**Article ID:** 1003 - 6326(2000)03 - 0298 - 06

# A new development of Al-Ti-C grain refining master alloys[①]

ZHANG Bai-qing(张柏清), LI Jian-guo(李建国), MA Hong-tao(马洪涛),
FANG Hong-sheng(方鸿生)
*Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China*

**Abstract:** Al-Ti-C master alloys have been prepared with a novel production method. A combination of X-ray phase analysis, SEM and EDS was used to examine the phases and microstructures of the master alloys. The master alloys have block-like $Al_3Ti$ particles and submicron size $TiC_X$ with $X$ ranging from 0.49 to 0.78 and show excellent grain refining performance for commercially pure aluminum. Titanium carbides were observed at the crystallization centers in refined castings.

**Key words:** Al-Ti-C; master alloy; microstructure; grain refinement **Document code:** A

## 1 INTRODUCTION

It is now a common practice to add grain refiners to molten Al before casting to produce fine grain structures in the solidified ingots or cast products. A lot of advantages are provided by grain refinement, including improved mechanical properties[1,2], reduced cracking in ingots and increased casting speed[3], improved homogeneity and reduced porosity in castings, and better mechanical deformation characteristics[4,5]. Especially, for alloys used in rolled or extruded form for architectural applications, surface defects will be remarkably reduced through grain refinement of cast ingots[3~5].

As the most widely used grain refiner, Al-Ti-B master alloys have a good grain refining performance in some aluminum and aluminum alloys. But there are some problems with this kind of grain refiner. First, borides in Al-Ti-B master alloys will coarsen by coalescence or agglomeration to form big particles, which will accelerate the sediment process of these particles in aluminum melt because of their higher density compared with that of aluminum. The sediment of borides is believed to be the main reason for the fading behavior of Al-Ti-B master alloys during the grain refining practice[6,7]. What's more, these large hard particles are very unfavorable for products intended for extrusion, deep drawing, or high performance structural applications[8~12]. In addition, elements like Zr, Cr, Li and Mn are believed to poison the nucleating boride particles which make Al-Ti-B master alloys very difficult to refine those aluminum alloys with dilute compositions of any one of the above-mentioned elements or combination of them[13~21]. In recent years, some further work has been done to improve the efficiency and consistency of the conventional Al-Ti-B products[22~27]. Some commercial producers of grain refiners have introduced statistical process control (SPC) technique to guarantee the consistent quality and consistent performance of grain refiners[22,27]. But the problems above-mentioned are still virtually hindering Al-Ti-B master alloys from being an excellent grain refiner.

Since the early extensive work of Cibula[28], TiC has been well known as an excellent potential nucleant for aluminum and its alloys[29~33]. some work[34~37] has been done to find a method to produce Al-Ti-C master alloys, but little success has been made. In mid 1980s, Banerji et al[38,39] reported that they had successfully produced Al-Ti-C master alloys which had adequate quantity of TiC particles and showed good grain refining performance. But till now, there is no any commercial product of Al-Ti-C master alloy used as grain refiners. The reason is believed to be the high production cost of their method, which has made them difficult to be applied on large scale. In order to elaborate the excellent grain refining characteristics of Al-Ti-C master alloys, new methods should be explored to produce the master alloy at a competitively low cost compared with the conventional Al-Ti-B grain refiners.

Our recent work has been focusing on exploring new method to produce Al-Ti-C master alloys at a low production cost and a novel method has been developed[40]. which is remarkably different from the previous methods[38,39]. The main characteristics of the present method are the low production temperature (750 ~ 850 ℃) and short production time (15 ~ 30 min), which leads to a low production cost and high competence compared with the conventional Al-Ti-B master alloys. The present paper summarizes some results of our work.

## 2 EXPERIMENTAL

Phases in the Al-Ti-C master alloys were ana-

① **Received date:** May 21, 1999; **accepted date:** Nov. 8, 1999

lyzed with D/MAX/RD-12kW-Cu type XRD analyzer. Master alloy samples ground and polished using standard procedure were used for XRD analysis. Extracted second phases powders after aluminum matrix was dissolved in an iodine-methanol-tartaric acid mixture[41] were also detected on XRD to further examine the second phases in master alloys. Chemical analysis (except for carbon) of the master alloys was done with an atomic absorption spectrometer. Carbon was determined by an automatic combustion apparatus, where the sample is combusted in a stream of oxygen and the carbon of the specimen is converted into $CO_2$, which is then fed into a measuring chamber where the concentration peak is detected with a non-dispersive spectrometer. The linear signal is integrated and displayed digitally after weight compensation and blank value correction. Electropolished samples were examined in a JSM-6301 Scanning Electron Microscope equipped with a Link ISIS energy dispersive X-ray spectrometer (EDS) to investigate the microstructures and second phases in the master alloys.

The Al-Ti-C master alloys were also tested for grain refinement efficiency of commercially pure aluminum (99.7% Al). To each 100 g melt of aluminum, different amounts (0.05% to 0.2%) of master alloys were added at a melt temperature of 720 ℃, and the melts with various holding times were poured into a permanent mold schematically shown in Fig.1. For comparison, similar castings were also prepared with additions of Al-6Ti and Al-5Ti-1B commercial grain refiner rods (procured from LSM-London and Scandinavian Metall. Co.). The cast structures were microscopically studied and grain size determined using a line intercept method from a large number of non-overlapping measurements.

## 3 RELSULTS

### 3.1 Phases and microstructures of Al-Ti-C master alloys

Table 1 summarizes the compositions of some Al-Ti-C master alloys and their respective typical microstructures are illustrated in Fig.2.

**Table 1** Typical compositions of Al-Ti-C master alloys

| Master alloys | w(Ti)/% | w(C)/% |
|---|---|---|
| Al-5Ti-0.2C | 4.97 | 0.21 |
| Al-6Ti-0.5C | 5.92 | 0.48 |
| Al-6Ti-0.8C | 6.06 | 0.78 |

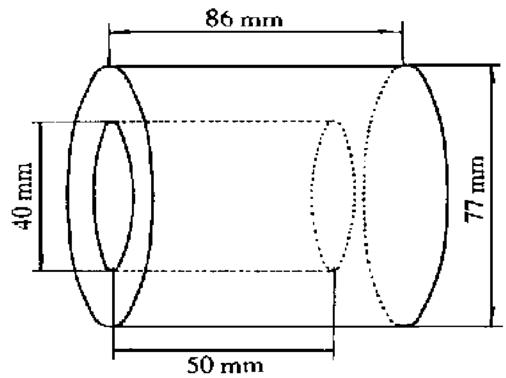


**Fig.1** Schematic diagram of permanent mold

The microstructures of master alloys include block-like particles and another particulate phase which segregates generally at the grain boundaries. The block-like particles usually have a size of 10 ~ 50 μm. The latter phase consists of fine particles with size between dozens of nanometers to 1 μm. Fig.3 shows a secondary electron image (SEI) of a selected typical region of the microstructure and its corresponding X-ray mappings of Ti and C. It is shown that the block-like particles enrich in Ti and the submicron size particles enrich in both Ti and C. Further EDS analysis shows that the block-like particles have a precise composition of Ti∶Al = 1∶3 (atom ratio) and the submicron size particles do not have a unique composition but a composition range with $X$ in $TiC_X$ varying from o.49 to 0.78. Fig.4 shows the typical EDS results of block-like particles and submicron particles. Fig.5 shows the XRD results of electropolishedsamples and extracted second phases powders. It is shown that there exist two phases of $Al_3$ Ti and ti-

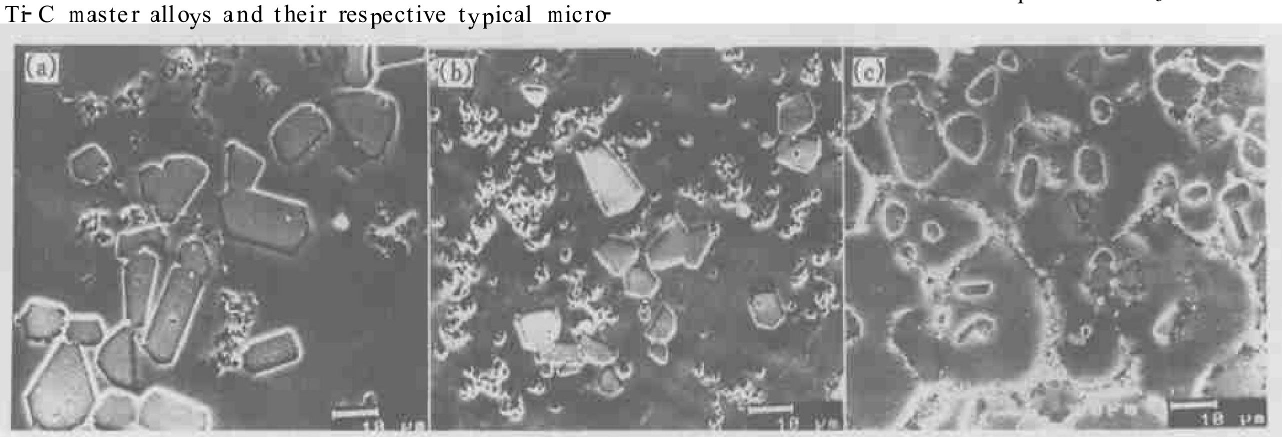


**Fig.2** Typical microstructures of master alloys with different compositions
(a) —Al-5Ti-0.2C; (b) —Al-6Ti-0.5C; (c) —Al-6Ti-0.8C

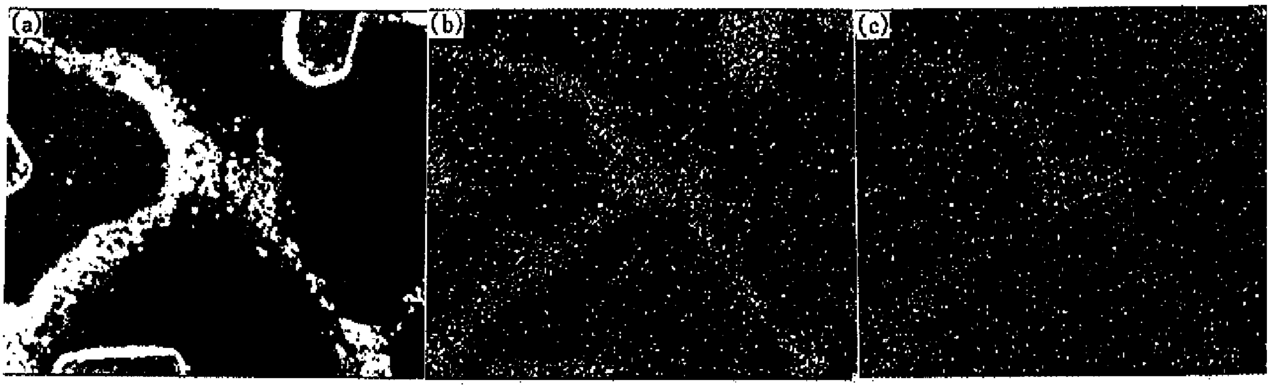


**Fig.3** Scanning electron microscope analyses of selected area of master alloys
(a) —SEI image; (b) —Ti X-ray mapping; (c) —C X-ray mapping

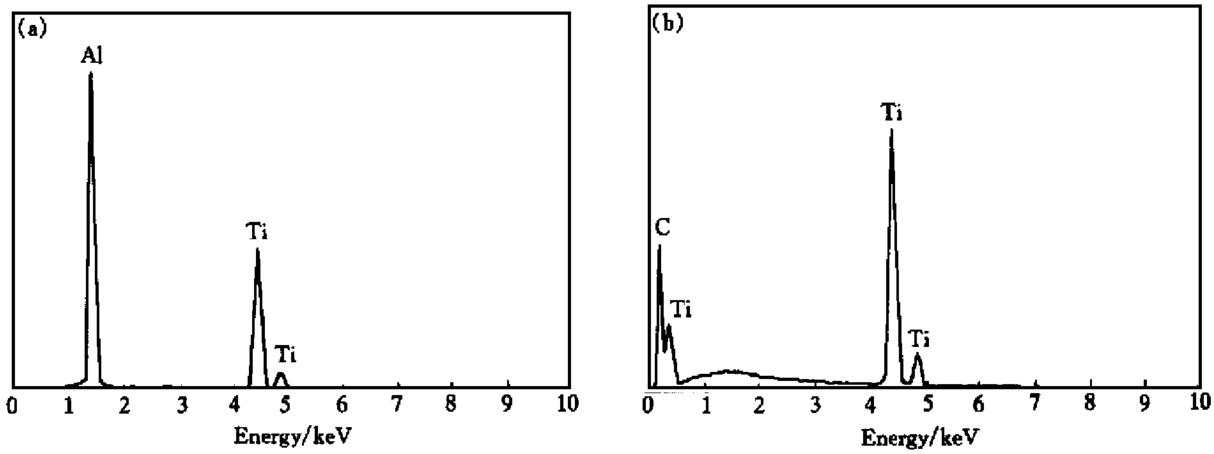


**Fig.4** EDS analyses of particles in master alloys
(a) —Block-like particles; (b) —One typical composition of submicron particles

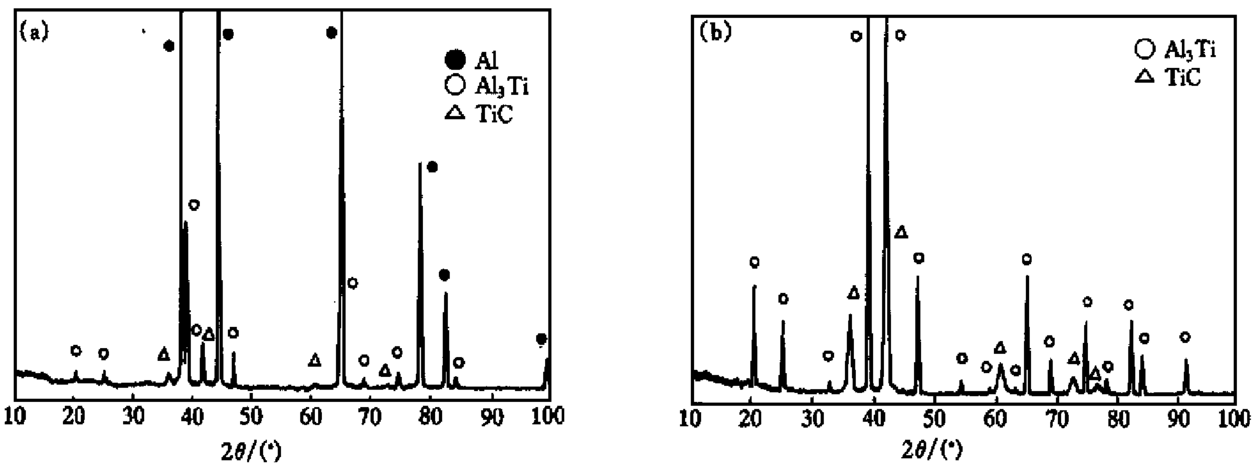


**Fig.5** X-ray diffraction patterns
(a) —Electropolished sample; (b) —Extracted second phases powder of master alloys

tanium carbides apart from the matrix aluminum in the master alloys. XRD on the extracted second phases powders shows more clearly that peaks of $Al_3Ti$ are in a good correspondence with the standard peaks, while the peaks of titanium carbides are broadened.

### 3.2 Grain refining performance of Al-Ti-C master alloys

Fig.6 shows the macrographs of commercially pure aluminum castings refined by Al-6Ti-0.8C master alloy ingot and procured Al-6Ti, Al-5Ti-1B with increasing addition level from 0.05% to 0.2%.

It can be seen that both the fraction of columnar grains and the size of equiaxed grains decrease with the increase of the addition level of all the three master alloys. In the case of Al-Ti-C master alloy, the

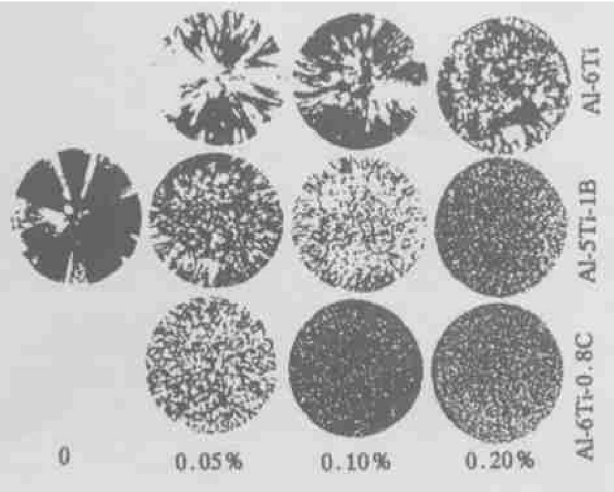


**Fig.6** Macrographs of aluminum castings refined with different addition level of Al-6Ti, Al-5Ti-1B and Al-6Ti-0.8C master alloys
(Refining temperature = 720 ℃; holding time = 5 min; Magnification = 0.35)

columnar grain zone decreases rapidly with increasing addition level and disappears virtually at the addition level of 0.2%, attaining the average equiaxed grain size of about 150 μm, which is obviously much better than the Al-6Ti master alloy and even some what better than the Al-5Ti-1B master alloy.

Fig.7 shows the variation of average grain size with increasing holding time of commercially pure aluminum refined by these three refiners at an addition level of 0.2%. In the case of the Al-6Ti master alloy, the grain size decreases with increasing holding time during the first 5 min and then increases sharply. In the case of the Al-5Ti-1B and Al-6Ti-0.8C master alloys, good fading behaviors were observed, especially for the latter there is no evident fading even up to 120 min.

### 3.3 Nuclei observation in aluminum castings refined with Al-Ti-C master alloys

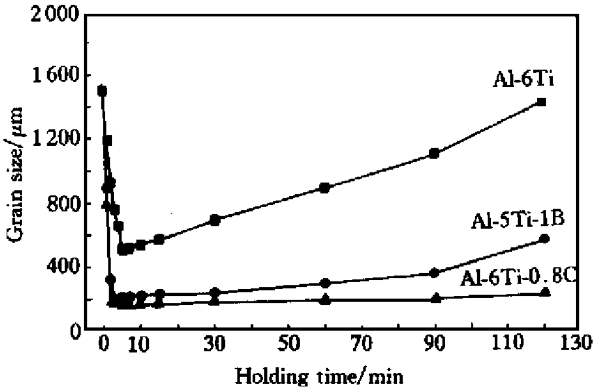


**Fig.7** Fading behaviors of Al-6Ti, Al-5Ti-1B and Al-6Ti-0.8C master alloys
(Refining temperature = 720 ℃; addition level = 0.2%)

Crystallization nuclei in aluminum grains refined with Al-Ti-C master alloys were examined. Titanium carbides of different compositions were frequently observed at the crystallization centers of aluminum grains. They usually exist with only one single particle or particle clusters composed of several particles less than 1 μm. Fig.8 shows a typical result of crystallization center in a refined casting. Fig.8(a) shows a subgrain structure with a nucleus at its center and dendritic structure around the nucleus, followed by magnified SEI of the nucleus (Fig.8(b)). Typical X-ray linings show that the nucleus enrich in Ti and C (Fig.8(c)).

## 4 DISCUSSION

$Al_3Ti$ particles in Al-Ti-C master alloys have block-like morphology, which is in accordance with the observations of Arnberg et al[41] and Blake et al[42] in Al-Ti and Al-Ti-B master alloys. The morphologies of $Al_3Ti$ particles are mainly determined by the melt temperature. If the mater alloys were pro-

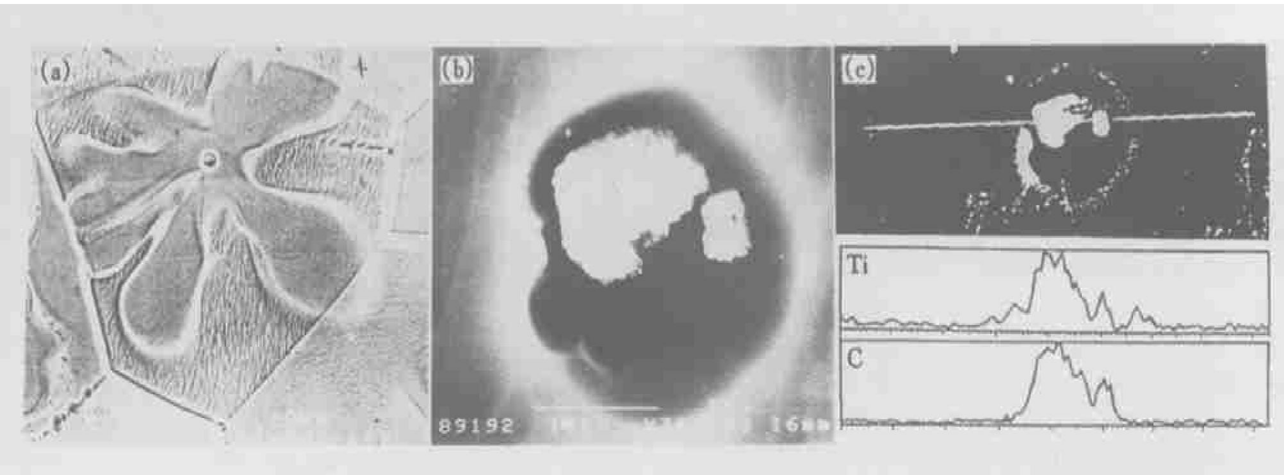


**Fig.8** Crystallization nuclei observations
(a) —SEI of subgrain structure; (b) —SEI of nucleus; (c) —X-ray linings of Ti and C

duced at a lower temperature ( < 900 ℃) , a compact block-like morphology was produced. While they were produced at a higher temperature ( > 1 000 ℃) , a two-dimensional flake or plate like morphology was resulted. The $Al_3Ti$ particles in Al-Ti-C master alloys prepared by Banerji et al's patented method had a typical plate morphology[38,39], which confirmed the higher production temperature in their method.

The broadening of XRD peaks of powder samples may have two reasons. One is the refinement of the detected crystal particles, the other is the occurrence of a range of the lattice parameters which result from either crystal distortion or composition change of the crystal[43]. From the above-mentioned composition analysis of titanium carbides in Al-Ti-C master alloys, it can be reasonably concluded that the broadening phenomenon of the peaks of titanium carbides( Fig.5 (b)) is at least partly due to the existence of composition range of titanium carbides, because composition range of the titanium carbides will result in a lattice parameter range[44]. In addition, the submicron size of titanium carbides, especially those with size below 100 nm has also an effect on the broadening of XRD peaks[43]. So the broadening phenomenon may be the combination effects of these two reasons. But it is difficult to quantitatively separate the single effects of these two sources.

From the excellent grain refining performance of Al-Ti-C master alloys and the frequently observed titanium carbides at the crystallization centers of the refined aluminum castings, it is confirmed that titanium carbides have an excellent potential to inoculate α-Al during the solidification process of aluminum melts. The good fading behaviors of the master alloys show that titanium carbides are stable in aluminum melts at the melt temperature in common grain refinement practice. Further work is under way to comprehensively investigate the characteristics of these Al-Ti-C master alloys.

## 5 CONCLUSIONS

The Al-Ti-C master alloys prepared by our novel method have block-like $Al_3Ti$ particles and submicron size titanium carbides with a composition range of $X$ in $TiC_X$ varying from 0.49 to 0.78. They exhibit excellent grain refining performance. Titanium carbides were observed at the crystallization centers in refined aluminum castings, which confirms the potential ability of titanium carbides to be nuclei for α-Al during the solidification process of aluminum melts.

## REFERENCES

[1] Granger D A and Liu J. Occurrence effect and control of twinned columnar growth in aluminum alloys [J]. J Met, 1983, 35(6): 54.

[2] Labarre L C, James R S, Witters J J, et al. Grain refinement of aluminum alloys [J]. J Phys (Orsay), 1987, 48(9): 93.

[3] Granger D A. Proc Int Seminar on Refining and Alloying of Liquid Aluminum and Ferro-Alloys [C]. Trondheim, Norway, 1985. 231.

[4] Apelian D, Sigworth G K and Whaler K R. Grain refinement of aluminum by Al-Ti-B master alloys [J]. Trans AFS, 1984, 92: 297.

[5] Hashemi-Ahamady S H. Research on grain refinement of aluminum and its alloys [D]. UK: University of Southampton, 1988.

[6] Gerloff R, Reif W, Heyroth W, et al. The agglomeration of the $TiB_2$ phase which has been added to molten aluminum for the grain refinement [J]. Metall, 1996, 50 (2): 97 ~ 101.

[7] Mohanty P S, Guthrie R I L and Gruzleski J E. Studies on the fading behavior of Al-Ti-B master alloys and grain-refinement mechanism using limca [J]. Light Metals, 1995: 859 ~ 868.

[8] Maxwell I and Hellawell A. The morphology of aluminides in Al-Ti alloys [J]. Acta Metall, 1975, 23: 229 ~ 237.

[9] Hellawell A. Grain refining performance of Al-Ti-B master alloys [A]. Solidification and Casting of Metals [C]. London: The Metals Society, 1979. 161 ~ 168.

[10] Pearson J, Birch M E J and Hadlet D. Study on the grain refining efficiency of aluminum grain refining alloys [A]. Solidification Technology in the Foundry and Casthouse [C]. London: The Metals Society, 1983. 74 ~ 78.

[11] Pearson J and Birch M E L. Effect of the Ti:B ratio on the efficiency of aluminum grain refining alloys [J]. J Met, 1979, 31(11): 27 ~ 31.

[12] Pearson J and Birch M E L. Geer J P. Light metals [C]. Warrendale, PA: Metallurgical Society of AIME, 1984. 1217 ~ 1229.

[13] Labarre L C, James R S, Witiers J J, et al. Grain refinement of aluminum alloys [J]. J Phys (Orsay), 1987, 48, C3, Suppl(9): 93 ~ 102.

[14] Kirby J L. Proc 1st Int Conf on Aluminum Alloys-their Physical and Mechanical Properties [C]. Charlottesville, VA, Aluminum Association, June 1986. 61 ~ 79.

[15] Birch M E J and Fisher P. Sheepard T. Aluminum Technology '86. London: The Institute of Metals, 1986. 117 ~ 124.

[16] Birch M E J and Cowell A J J. Grain refining performance of Al-Ti-C on aluminum alloys with Zr and Cr [J]. J Phys (Orsay), 1987, 48, C3, Suppl(9).

[17] Abdel-Hamid A A. Effect of other elements on the grain refinement of Al by Ti or Ti and B( Ⅱ) [J]. Z Metallkd, 1989, 80: 643 ~ 647.

[18] Abdel-Hamid A A. Effect of other elements on the grain refinement of Al by Ti or Ti and B ( Ⅰ ) [J]. Z Metallkd, 1989, 80: 566 ~ 569.

[19] Jones G P and Pearson J. Factors affecting the grain-refinement of aluminum using titanium and boron additives [J]. Metall Trans, 1976, 7B: 223 ~ 234.

[20] Marcantonio J A and Mondolfo L F. The nucleation of aluminum by several intermetallic compounds [J]. J Inst Metals, 1970, 23 ~ 27.

[21] Abdel-Reiheim M, Hess N and Reif W. Kornfeinung von titanhaltigem technischen aluminum durch erdalka-

lielemente [J]. Metall, 1984, 38: 520 ~ 525.

[22] Shaw A D and Barber A D. Consistent quality reduces grain refining costs [J]. Aluminum Today, 1994, 6: 31 ~ 33.

[23] Meredith M W, Greer A L and Evans P V. Effect of grain-refining additions on intermetallic selection in dilute aluminum alloys [J]. Light Metals: Proceedings of Sessions [C], TMS Annual Meeting (Warrendale, Pennsylvania), 1997: 977 ~ 982.

[24] Pearson J and Kearns M A. Optimisation of grain refiners in the cast house based on recent development programmes [A]. Fifth Australian Asian Pacific Conference. Aluminium Cast House Technology: Theory and Practice [C], 1997. 87 ~ 101.

[25] XIAO Y, MA H, LU J, et al. Effective nucleation particles in grain refining of Al-Ti-B master alloy [J]. The Chinese Journal of Nonferrous Metals, 1997, 7(3): 137 ~ 139.

[26] HU B and LI H. Effects of processing parameters on the performance of Al grain refinement master alloys Al-Ti and Al-B in small ingots [J]. Journal of Materials Processing Technology, 1998, 74(1 ~ 3): 56 ~ 60.

[27] Vader M and Noordegraaf J. Control the quality of master alloy grain refiners [J]. Light Metals, 1988: 463.

[28] Cibular A. The mechanism of grain refinement of sand casting in aluminum alloys [J]. J Inst Met, 1949 ~ 1950, 76: 321.

[29] Hardman A and Young D. Grain refining performance of TICAR master alloys [J]. Light Metals, 1997: 983.

[30] Schneider W, Kearns M A, McGarry M J, et al. Comparison of the behaviour of AlTiB and AlTiC grain refiners [J]. Light Metals, 1997: 953.

[31] Hadia M A, Ghaneya A A and Niazi A. Development and evaluation of Al-Ti-C master alloys as grain refiner for aluminum [J]. Light Metals, 1996: 729.

[32] FENG Q L and WANG C M. Posioning of TiC particles in Al-Ti-C master alloy [J]. J Tsinghua University, 1994, 34: 106.

[33] Mayes C D, McCartney D G and Tatlock G J. Observation on the microstructure and performance of Al-Ti-C grain refining master alloy [J]. Mater Sci Eng A, 1994, 188A: 283.

[34] Marcantonio J A and Mondolfo L F. Grain refinement in aluminum alloyed with Ti and some other elements [J]. Metall Trans, 1971, 2: 465.

[35] Nakao Y. Preparation of Al-Ti-C master alloy through the addition of TiC to Al-Ti melts [J]. J Japan Inst Light Metals, 1967, 17: 65.

[36] Lihl F and Sagoschen J. Grain refinement of aluminum with titanium and carbon [J]. Metall, 1957, 11: 179.

[37] Thury W. Beitrag zur kornfeinung von aluminum [J]. Metallkde W, 1955, 46: 488.

[38] Banerji A and Rohatgi P K. Cast aluminum alloy containing dispersions of $TiO_2$ and $ZrO_2$ particles [J]. J Mater Sci, 1982, 17: 335.

[39] Banerji A and Reif W. Development of Al-Ti-C grain refiners containing TiC [J]. Metall Trans A, 1986, 17A: 2127.

[40] FANG Hong-sheng, MA Hong-tao, ZHANG Bai-qing, et al. A method to prepare a kind of aluminum based master alloys containing Ti and C [P]. China Patent Application No. 98119378.1.

[41] Arnberg L, Backerud L and Klang H. Production and properties of master alloys of Al-Ti-B type and their ability to grain refine aluminum [J]. Met Technol, 1982, 9(1): 1 ~ 6.

[42] Blake R and Smith J. Solidification Technology in the Foundry and Casthouse [C]. London: The Institute of Metals, 1980. 83 ~ 88.

[43] Warren B F. X-Ray Diffraction [M]. Addison-Wesley, 1969.

[44] Timofeeva I I and Klochkov L A. Samsonov G V. Refractory Carbides [C]. New York: Consultants Bureau, 1974.

**(Edited by PENG Chao-qun)**