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# Structural heredity of TiC and its influences on refinement behaviors of AlTiC master alloy①

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**Abstract:** Heredity of microstructure in AlTiC master alloy, grain refiners, was analyzed. It is found that, for morphologies and distributions of TiC particles, there are visible heredity which originates from raw materials or processing methods of Al melt, and will ultimately be transferred to the solid state structure through the melt stage, and this phenomenon can cause hereditary influences on refinement: formation of chain-like TiC morphology results in rapid refinement fading behavior; distribution of TiC along grain boundaries greatly reduces refinement efficiency. Controlling of structural heredity through proper selections of raw materials and processing parameters is of great importance in obtaining ideal microstructures and improving refinement behaviors of AlTiC master alloys.

**Key words:** heredity phenomenon; AlTiC master alloy; TiC; grain refinement
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## 1 INTRODUCTION

Preparation of most alloys is achieved through processing in three stages: solid-liquid-solid. During every processing stage, processing methods or parameters may result in some changes in the microstructures or properties of the alloy which will be transferred stably to the subsequent stages and influence properties of the ultimate product, and this may be called hereditary phenomenon of microstructures and properties. Heredity phenomenon in metal alloys has been noticed as early as in 1920[1], recently works were carried out to study its regularities in iron/steel and nonferrous metals, and significant results were obtained in understanding the melt structures, crystallization, and physical properties of solid-state materials[2-4].

A new method to produce AlTiC master alloy, i.e. the grain refiner for Al and its alloys has been developed recently[5]. Visible heredity has been found in this master alloy produced under different parameters, this paper mainly presents the microstructure heredity of TiC particles in the master alloy and its hereditary influence on the refinement behaviors of this master alloy in pure Al.

## 2 EXPERIMENTAL

AlTiC master alloys were prepared under different processing parameters according to Ref. [5], microstructures of AlTiC master alloys and pure Al refined were observed using Hitachi S－570 or JXA－840 Scanning Electron Microscope (SEM) and KH－2200 Hi-Scope Video Microscope.

Refinement efficiencies of the master alloys were tested as follows: to each 160g of pure commercial Al (99.7%), different master alloys with the addition level of 0.2% were added at 720 ℃, after different holding times the melts were stirred for 15 s and then poured into a steel ring put on a ceramic fiber block. The steel ring is 50 mm in inner diameter and 25 mm in depth. After solidification the bottom surface of the refined cast in contact with the ceramic fiber block was etched through a reagent (60%HCl+ 30% $HNO_3$+ 5%HF+ 5%$H_2O$), and the grain size determined using line intercept method.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Microstructure and refinement efficiency of AlTiC master alloy

As a grain refiner for Al and its alloys, AlTiC master alloy with titanium content of 3%－12% and carbon content of 0.1%－1.5% usually contains two secondary phases, i.e. $TiAl_3$ and TiC, in the Al matrix. Identification of the two phases through X－ray diffraction and EPMA (electron probe micro analysis) has been confirmed in our previous work. $TiAl_3$ pre-

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sents needle or blocky morphologies with the length ranging between 5 and 200 μm and width between 3 and 15 μm, and will dissolve into Ti and Al after the master alloy is added into pure Al melt to be refined[6, 7]. While TiC phase has a melting point as high as 3 683 K and the same fcc (face centered cubic) crystal structure as that of α-Al, so it is generally accepted[8-10] that the stable TiC particle acts as the nucleating substrate of α-Al and refines the grains.

The previous work[11] reported the good refinement efficiency of AlTiC master alloy on pure Al, and found that excessive Ti provided by the dissolution of $TiAl_3$ also played an significant role in refinement. Fig. 1 presents an α-Al grain after the addition of Al-TiC master alloy, TiC particles surrounded by dendrite structure are located at the grain center, subsequent EPMA shows that Ti is enriched in the dendrite structure but near zero in the ambient Al matrix. So it is concluded that refinement of Al by Al-TiC refiner results from a combined action of TiC and excessive Ti, among which TiC particle acts as the nucleus of α-Al while Ti has some effects on the nucleation of α-Al on the surface of TiC particle and subsequent grain growth. Other factors such as addition level, the ratio of Ti to C, morphology and distribution of TiC particle which will be presented in the following sections, can also greatly influence the refinement behaviors.

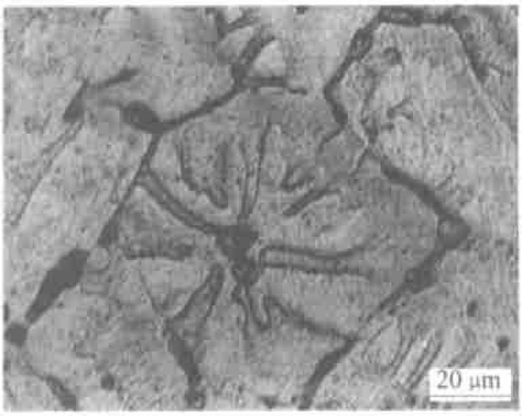


**Fig. 1** α-Al grain refined by Al5Ti0. 3C master alloy with 0. 1% Ti and 0. 006% C

## 3. 2 Hereditary effect of TiC morphology on refining performance of AlTiC master alloy

Two kinds of typical TiC morphologies, as shown in Fig. 2, can be found in produced AlTiC master alloys. In Fig. 2(a), fine TiC particles presenting polyhedron morphology are disconnected from each other and discretely dispersed in the Al matrix. In Fig. 2 (b), most of TiC particles are connected each other and form chain-like or other kinds of, e. g. star-like, morphologies. The presence of different TiC morphologies is due to different processing parameters and raw materials: the former one was formed through 3 min of reaction of Ti and C in the Al melt at 1 100 - 1 200 ℃, the latter one was formed through reaction of Ti and C in the Al melt with the aid of small amount of active elements at 780 - 1 050 ℃, and the reaction time was 8 min. Different processing parameters have created different melt structures which endower TiC particles with different growth and aggregating behaviors. It is apparent that individual TiC particles in Fig. 2(b) have the strong tendency to agglomerate and coalesce in the Al melt.

Fig. 3 shows the refinement behaviors of two Al5Ti0. 3C master alloys with the two different kinds of TiC. Within ten minutes of holding in the pure Al melt the two master alloys present similar refinement efficiency, but different fading behaviors with time prolonged: there is essentially no fading when TiC disperses in the Al matrix as indi-

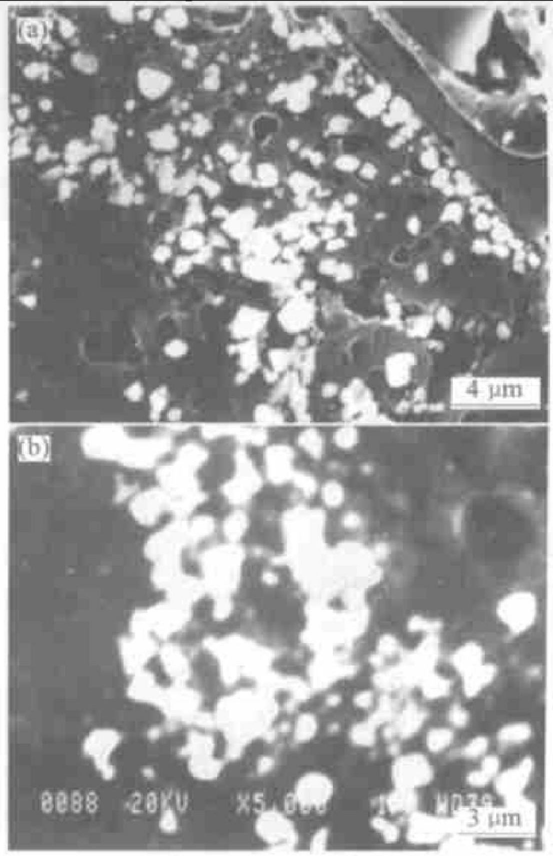


**Fig. 2** Two kinds of TiC morphologies
(a) —Discrete particles; (b) — Chain-like particles

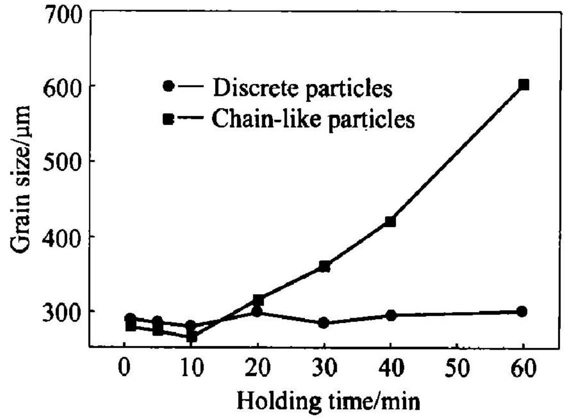


**Fig. 3** Refining behaviors of two Al5Ti0. 3C master alloys with different TiC morphologies

vidual fine particles, while grain size increases rapidly when TiC forms chain-like structure.

Pure Al with respective addition (1%) of the above two Al5Ti0.3C refiners was held at 720 ℃ for 60 min in a graphite crucible 20 mm in diameter and 60 mm in depth, after solidification the casts were sectioned along the longitudinal direction and examined under optical microscope and the bottom of the sections were shown in Fig. 4.

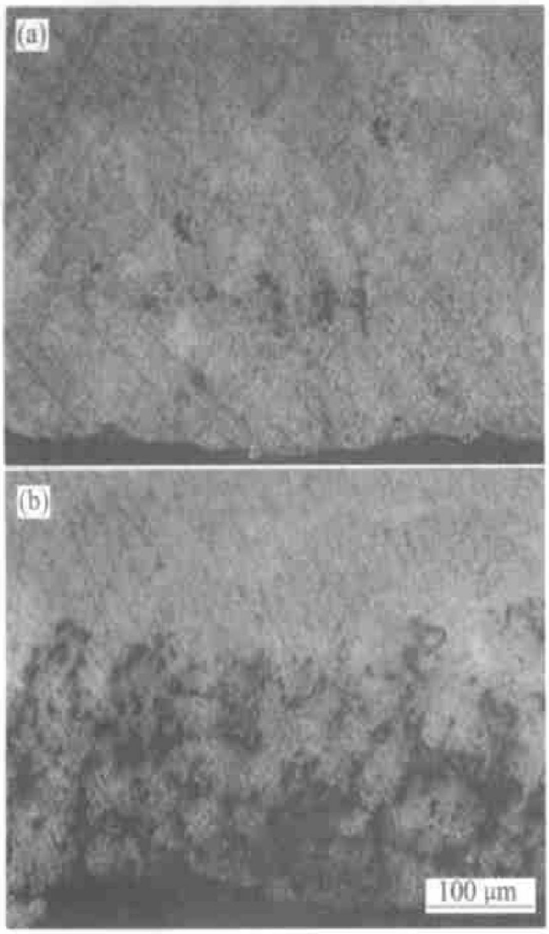

**Fig. 4** Bottom of pure Al(99.7%) after addition (1%) of two Al5Ti0.3C refiners with different TiC morphologies and held at 720 ℃ for 1 h.
(Black agglomerates are TiC particles)
(a) —Discrete particles; (b) —Chain-like particles

It is clear that TiC particles in Fig. 4 (b) aggregate together and sedimentate to the bottom of the melt during holding, while only very small amount of agglomerating TiC particles in Fig. 4 (a) is found. Apparently traits of two kinds of TiC to aggregate or not in master alloys are inherited to the pure Al melt to be refined. The aggregation of TiC particles greatly reduces the number of individual particles which act as the substrate for the nucleation of α-Al, and hence reduces the refinement efficiency.

### 3.3 Heredity of TiC distribution and its influence on refining efficiency of AlTiC master alloy

Fig. 5 shows the distribution of TiC particles in master alloys with different titanium and carbon contents. In Figs. 5(b), (d) and (e), TiC particles are agglomerated along the grain boundaries of α-Al, while needle or blocky $TiAl_3$ is located in the center of the α-Al grains; in Figs. 5 (a) and (c), both TiC and $TiAl_3$ particles are evenly dispersed in the Al matrix. Their refinement efficiencies are shown in Fig. 6, grain sizes of pure Al unrefined and refined by master alloys in Figs. 5 (a)−(e) are 4 200, 230, 1 900, 260, 2 200, and 2 900 μm respectively. Apparently, distribution of TiC particles along grain boundaries caused poor refinement efficiency.

Master alloys in Figs. 5 (a), (c) and those in (b), (d) were prepared respectively using the same raw materials, but different reaction temperatures (1 080 − 1 130 ℃ and 900 − 980 ℃ respectively). Though it was reported [12, 13] that solidification parameters could influence the distribution of particles in Al melt, the solidification conditions were controlled to be the same in this work, so the difference of TiC distribution was sure to result from the difference in reaction temperatures. Different melt temperatures result in different liquid structures, different formation mechanisms of TiC, and hence different wettabilities of TiC particle by the Al melt. TiC particles poorly wetted by Al were pushed to grain boundaries during solidification of the master alloys, and when this characteristic was inherited to the pure Al to be refined, TiC particle cannot act as nucleus of Al, and poor refining performance was presented.

The master alloy in Fig. 5 (e) was made in the temperature range of 750 − 900 ℃, with the hope to change the wettability of TiC, it was remelted in the temperature range of 1 000 − 1 300 ℃. Despite the turning of blocky morphology of $TiAl_3$ into needle type, the distribution of TiC particles along the grain boundaries does not change and the master alloy presents the same poor refinement efficiency. From the above analysis, it can be seen that some characteristics formed in the liquid structure can be stably inherited to the solid structure and difficult to be changed in the subsequent melt processing. So the controlling of melt structure through different processing methods and parameters is of great importance in obtaining ideal microstructures and refinement properties of Al-TiC master alloy grain refiners.

## 4 CONCLUSIONS

1) Morphologies of TiC particles, formed due to different processing parameters, can influence the fading behaviors of AlTiC master alloys due to its heredity from AlTiC master alloy (grain refiners) to the Al melt to be refined.

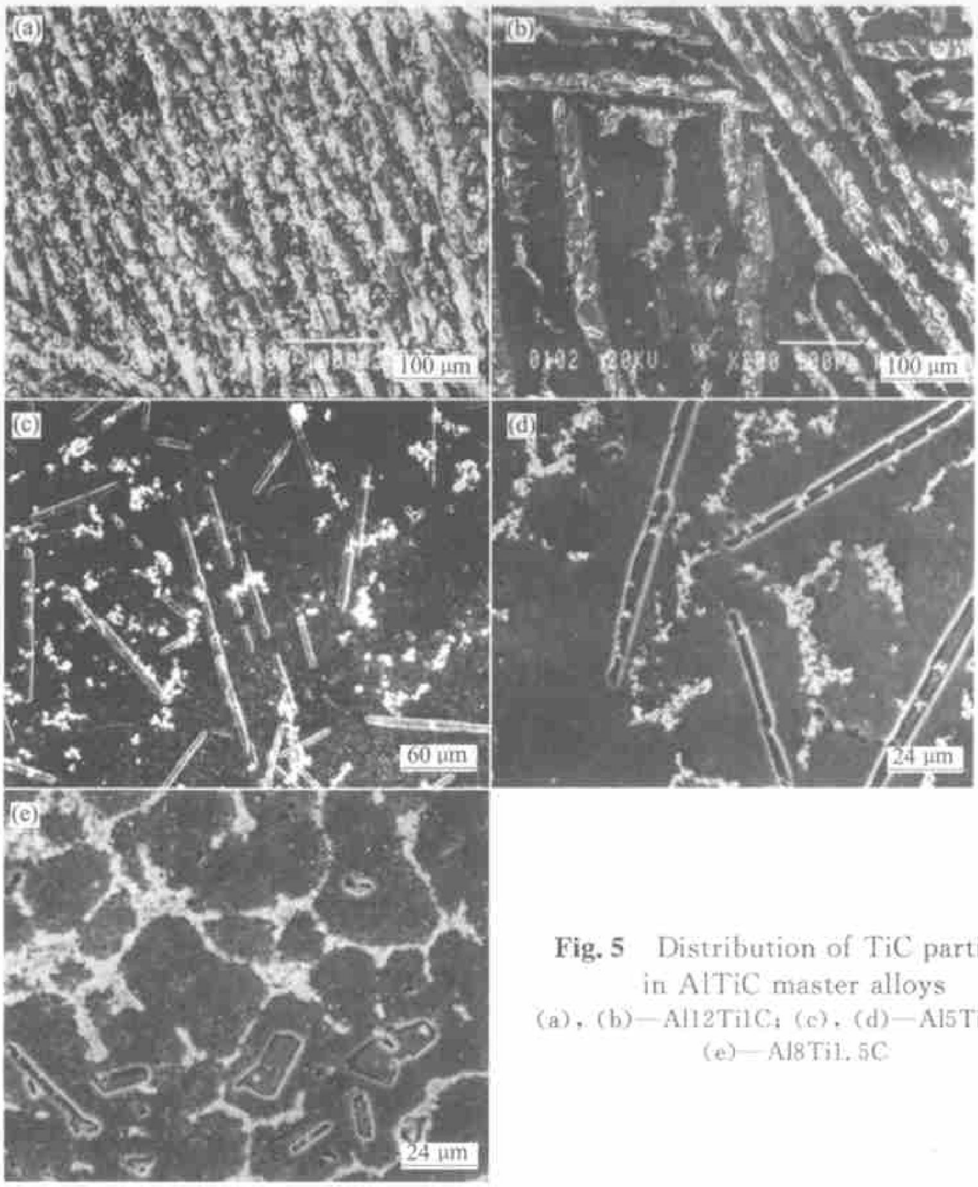


**Fig. 5** Distribution of TiC particles in AlTiC master alloys
(a), (b)—Al12Ti1C; (c), (d)—Al5Ti0.3C; (e)—Al8Ti1.5C

2) Distribution of TiC along grain boundaries will greatly reduce the refining efficiency of AlTiC master alloys due to the hereditary poor wettability of TiC particles in Al melt.

3) Controlling of liquid structure is of great importance in obtaining ideal microstructures and refinement properties of AlTiC master alloy.

## REFERENCES


[1] Levi A. Heredity in Cast Iron [J]. The Iron Age, 1927 (6): 960−965.

[2] Margerie J C. The notion of heredity of cast iron [J]. The Metallurgy of Cast Iron, 1974: 546−550.

[3] BIAN Xiu-fang, LIU Xiang-fa, MA Jia-ji. Heredity in Cast Metals [M]. Ji′nan: Shandong Science and Technology Publishing House, 1999.

[4] LI Pei-jie, ZHANG Yan-fei, Nikitin V I, et al. Hereditary effect of Al-based modifiers and grain refiners on structure and properties of A356.2 alloys [J]. Trans Nonferrous Met Soc China, 2002, 12(2): 233−237.

[5] LIU Xiang-fa, WANG Zhen-qing, BIAN Xiu-fang. A method to produce AlTiC master alloy grain refiner [P]. CN ZL00123953.8, 2000.5.

[6] Guzowski M M, Sigworth G K, Sentner D A. The role of boron in the grain refinement of aluminum with titanium [J]. Metall Trans A, 1987, 18A(4): 603−619.

[7] Marcantonio J A, Mondolfo L F. Grain refinement in aluminum alloyed with titanium and boron [J]. Metall Trans A, 1971, 2A(2): 465−471.

[8] Cibula A. The mechanism of grain refinement of sand castings in aluminum alloys [J]. J Inst Met, 1949−1950, 76: 321−360.

[9] Banerji A. Reif W. Development of Al-Ti-C grain refiners containing TiC [J]. Metall Trans A, 1986, 17A (12): 2127−2137.

[10] JIANG Wen-hui, HAN Xing-lin. Preparation of Al-Ti-C master alloys and their grain refining properties [J]. The Chinese Journal of Nonferrous Metals, 1998, 8 (2): 268−271. (in Chinese)

[11] WANG Zhen-qing, LIU Xiang-fa, BIAN Xiu-fang. Phases and refinement performances of AlTiC master alloys [J]. Foundry, 2001, 50(6): 316−320. (in Chinese)

[12] Carcea I, Agop M. Transition and equilibrium process in metal-ceramic particle system [J]. Metall Mater Trans A, 1995, 26A(11): 3021−3025.

[13] Kaptay G. Interfacial criterion of spontaneous and forced engulfment of reinforcing particles by an advancing solid/liquid interface [J]. Metall Trans A, 2001, 32A(4): 993−1005.


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