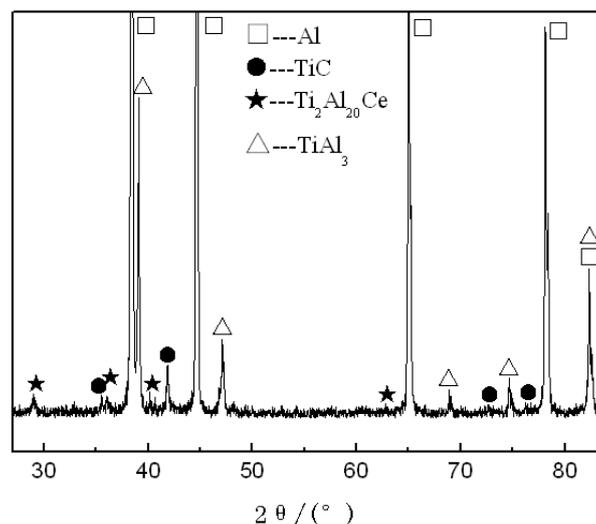


Figure 1. XRD pattern of Al-5Ti-0.62C-0.2Ce master alloy.

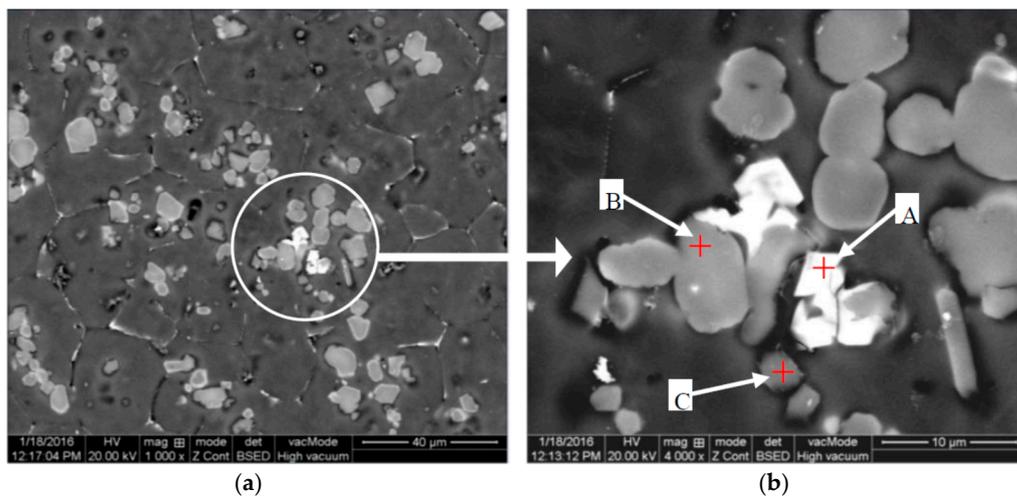


Figure 2. Microstructures of Al-5Ti-0.62C-0.2Ce master alloy: (a) SEM image; (b) SEM image of titanium compounds at higher magnification.

Figure 3 shows the EDS pattern of Point A in gray blocky particles, Point B in bright-white blocky particles and Point C in granule. As shown in Figure 3, Point A is composed of Ti, Al, Ce elements, Point B is composed of Al, Ti elements, and Point C is composed of C, Ti, Al elements. According to the analysis results of the XRD pattern of the Al-5Ti-0.62C-0.2Ce master alloy, we can see that the bright-white blocky particle in Figure 2b is $Ti_2Al_{20}Ce$, the gray blocky particle is $TiAl_3$ and the granule is TiC. The small size of TiC particles results in the detection of Al element in matrix by the energy spectrum.

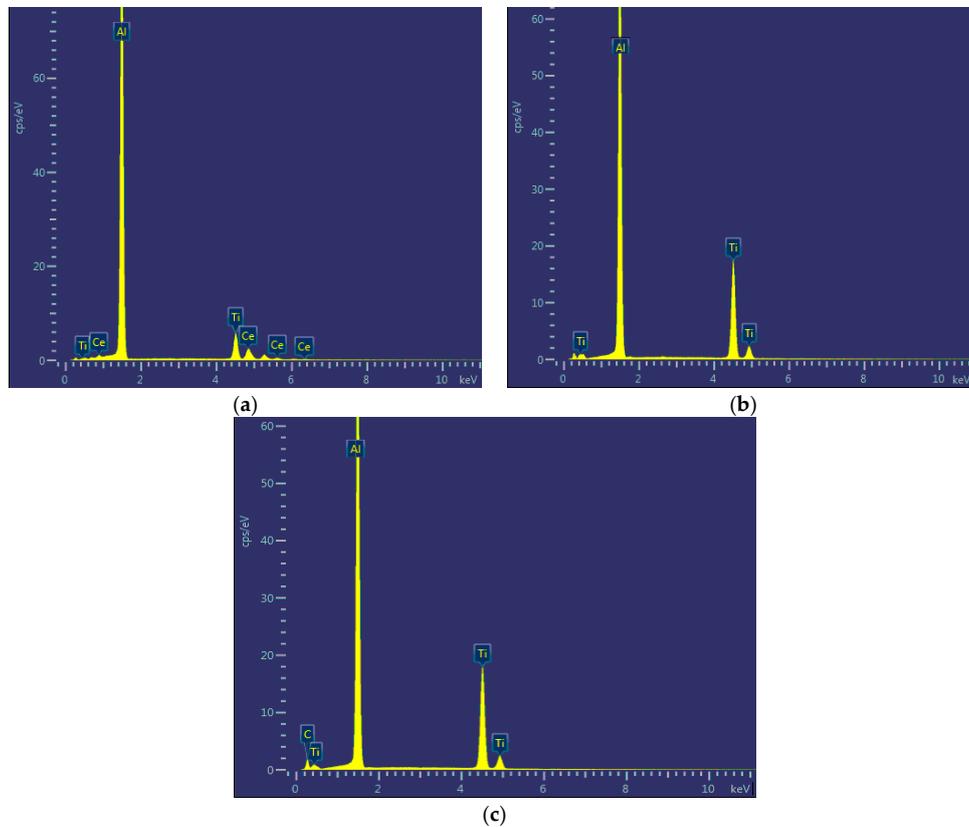
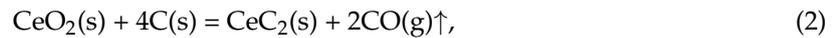


Figure 3. EDS composition analysis of points A, B and C in Figure 2: (a) Point A; (b) Point B; and (c) Point C.

In the reaction with the addition of CeO_2 , adding CeO_2 to aluminum liquid improves the wettability of Al powder, Ti powder, C powder and molten aluminum [17]. The thermite reaction between Al and Ti produces TiAl_3 phase and some free-state Ti. With energy supplied by a thermite reaction, CeO_2 can have a carbothermal reaction with C. Constant heat from the reaction results in the production of TiC particles and the active Ce element. The reaction equations are as follows [18]:



To conclude, the reaction of TiAl_3 with Ce produces a $\text{Ti}_2\text{Al}_{20}\text{Ce}$ new phase in the solidification of molten alloy. CeO_2 functions as both reactant and reaction promoter.

3.2. The Effect of Al-5Ti-0.62C-0.2Ce Master Alloy on Microstructure of Commercial Pure Al

Figure 4 shows the different additions of Al-5Ti-0.62C-0.2Ce master alloy (0.2%, 0.3%, 0.5%, 0.7%) on the grain size of commercial pure aluminum with the holding time of 5 min. It can be seen that the grain of the commercial pure aluminum prior to the addition is coarse and its macrostructure is composed of columnar grain and coarse equiaxed grain (Figure 4a). The grains with the addition of 0.2% Al-5Ti-0.62C-0.2Ce master alloy are significantly refined, and columnar grain and coarse equiaxed grain are replaced by small equiaxed grain (Figure 4b). Equiaxed grain is further refined with the addition of 0.3% Al-5Ti-0.62C-0.2Ce (Figure 4c). Figure 5 shows the relation curve between the content of Al-5Ti-0.62C-0.2Ce master alloy and the average grain size of solidified commercial pure aluminum samples. It can be seen that, when the addition level of master alloy is growingly increased, the grain size is increasingly decreased. However, a further increase in the addition level of Al-5Ti-0.62C-0.2Ce master alloy shows no significant improvement in grain-refining efficiency. When the addition amount of master alloy increases to a certain degree, refinement reaches the state of saturation and the grain size is not reduced any longer. The addition amount of a Al-5Ti-0.62C-0.2Ce master alloy (0.3%) is a critical point at which grain size can be refined to meet the demand of industrial production and the refiner will not be wasted. In terms of cost and benefits, the best addition amount of Al-5Ti-0.62C-0.2Ce master alloy is 0.3% in the refinement of commercial pure aluminum.

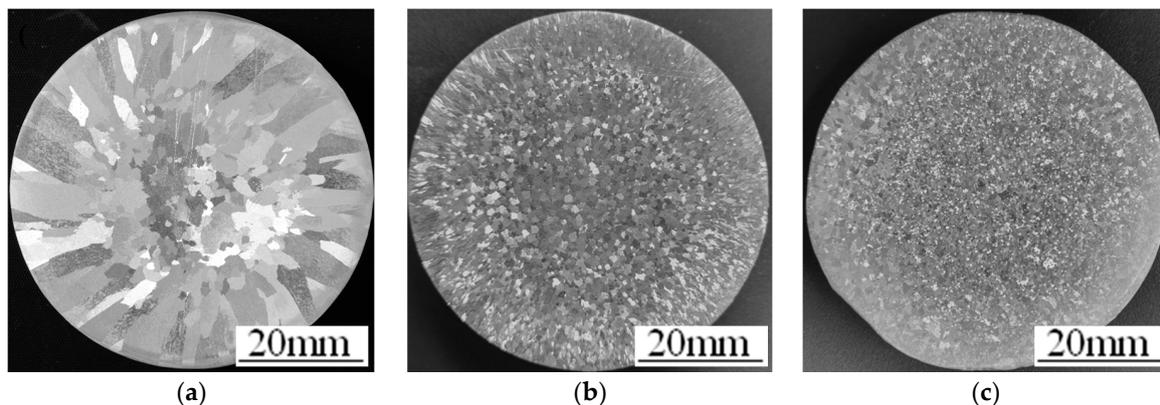


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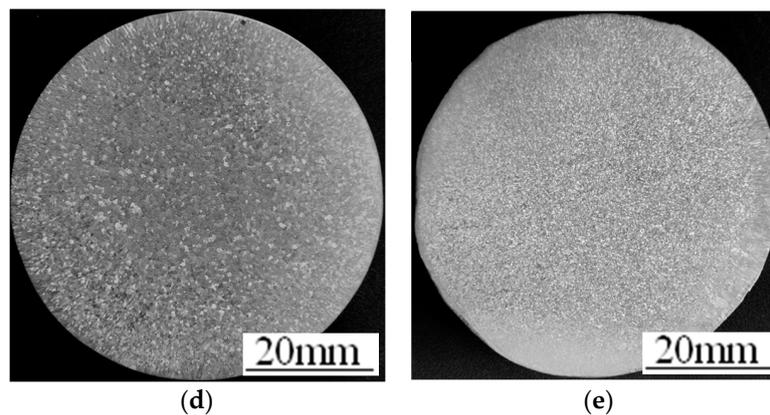


Figure 4. Effects of different additions of Al-5Ti-0.62C-0.2Ce master alloy on grain size of solidified commercial pure aluminum sample (holding for 5 min): (a) unmodified; (b) 0.2%; (c) 0.3%; (d) 0.5%; and (e) 0.7%.

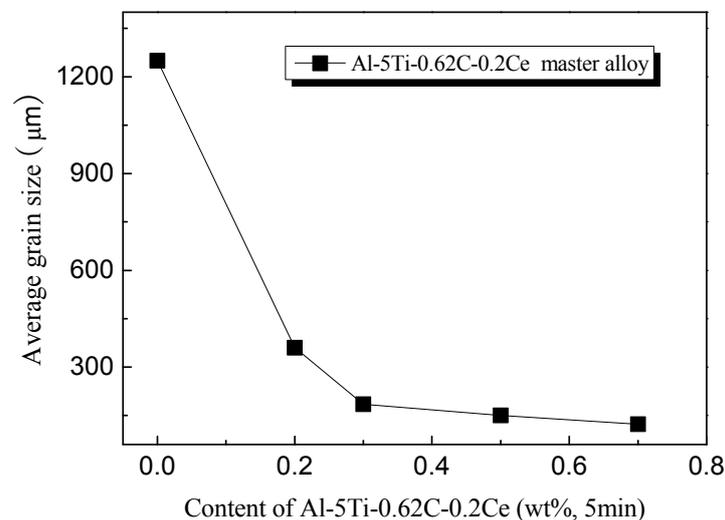


Figure 5. The relation curve between the content of Al-5Ti-0.62C-0.4Ce master alloy and the average size of solidified commercial pure aluminum samples.

Figure 6 shows the macrostructure of commercial pure aluminum refined with 0.3% Al-5Ti-0.62C-0.2Ce master alloy and then heat preserved for different times. As can be seen from Figure 6, after heat preserved for 30 min, commercial pure aluminum macro grains are equal-sized and small equiaxial structure and the refinement effect of grains do not fade, as shown in Figure 6a. As shown in Figure 6b, the holding time of 60 min results in slight fading of the refinement effect. The holding time of 90 min leads to significant fading of the refinement effect as shown in Figure 6c. The further increase of the holding time results in more significant fading of the refinement effect, as shown in Figure 6d. Figure 7 shows the fading curve of refinement effect of commercial pure aluminum samples refined with 0.3% Al-5Ti-0.62C and Al-5Ti-0.62C-0.2Ce master alloy. It can be seen that, with the same addition amount of master alloy, the resistance to the fading of refinement of Al-5Ti-0.62C-0.2Ce master alloy is better than that of Al-5Ti-0.62C master alloy.

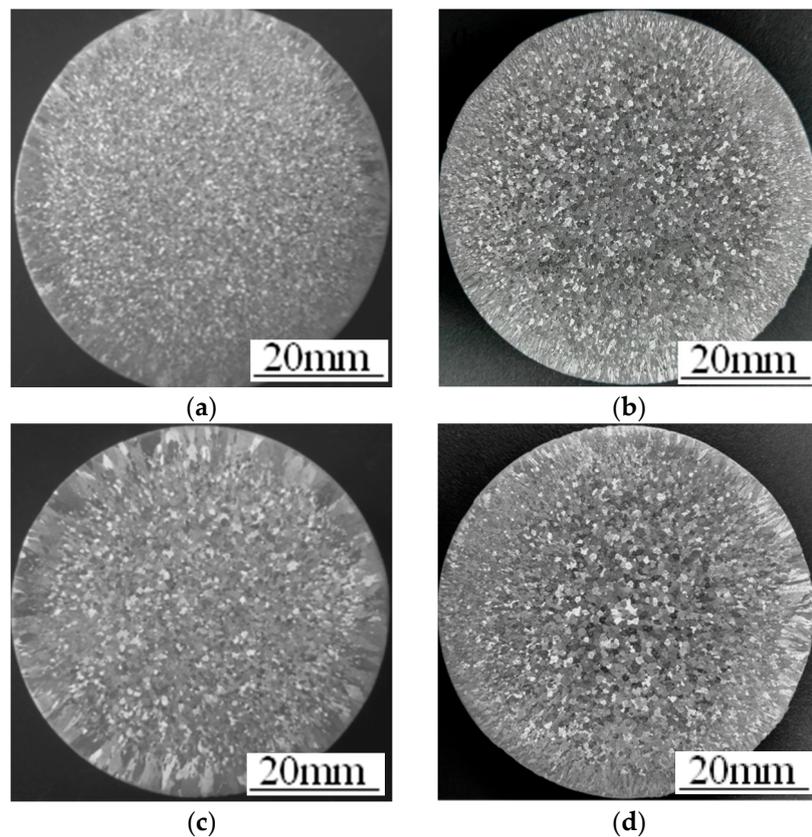


Figure 6. Effects of holding time on refinement effect of pure aluminum refined with 0.3% Al-5Ti-0.62C-0.2Ce master alloy: (a) 30 min; (b) 60 min; (c) 90 min; and (d) 120 min.

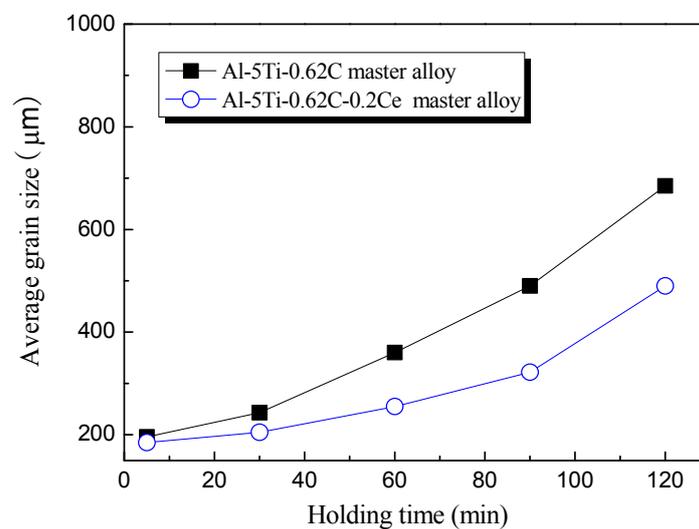


Figure 7. The relation curve between holding time and the average size of solidified commercial pure aluminum samples refined with 0.3% Al-5Ti-0.62C and Al-5Ti-0.62C-0.2Ce master alloy.

Despite the fact that there exist many differences about the grain refinement mechanism of Al-Ti-C master alloy, according to the previous research by the author [19] and relevant literature analysis [1,14], TiC particles can act as sites of heterogeneous nucleation and display better refinement effect with active Ti element in melt. The amount and activity of TiC particles have an important effect on the refinement effect of Al-Ti-C master alloy. It is a significant objective that the technique conditions can

be controlled and plenty of tiny and uniform-distribution TiC particles are prepared in Al-Ti-C master alloy. The activity and stability should be ensured in the refinement. It is extremely important to make full use of heterogeneous nucleation.

Adding CeO_2 promotes the formation of TiC particles, the nucleus of heterogeneous nucleation [17]. After adding Al-Ti-C-Ce master alloy to molten aluminum, as the holding time of molten liquid extends, $\text{Ti}_2\text{Al}_{20}\text{Ce}$ will melt before TiAl_3 . The melting of $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase can not only release free-state Ti atom earlier but also provide plenty of free-state Ce atom for molten aluminum. Ti atom and Ce atom of high activity produce a Ti-Ce compound protective layer around TiC particles. This layer improves the structural adaptability between TiC particles and α -Al, strengthens the wettability of them, and intensifies the heterogeneous nucleation capability of TiC particles. In addition, the presence of a protective layer ensures that TiC particles are equal-sized and tiny, and difficult to gather and deposit. Uniform-distribution TiC particles in a state of suspension in molten aluminum can not only make full use of the nucleus of heterogeneous nucleation, but also achieve sound resistance to the fading of refinement and ensure the long-term refinement effect [20].

3.3. The Effect of Al-5Ti-0.62C-0.2Ce Master Alloy on Microstructure of Hypoeutectic Al-8Si Alloy

Figures 8 and 9 show the as-cast microstructure of hypoeutectic Al-8Si alloy refined with different amount of Al-5Ti-0.62C-0.2Ce master alloy. As can be seen from Figures 8a and 9a, the α -Al grains are in the shape of coarse dendrites before the addition of refiner; and eutectic Si are distributed among α -Al dendrite in the shape of needle and strip. Figures 8b and 9b show hypoeutectic Al-8Si alloy modified with 0.8% Al-5Ti-0.62C-0.2Ce master alloy. Compared with those of Figures 8a and 9a, α -Al grains in Figures 8b and 9b are refined, dendrite become coarser and shorter, and plenty of eutectic Si becomes short rod-like. Figures 8c and 9c shows the addition of 1.0% Al-5Ti-0.62C-0.2Ce master alloy. It can be seen that α -Al grains are obviously refined. In terms of Al-8Si alloy without the addition of master alloy, sharp edges of some eutectic Si disappear and eutectic Si is in the shape of short rods or small blocks. Figures 8d and 9d are hypoeutectic Al-8Si alloy modified with 1.5% Al-5Ti-0.62C-0.2Ce master alloy. It can be seen that α -Al grains become smaller and eutectic Si is in the shape of short rods and grains. Figure 10 shows the relation curve between the content of Al-5Ti-0.62C-0.2Ce and the secondary dendrite arm spacing and eutectic Si in Al-8%Si alloy. It can be seen that, when the addition of Al-5Ti-0.62C-0.2Ce master alloy was further increased to 2.0%, the average size of the eutectic Si and secondary dendrite arm spacing increased and the morphology of the eutectic Si structure was transformed into a coral-like fibrous structure with coarse needles and platelets. Thus, the best addition amount of hypoeutectic Al-8Si alloy refined and modified with Al-5Ti-0.62C-0.2Ce master alloy is 1.5%.

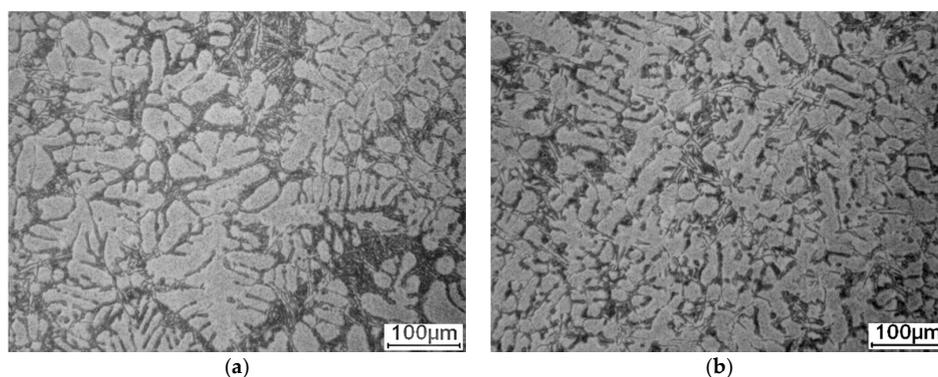


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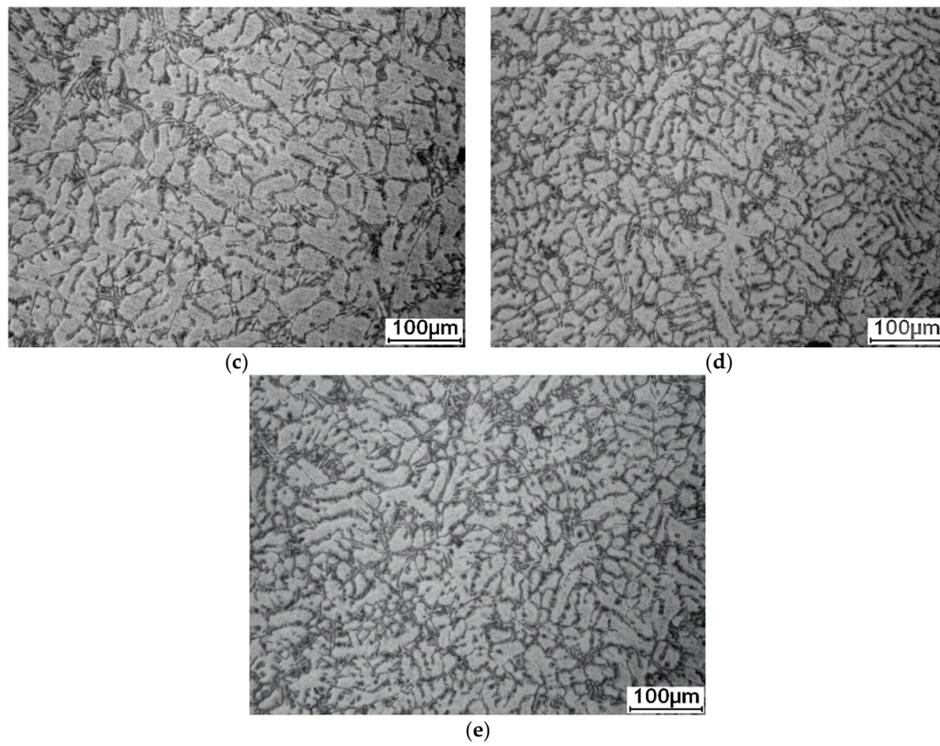


Figure 8. The α -Al in Al-8Si alloy modified with different amount of Al-5Ti-0.62C-0.2Ce master alloy: (a) unmodified; (b) 0.8%; (c) 1.0%; (d) 1.5%; and (e) 2.0%.

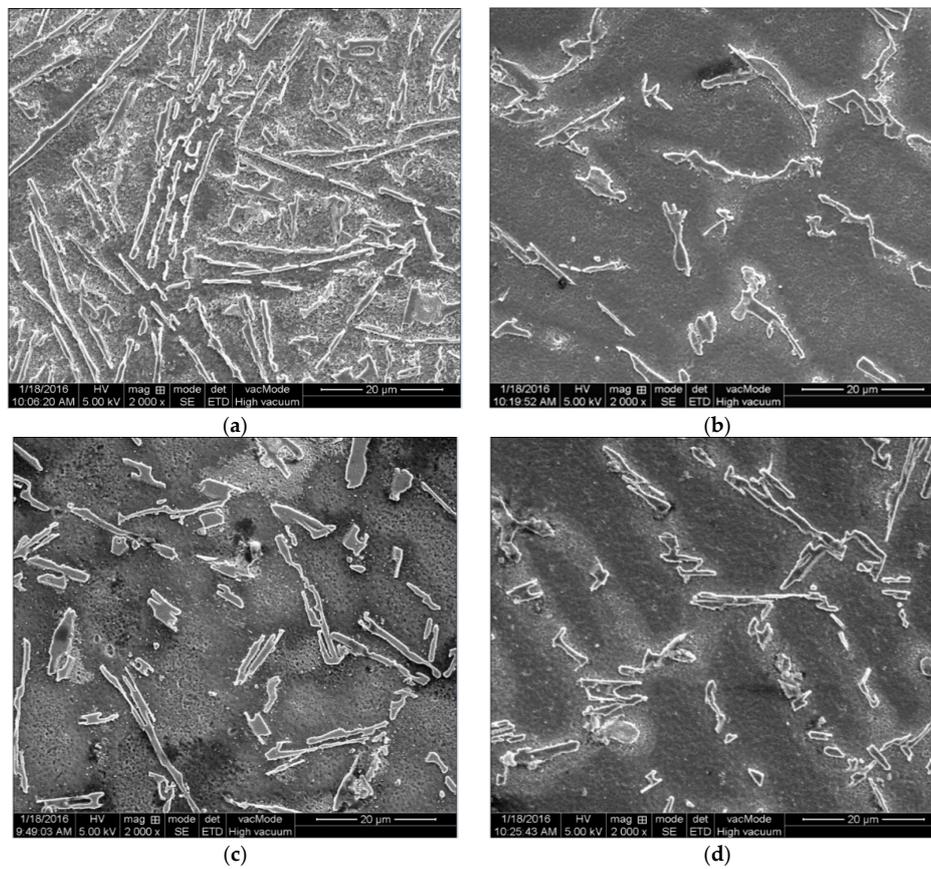
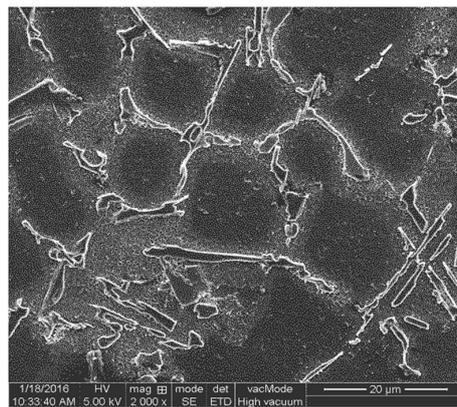


Figure 9. Cont.



(e)

Figure 9. Eutectic Si in Al-8Si alloy with different amount of Al-5Ti-0.62C-0.2Ce master alloy (a) unmodified; (b) 0.8%; (c) 1.0%; (d) 1.5%; and (e) 2.0%.

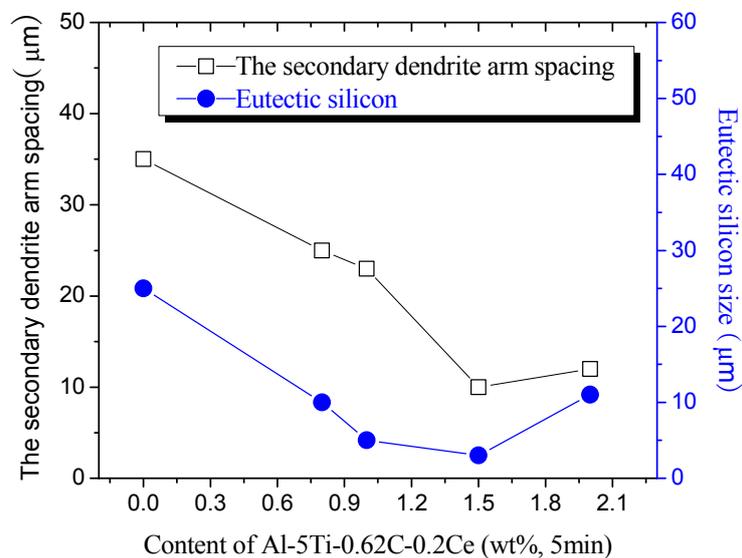


Figure 10. The relation curve between the content of Al-5Ti-0.62C-0.2Ce and the secondary dendrite arm spacing and eutectic Si in Al-8%Si alloy.

The research by Barerji and Reif at the University of Berlin, Germany indicates that, since $TiAl_3$ is thermodynamically unstable, it will be dissolved in aluminum liquid at a rate of $40 \mu\text{m}/\text{min}$. Due to the high melting point of TiC , it can be kept stable in molten aluminum and function as a nucleating agent [21]. The modification mechanism of Si in Al-8Si alloy modified with Al-Ti-C-Ce master alloy is mainly investigated from the perspective of twin geometric growth [22]. When the radius proportion of alternative and Si atom is 1.648:1, the modification effect of Si phase is the best. After the addition of molten aluminum to Al-Ti-C-Ce master alloy, the melting of $Ti_2Al_{20}Ce$ phase can provide a large amount of free-state active Ce atom for molten aluminum. The radiuses of Ce and Si atom are, respectively, 0.183 nm and 0.143 nm. The proportion of the two is 1.280:1, approaching 1.648:1. Thus, Ce atom plays a dominant role in the modification of Si phase.

3.4. The Effects of Al-5Ti-0.62C-0.2Ce Master Alloy on Mechanical Properties of Commercial Pure Al and Hypoeutectic Al-8Si Alloy

Figure 11 shows the tensile strength and ductility of commercial pure aluminum change with the addition amount of Al-5Ti-0.62C-0.2Ce master alloy. It can be seen that, before the addition of master

alloy, the tensile strength and ductility of commercial pure aluminum are, respectively, 55.72 MPa, 24.31% while the tensile strength and ductility of commercial pure aluminum are, respectively, 66.45 MPa, 39.34% after the addition of 0.3% Al-5Ti-0.62C-0.2Ce master alloy, a respective increase of 19.26% and 61.83%. The experiment shows that Al-5Ti-0.62C-0.2Ce master alloy can exert a significant effect on the tensile properties of Al-8Si alloy, as the Figure 12 shows. Before the addition of master alloy, the tensile strength and ductility of Al-8Si is, respectively, 151 MPa and 3.4%. As the amount of master alloy increases, the tensile strength and ductility of Al-8Si firstly increases and then declines. When the amount of master alloy is 1.5%, its tensile strength and ductility reach the peak, 182 MPa and 5.1%, an increase of 20.53% and 50%, respectively. Then, continue to increase the amount of Al-5Ti-0.62C-0.2Ce master alloy and the tensile strength and ductility of Al-8Si declines slightly.

Following the Hall–Petch type equation:

$$\sigma_s = \sigma_0 + kd^{-1/2}, \quad (5)$$

where σ_s is the yield stress, σ_0 is the force needed to move a single dislocation to overcome the lattice friction, k is a constant, and d is the average grain diameter. It can be seen that the yield strength of the material is proportional to the square root of the reciprocal of the grain size. Therefore, grain refinement can not only improve the strength of the material, but also improve the plasticity of the material.

The reduction of secondary dendrite arm spacing (SDAS) in the above range also caused a substantial increase in fatigue life. According to fractography, the tensile cracks propagated mainly through the eutectic Si and primary phases. The presence of fatigue striations on the plate-shaped intermetallics proved their ductile nature and had a positive effect on fatigue life [23].

Al-Ti-C-Ce master alloy refines α -Al and Si. On the one hand, the reduction in size of Si and the increase of circularity reduce the chance of dehiscence of Si and increase the resistance of micro crack formation [24]. On the other hand, the refinement of α -Al phase results in the resistance increase of dislocation movement, enhancing the hardening rate of α -Al matrix processing in an alloy [25]. An alloy can be deformed in a more coordinated way to effectively prevent the gathering and growth of micro cracks [26]. Therefore, due to the tensile load, the alloy can stand greater deformation and its tensile strength and plasticity are significantly improved.

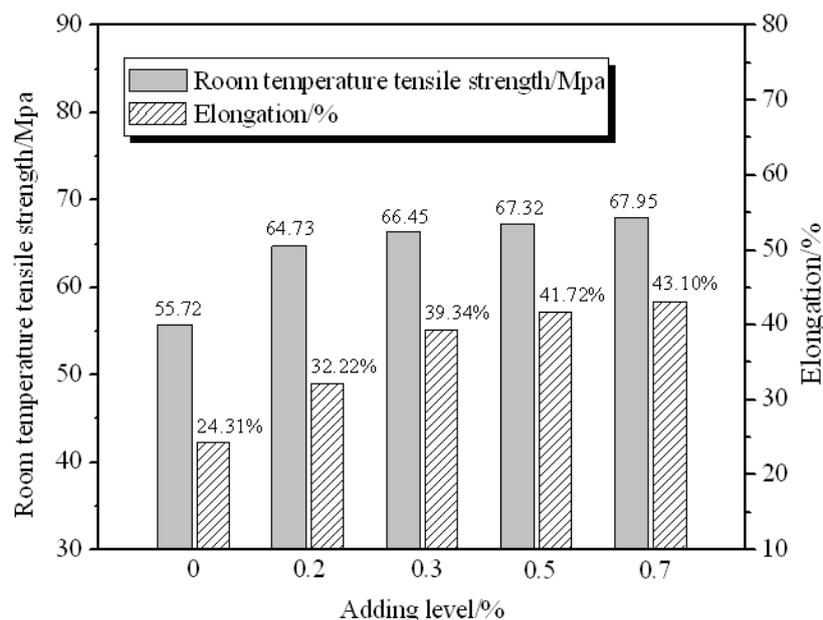


Figure 11. Tensile properties of commercial pure aluminum with different adding levels of Al-5Ti-0.62C-0.2Ce master alloy.

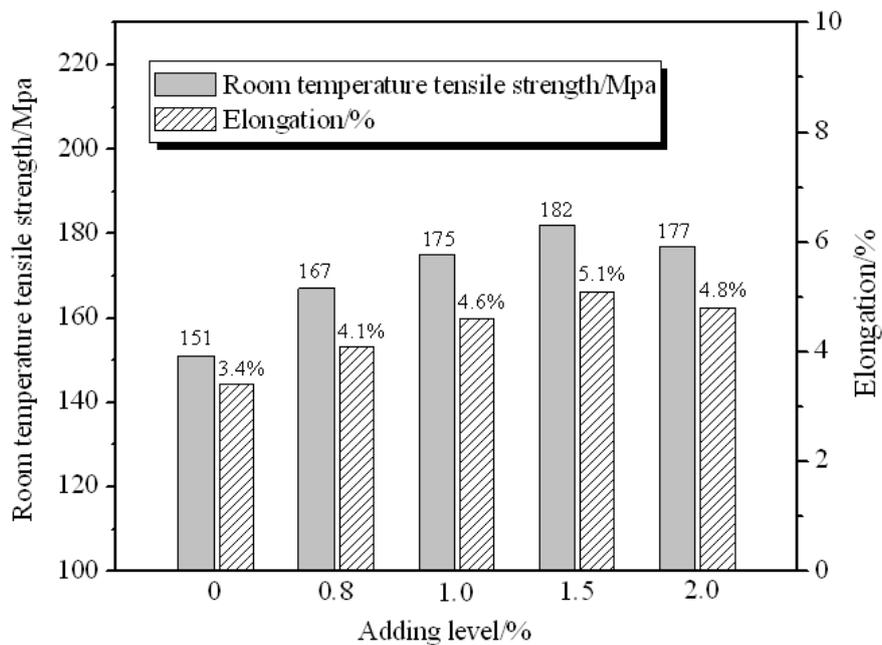


Figure 12. Tensile properties of Al-8Si alloy with different adding levels of Al-5Ti-0.62C-0.2Ce master alloy.

4. Conclusions

(1) The new-type Al-5Ti-0.62C-0.2Ce master alloy prepared with molten aluminum in situ reaction is composed of Al, TiAl₃, TiC, and Ti₂Al₂₀Ce phase.

(2) Al-5Ti-0.62C-0.2Ce master alloy has a sound effect on the refinement of commercial pure aluminum. Pure aluminum macro grains with the addition of 0.3% Al-5Ti-0.62C-0.2Ce master alloy are refined into tiny equiaxed grains and display good resistance to the fading of refinement. Its tensile strength and ductility increase by roughly 19.26% and 61.83%, respectively.

(3) Al-5Ti-0.62C-0.2Ce master alloy has a sound effect on the refinement and modification of hypoeutectic Al-8Si alloy. When the addition amount is 1.5%, Al-5Ti-0.62C-0.2Ce not only refines the coarse dendrite α -Al grains in hypoeutectic Al-8Si alloy into tiny equiaxed grains but also modifies coarse needle-shaped or strip-shaped eutectic Si into the short rod-like or grain-like eutectic Si. The tensile strength and ductility of the alloy increase by roughly 20.53% and 50%, respectively.

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Conflicts of Interest: The authors declare no conflict of interest.

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