Grain Refinement Behavior of Al-Zn-Si Alloy by Inoculation in Hot-Dip Coating

Wangjun Peng[1], Guangxin Wu[1*], Xuan Dai[1], Jieyu Zhang[1], Weidong Hu[1], Kuochih Chou[1,2]

(1 Shanghai Key Laboratory of Modern Metallurgy and Materials Processing, Shanghai University, Shanghai, 200072, China;
2 Department of Physical Chemistry, University of Science and Technology Beijing 100082, China)

Keywords: Al-Ti-B; high-temperature liquid quenching; grain size

Abstract

Grain refinements were an effective method to improve the mechanical properties of aluminium alloy, and heterogeneous nucleation was widely applied in industry to achieve a grain-refined. In this study, grain refinement behavior of 55%Al-Zn-1.6%Si alloy by Al-Ti-B was investigated. In order to obtain the microstructure *in situ*, high-temperature liquid quenching by stainless steel pipe was used to capture the sample snapshots. Then, the effect of Al-5Ti-0.2B on the alloy was analyzed by microstructure, solid fraction and grain size. Our results show that the grain size of 55Al-Zn-Si alloy decreased after the Al-5Ti-0.2B addition to some extent, and in order to understand the effect of refinement, it was necessary to analyze the mechanisms of Ti in 55Al-Zn-Si alloy. Meanwhile, during the process of solidification, the solid fraction of 55Al-Zn-Si alloy was further increased with the temperature decreasing, and the result was consistent with our calculation of phase diagram. Finally the reactions were identified using calculation of phase diagram.

Introduction

Hot dip is an effective protective means for metal material. In addition, in all kinds of hot-dip coating, hot dip 55Al-Zn-Si (Galvalume) is a method for obtaining excellent and comprehensive performance. The 55Al-Zn-Si alloy was used in this study because of its industrial importance. With the hot-dip steel plate entering the market of household appliances, more and more manufacturer concern about the surface quality of hot-dip steel plate. In these factors we need to considered, flat surface and high corrosion resistance were very important and these should be considered. These properties are both associate with grain size, and based on the relationship between microstructures and properties, grain refinement is an effective method to improve the tensile strength, plasticity, and ductility. The addition of a small amount of grain refiner to the aluminium melt can promote the formation of equiaxed grains, which improves the mechanical properties and reduces the ingot cracking [1]. And the method most widely used in industry to achieve fine and uniform grain structure is inoculation [2]. Mainly to added Ti in the grain refinement of 55Al-Zn-Si. The size of spangle particles on the surface of Ti-treated galvalume (Hot dip 55Al-Zn-Si) appeared much finer than that of not-Ti-treated galvalume [3]. Garcia. F [4] added small amounts of Ti to 55Al-Zn-Si, and result in decreasing the grain size. Ti inoculation was known to produce grain refining during solidification of liquid Al-alloys by many researchers [5].

In fact, for Ti inoculation, generally Al–Ti–B master alloys were added to the aluminum alloys to refine the grain size of the solidified product[6], and widely used in high-strength aluminum alloy and hot dip 55Al-Zn-Si. Al-Ti-B master alloys contain microscopic TiB_2 and $TiAl_3$ nucleating particles. Although various theories regarding the grain refining mechanisms are proposed (e.g. the particle theory, the phase diagram theory, the duplex nucleation theory, and the peritectic hulk theory) [7]. The mechanism of grain refinement remains a problem of considerable controversy in the scientific literature [6]. Especially in the 55Al-Zn-Si alloy, the report on refinement mechanism of Al-5Ti-0.2B was few, and there are few researches about mechanism of Al-5Ti-0.2B in 55Al-Zn-Si alloy.

Therefore, the purpose of present work is to understand the grain refinement behavior of a 55Al-Zn-Si under the influence of inoculation nucleation. In order to achieve this objective, the high-temperature quenching method is used in this paper. The quenching samples which contain 0% Al-5Ti-0.2B and 1% Al-5Ti-0.2B were used to contrast the grain size. During the process of solidification, the solid fraction was further increased with the temperature decreasing, and the result was consistent with our calculation of phase diagram. The database was Al-Zn-Si-Ti database optimized by our research group, The reactions were identified using calculation of phase diagram.

Experimental

Materials

The 55Al-Zn-1.6Si alloy for experiment was taken from commercial products manufactured by Zhuzhou Smelter Group (Zhuzhou City, China). The actual element compositions of the 55Al-Zn-Si alloy detected by chemical analysis method were given in Table 1.The grain refiner added to the 55Al-Zn-Si alloy used in this investigation is a master alloy with the composition Al-5Ti-0.2B manufactured by Central Aluminum Ltd(Xuzhou, China).

Table 1 Chemical composition of Al-Zn-Si alloy

element	Al	Zn	Si	la	Ce	Fe
wt%	52.687	45.7	1.31	0.2	0.01	0.093

Furnace

The experiments were carried out in electrically heated crucible furnace. The furnace had the following characteristics:

Volts=380, Watts=7.5KW, Phase=3, Hertz=50 Temperature range=1200°C

* Corresponding author. Tel.: +86 021 56337920; fax.: +86 021 56337920
E-mail address: gxwu@shu.edu.cn (Guangxin Wu)

Crucible

A clay graphite crucible having the following dimension was used;

Height: 160mm; Top OD: 140mm; Top ID: 115mm

Thermocouple

Bath temperature was one of the most important parameter in refinement experiment. In order to have a better monitoring the bath temperature, a high-sensitive K-type thermocouple with a high-speed data acquisition system (A/D converter) linked to a notebook computer was used.

Covering flux

There was high volatility near the melting point of 55Al-Zn-Si alloy, so a quality of flux was covered on the top of bath. The composition of the covering flux was showed in Table 2.

Table 2.The composition of the covering flux

	NaCl	KCl	NaF
wt%	47.5	47.5	5

Experimental procedure

General process

The general process of experimental was showed in Figure 1. Step c was extra experiment of refinement

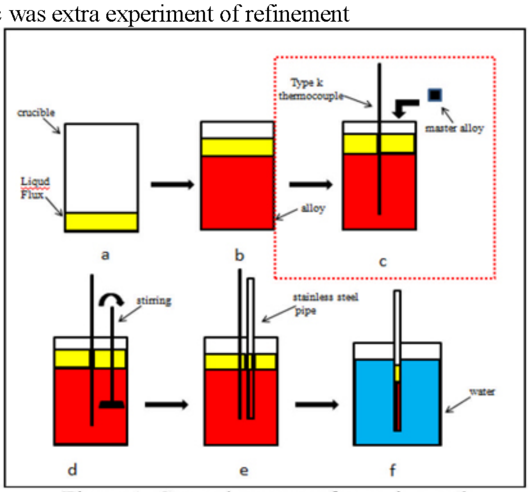


Figure 1. General process of experimental

a. Covering flux was added in a clay graphite crucible and heated it up to 700°C until it melts.
b. 55Al-Zn-1.6Si alloy was added in crucible and holding the temperature at 700°C for some time.
c. Master alloy was added into the bath.
d. The bath was stirred for some time.
e. The sample was taken from the bath by stainless steel pipe at a certain temperature.
d. High-temperature quenching.

Specific processes

Firstly, a covering flux charge of 352g was melted in clay graphite crucible using an electrically heated crucible furnace. Secondly, once the temperatures up to 700°C, the 55Al-Zn-Si alloy charge of 1506g were added into the crucible and hold the temperature for fifty minutes. Thirdly, the master alloys of Al-5Ti-0.2B charge of 15.42g (1%) were later added and the contact time was five minutes after Al-5Ti-0.2B completed melting. Fourthly, the crucible was moved from the furnace and a K-type thermocouple was inserted immediately and cooling it in the air. Finally, once the bath temperature arrived at a certain point, some melt was taken from crucible by stainless steel pipe and quenched it in the water as soon as possible. The samples were cut into Φ11×5mm. Next samples were mechanically grinded with 320 to 2000 mesh SiC papers in order and then polished it using a 0.5μm diamond paste on a napless polishing cloth. The microstructures of section were revealed by 4% Nitric acid-alcohol (3ml Fuming nitric acid [concentration], and 47ml alcohol). Optical microscopy (DM6000 M, LEICA MICROSYSTEMS LTD) was used to characterize the morphologies. Two kinds of 55Al-Zn-1.6Si alloys were investigated: untreated, 1% Al-5Ti-0.2B master alloy addition.

Results and Discussion

Characterization of Al-5Ti-0.2B Master alloy

The Microstructure of master alloy was presented in Fig 2. From this picture, there were three kinds of phase appeared in the picture. In order to know its composition, the energy dispersive spectrum analysis was used (as show in Figure 3). There were high contents of Ti and Al appeared in grey phase, the black phase was pure aluminum, and bright phase is a complex mixture containing Al, Ti, Si and B. The shape of gray phase was quadrilateral, and the result was consistent with the literature [8]. The average atomic ratio of Ti: Al was 1:3. The gray phase was identified as $TiAl_3$.

The quality of Si was too low for the Al-5Ti-0.2B master alloy, so it was regarded as trace element and no longer considered. In order to know the mixture of four elements, the X-ray diffraction analysis was used (As show in Figure 4). The result showed there were three phase in Al-5Ti-0.2B master alloy, Al, $TiAl_3$ and TiB_2. Therefore, the bright phase appeared in Figure 2 were a mixture of Al, $TiAl_3$, and TiB_2. TiB2 clusters aggregated along the grain boundary, and this was consistent with ZHU Man [8].

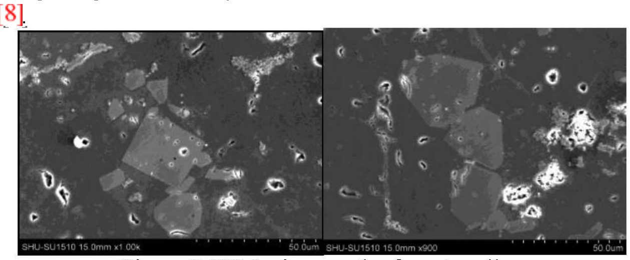
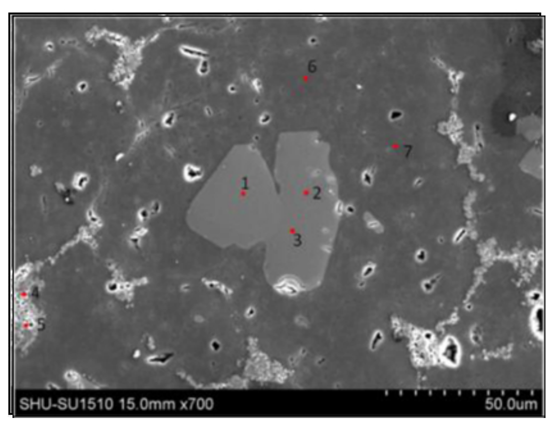


Figure 2 SEM micrograph of master alloy



point	Al		Ti		Si		B	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
point 1	61.68	73.87	37.72	25.44	0.6	0.69	-	-
point 2	61.80	74.01	37.72	25.44	0.48	0.55	-	-
point 3	61.82	74.03	37.73	25.45	0.45	0.51	-	-
point 4	41.62	26.42	15.28	5.46	0.18	0.11	42.92	68.00
point 5	30.81	20.51	27.46	10.34	0.31	0.16	41.31	68.96
point 6	100	100	-	-	-	-	-	-
point 7	100	100	-	-	-	-	-	-

Figure 3 EDS analysis of masteralloy

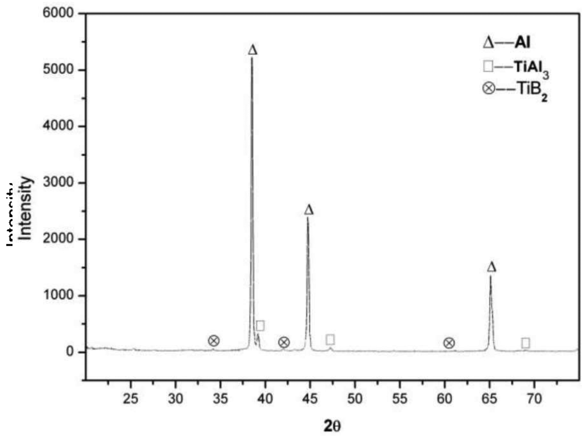


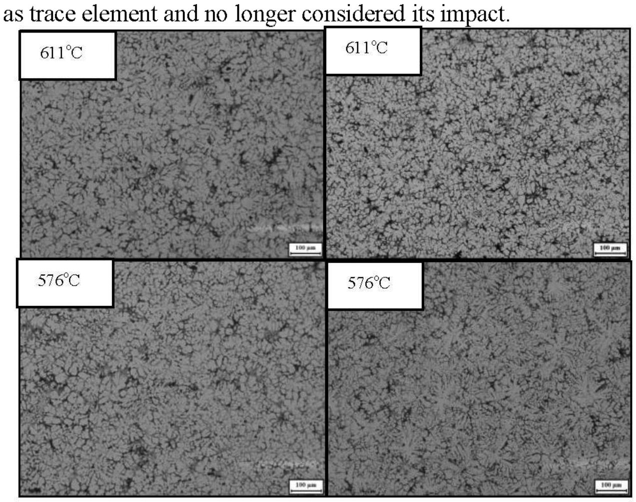
Figure 4 XRD pattern of Al-5Ti-0.2B master alloy

Structure of 55Al-Zn-Si alloy and added inoculation

In order to learn the relationship phase composition with temperature, the Pandat software package [9] was used to simulate the solidification process with the Scheil–Gulliver model [10], which was closer to the real solidification processes taking place in the melt. And thermodynamic database of the Al–Zn–Si-Ti quaternary was built by our group. [11] The samples were taken from the bath by stainless steel pipe at different temperature of 611°C、576°C、540°C、525°C、510°C, and the microstructures of 55Al-Zn-Si alloy with Al-5Ti-B and without were given in Figure 5.

In Figure 5, once the temperature arrived at 611°C, a crystallizing reaction (L→$TiAl_3$) which the formation of $TiAl_3$ have been occurred, but the primary α phase was not found in the quenching structure, and liquid alloys have yet to start solidification. After a period of time, the temperature was 576°C, the reaction still was a crystallizing reaction (L→$TiAl_3$), but some small newborn equiaxed dendrite was found in quenching structure, it showed that alloy had already begun solidification. In 540°C, peritectic reaction (L+$TiAl_3$→Fcc-Al) have occurred, and the newborn equiaxed dendrite had grown up. Then the temperature arrived at 525°C, Fcc-Al was appeared in the picture peritectic peritectic (L+Al-Zn-Si→ Fcc-Al) have been occurred, and the grain grew up further, but some grain begun to contact with each other, mutual interference and limited it grew up. With the temperature decreasing, most of the molten metal in the crucible had solidified, and taking the samples from bath by stainless steel pipe becoming difficult, The final sample was taken at 510°C. The kinds of phase did not change anymore. But the equiaxed dendrites to grow further, all grain touch each other and grew up difficultly. The observation exhibited that the final solidification structure was composed of the Diamond-Si phase, the primary Fcc-Al phase and the $TiAl_3$ phase, which was consistent with the predicted one under a non-equilibrium path.

During solidification process, the solid fraction was further increased with the temperature decreasing, this was consistent with the curve of solidification calculated by phase diagram, and the phase composition of samples at difference temperature in accord with the results of calculation (as show in Figure 6), the quality of boron was too low in this master alloy, it was regarded as trace element and no longer considered its impact.



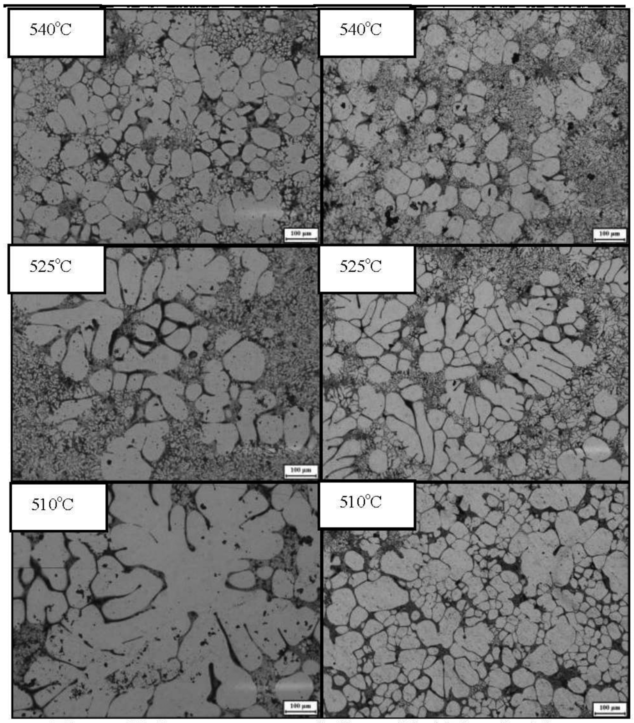


Figure 5 Macrostructures of alloy added Ti and without

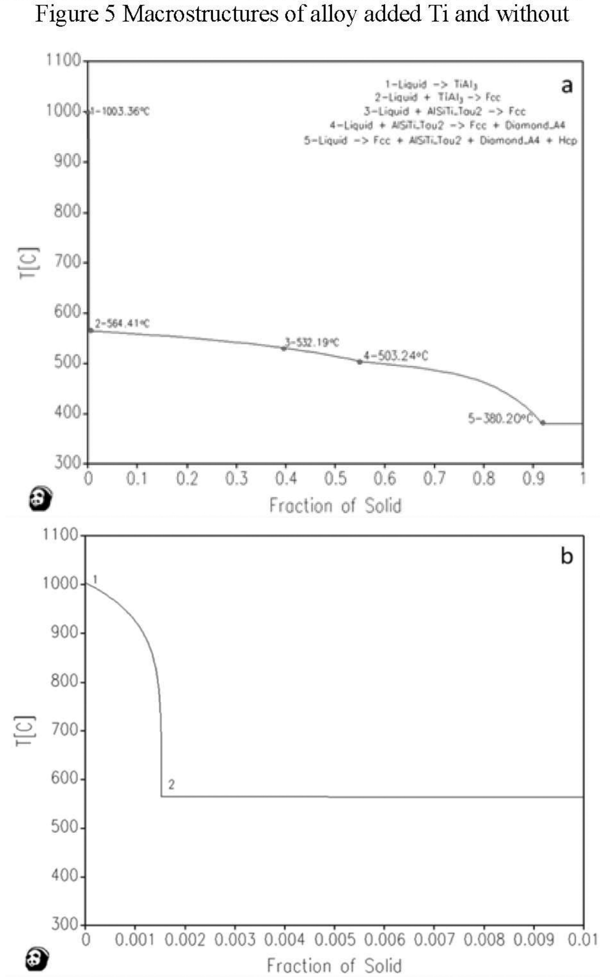


Figure 6 the curve of 55Al-Zn-1.6Si-0.05Ti solidification: b is a part of a (0-0.01)

The grain size of primary α phase at 540°C was analyzed by Image-pro Plus 6.0 software. The shape of primary α phase was irregular, therefore the area of α phase stand for grain size was measured (As show in Figure 7). And the grain size of primary α phase in 55Al-Zn-1.6Si alloy with Al-5Ti-0.2B and without at 540°C was contrasted. The results showed grain size was decreased after added master alloy.

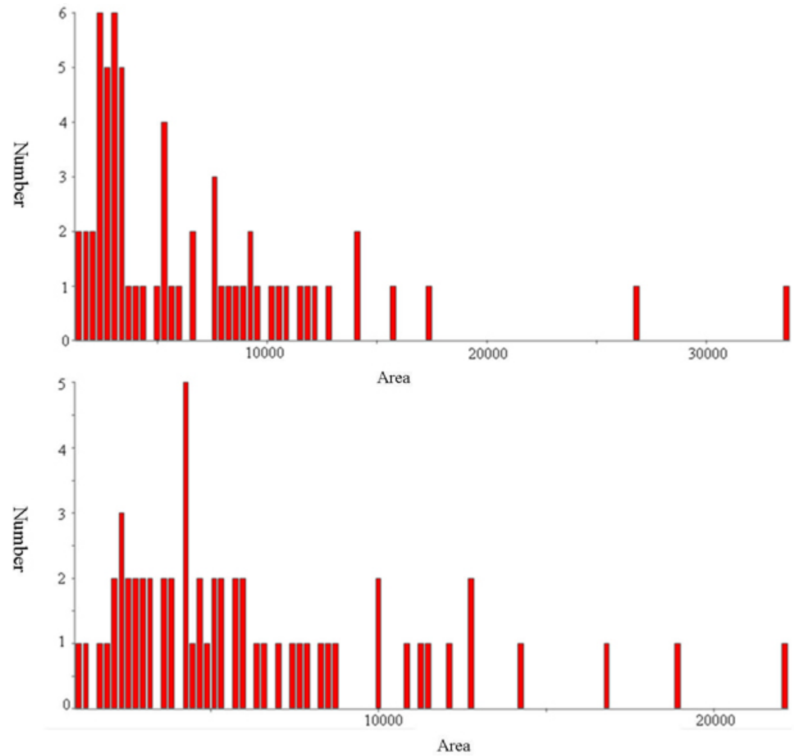


Figure 7 the distribution of grain size

At high magnification, some unique particles could be observed clearly at the center of primary aluminum (α -Al) phase. (As show in Figure 8) And these particles stood for nucleus of primary aluminum. This phenomenon was confirmed by Honda K et [12]. In order to obtain the composition of nucleus, the EDS analysis was used (show in Figure 9). The composition of nucleation was composed of element Ti, Al, Si and Zn. Only a little of nucleation center were found in the sample, but the grain size was reduced indeed. Once the master alloy was added to the melt, the Al matrix dissolved and then released the $TiAl_3$ and TiB_2 into the melt to act as nucleates, but if the contact time was too long, the $TiAl_3$ and TiB_2 would precipitate down at the bottom of crucible, many investigators [13, 14] have made an assumption. The average atomic ratio of Ti: (Al, Si) in point 1, 2 and 3, were respectively 24.20% : 74.92%, 24.16% : 76.1% and 23.14% : 75.92%, corresponding to atomic ratio of Ti (Al, Si) $_3$ phase. The non-integer stoichiometry of this phase was close to that of the ternary Ti $(Al_{1-x}, Si_x)_3$; $x \leq 0.15$ phase identified in the literature [15, 16]. The reason for formation of this phase was the element of Si which existed in 55Al-Zn-1.6Si displaced the lattice of $TiAl_3$. The existence of Si did not significantly alter the lattice parameters of Al [17], therefore, the ternary Ti $(Al_{1-x}, Si_x)_3$ was treated as a binary $TiAl_3$ phase in this study and play an important role for heterogeneous core.

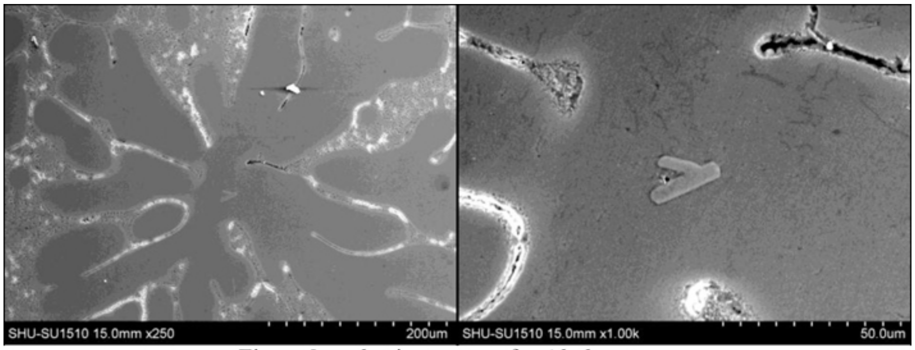
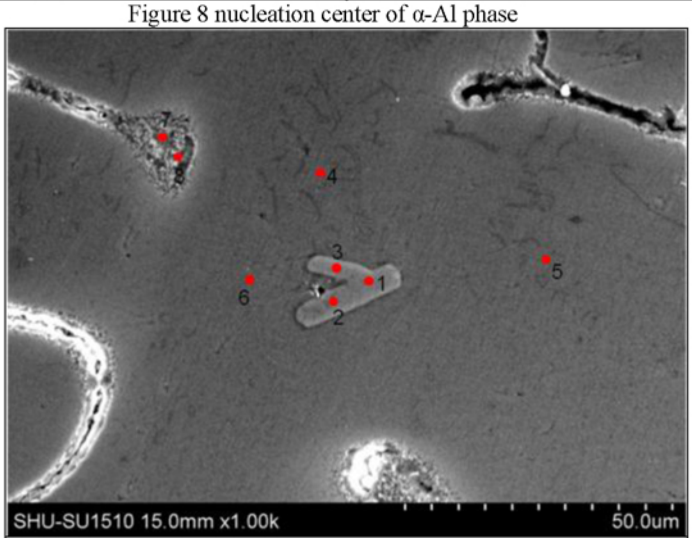


Figure 8 nucleation center of α-Al phase



point	Al		Si		Ti		Zn	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
point 1	51.28	61.82	11.31	13.10	35.64	24.20	1.77	0.88
point 2	51.38	61.82	11.49	13.28	35.65	24.16	1.48	0.74
point 3	51.87	62.16	11.95	13.76	34.28	23.14	1.90	0.94
point 4	72.75	86.61	-	-	-	-	27.25	13.39
point 5	72.58	86.51	-	-	-	-	27.42	13.49
point 6	71.87	85.83	0.47	0.54	-	-	27.66	13.63
point 7	57.97	75.26	3.11	3.87	-	-	38.93	20.86
point 8	39.49	52.94	18.49	23.81	-	-	42.02	23.25

Figure 9 EDS analysis of nucleation

Conclusions

Several conclusions can be derived from this study:

1. The phase of master alloy was composed of pure aluminum, $TiAl_3$, and a small quantity of TiB_2 phase.
2. The quenching samples which contain 0% Al-5Ti-0.2B and 1% Al-5Ti-0.2B were used to contrast the grain size, and the efficiency of refinement was not obvious, however, after analyzed by the Image-pro plus 6.0 software, the result of refinement was obvious.
3. The nucleation was composed of Ti, Al, Si and Zn, and the non-integer stoichiometry of this phase was close to that of the ternary $Ti\ (Al_{1-x},\ Si_x)_3$; $x \leq 0.15$ phase. But the phase was identified a binary $TiAl_3$ phase in this study and it play an important role for heterogeneous core.
4 The reason for the fading of grain refinement was $TiAl_3$ and TiB_2 precipitated down at the bottom of crucible.

Acknowledgements

The work described in this paper was supported by the grant from the National Natural Science Foundation of China (Grant No. 51104098) and shanghai university scientific selection and cultivation for outstanding young teachers in special fund and Innovation Program of Shanghai University (SDCX2012011).

References

[1] Zhu M, Yang G, Yao L, et al "Influence of Al-Ti-B addition on the microstructure and mechanical properties of A356 alloys," *Rare Metals*, 28(2)(2009): 181-186.
[2]Wannasin J, Canyook R, Wisutmethangoon S, et al. "Grain refinement behavior of aluminum alloy by inoculation and dynamic nucleation," *Acta Materialia*, 61(10) (2013): 3897-3903.
[3]Cho N G. *Method of manufacturing a coated steel*: U.S. patent 5,571,566[p].1996-11-5.
[4] García F, Salinas A, Nava E. The role of Si and Ti additions on the formation of the alloy layer at the interface of hot-dip Al–Zn coatings on steel strips[J]. *Materials Letters*, 2006, 60(6): 775-778.
[5] Kashyap K T, Chandrashekar T. Effects and mechanisms of grain refinement in aluminium alloys[J]. *Bulletin of Materials Science*, 2001, 24(4): 345-353.
[6] Iqbal N, van Dijk N H, Offerman S E, et al. "In situ investigation of the crystallization kinetics and the mechanism of grain refinement in aluminum alloys," *Materials Science and Engineering: A*, 416(1) (2006): 18-32.
[7] Easton M, Stjohn D. Grain refinement of aluminum alloys: part I. The nucleant and solute paradigms—a review of the literature[J]. *Metallurgical and Materials Transactions A*, 1999, 30(6): 1613-1623
[8] ZHU Man, YANG Gencang, YAO Lijuan, et al. "Influence of Al-Ti-B addition on the microstructure and mechanical propertiesof A356 alloys," *RARE METALS*, 2009 Vol. 28, No. 2
[9] W. Cao, S. L. Chen, F. Zhang, K. Wu, Y. Yang, Y. A. Chang, R. Schmid-Fetzer, W. A. Oates: *Calphad*, 2009, Vol. 33, no. 2, pp. 328-42
[10] M. Rappaz, C. A. Gandin, A. M. Stoneham, M. McLean, M. S. Loveday: *Phil. Trans.*, 1995, Vol. 351, no. 1697, pp. 563-77.
[11] Luo Q, Li Q, Zhang J Y, et al. Experimental investigation and thermodynamic optimization of the Al–Zn–Ti system in the Al-rich corner[J]. *Intermetallics*, 2013, 33: 73-80.
[12] Honda K, Ushioda K, Yamada W, et al. Nucleation of the primary al phase on TiAl3 during solidification in hot-dip Zn-11% Al-3% Mg-0.2% Si-coated steel sheet[J]. *Materials transactions*, 2008, 49(6): 1401.
[12] Ussadawut Patakham , Julathep Kajornchaiyakul , et al. "Grain refinement mechanism in an Al–Si–Mg alloy with scandium," *Journal of Alloys and Compounds*, 542 (2012) 177–186.
[13] R. Gerloff, W. Reif, W. Heyroth, et al, *Metall*. Germany 2 (1996) 97.
[14] M.A. Kearns, S.R. Thistlethwaite, P.S. Cooper, *TMS Light Metals* (1996) 713.
[15] M. K. Hoffmeyer and J. H. Perepezko, *Light Metals 1991* (edited by E. L. Rooy), p. 1105. Metal. Sot. Of AIME, Warrendale, PA (1991).
[16]G. Petzow and G. Effenberg (eds) *Ternary Alloys*,Vol. 8. D. 283. VCH. Weinheim (1993).
[17]Mohanty P S, Gruzleski J E. "Mechanism of Grain Refinement in Aluminum," *Acta Metall Mater*, 1995, 43(5): 2001～2012.