

EFFECT OF TITANIUM ON DROSS FORMATION IN HOT-DIP 55%Al-Zn-Si-La BATH

Qin Li, Qian Li, Kuo Chih Chou*

Shanghai Key Laboratory of Modern Metallurgy & Materials Processing, Shanghai University, Shanghai 200072, China

Keywords: titanium addition, dross formation, 55%Al-Zn-Si-La bath

*Corresponding author: kcc126@126.com

Abstract

Both titanium (Ti) and lanthanum (La) can improve the quality of hot-dip 55%Al-Zn-Si coating. However, the authors found that the dross problem was very serious when titanium and lanthanum coexisted in the bath. In order to reveal the cause of this phenomenon, different contents of Ti were added into the 55%Al-Zn-Si-La bath to study its influence on the dross formation. The results indicated that La promotes the formation of Si-rich τ_5 ($\text{Fe}_2\text{Al}_3\text{Si}$ or $\alpha\text{-AlFeSi}$) phase in the bath while Ti has no influence on the Fe-Al phase. Furthermore, it was also found that the addition of Ti into the 55%Al-Zn-Si-La bath would lead to the precipitation of TiAl_3 and $\text{Ti}_2\text{Al}_{20}\text{La}$ type of intermetallic compounds, both of which are insoluble and become part of the dross, therefore increase the amount of dross in the bath.

Introduction

In order to improve the quality of coating, some alloy elements are added into the hot dip galvanized bath, which will change the bath's chemical composition and influence the dross formation in it. For example, Al is added into the bath to control the reaction kinetics between the molten Zn and the steel substrate. Due to the strong affinity of Al and Fe, the added Al will react with the dissolved Fe and FeZn_7 to form Fe_2Al_3 and finally become the floating dross in the bath [1]. When adding Ni into the galvanized bath, the FeZn_{13} will be change into $\text{Fe}_6\text{Ni}_5\text{Zn}_{89}$ [2] and adding Ti will change FeZn_{13} into $\text{TiFe}_2\text{Zn}_{22}$ or TiZn_{15} [3]. The transformation of dross will influence the amount of dross and the way to handle it. Therefore, it is necessary to study the influence the alloy elements to the dross formation. In the hot dip galvalume bath, the comprehensive quality can be improved by the addition of Ti and La. It was proposed that the size of spangle forms on the surface of the coating would be minimized and the corrosive resistance, durability and formability would be improved by the addition of Ti into the bath [4]. As for the La, Lai et al [5] and Wu et al [6] pointed out that the thickness of the intermetallic layer would be decreased after La was added into the bath. Yang et al [7] found that the corrosive resistance of the galvalume coating could be improved by proper amount of La addition. However, the existence of Ti and La will increase the amount of bottom dross in the bath, which will cause lots of problems in the operating line. A major problem with the operation disclosed in Europe Patent No. 1068369 B1 [8] is dross pick up on the strip which will cause some "print-through" show up in the painted appearance and other defects such as pimples on the surface of the product. The dross particles can also cause operational problems when they build-up on the sink roll. It will downgrade the quality of coating and/or lead to shutting down the line periodically to clean or change the affected roll resulting in lost production [8]. In order to reveal the cause of the heavy dross accumulation problem, this paper investigates the effect of Ti on the dross formation in the 55Al-Zn-Si-La bath.

Experiment

High purities of Al>99.9 wt.%, Zn>99.9 wt.%, Si>99.9 wt.%, La>99.9 wt.% were used as raw materials to prepare two galvalume pre-melting ingots with the nominal composition of 55wt.%Al-43.4wt.%Zn-1.6wt.%Si and 55wt.%Al-43.4wt.%Zn-1.6wt.%Si-0.1wt.%La. All the pre-melting ingots were prepared in a vacuum induction furnace. Sponge titanium (Ti>99.5wt.%) and iron panel (Fe>99.5wt.%) were added into the melted ingot to simulate the dross formation in the hot dip galvalume bath.

Total mass of 100g of the pre-melting ingot with the added Ti and/ or Fe were first heated in a resistance furnace to the temperature of 800 °C and kept for 20 h to ensure the dissolution of raw materials and homogeneity of the bath. They were then held at 600 °C for 10h to allow for the precipitation and segregation of intermetallic compounds. In case of the oxidation of the liquid metal, 100g of 60wt.% CaCl_2 +40 wt.%NaCl mixture was adopted to cover on the surface of the liquid bath. The samples were finally water quenched individually to prevent the precipitation of secondary intermetallic particles during solidification.

The bottom of each sample were sectioned, polished, and examined by optical microscopy for the existence of intermetallic particles. Sections rich in intermetallic particles were used for the observation of the morphology and determination of the chemical composition by a scanning electron microscope equipped with an X-ray energy dispersive spectroscope (SEM-EDS).

The microstructure of intermetallic phases was further confirmed by analyzing X-ray diffraction patterns generated by a D/max-2550 X-ray diffractometer (XRD), operating at 50 kV and 100mA with Cu K α radiation. The diffraction data were collected by a goniometer at in the scanning range of $10^\circ \leq 2\theta \leq 90^\circ$, $4^\circ/\text{min}$, with a step size of 0.02° . However, because the size and amount of intermetallic phases are much smaller than the matrix phases, it is very difficult to detect them directly. Therefore, we used the solution of 10g/l FeCl_3 +40g/l tartaric acid [9] to selectively dissolve the Al-Zn matrix and extract the intermetallic phases for the XRD analysis.

Results and discussion

The Influence of Ti and La on the Formation of Fe-Al Dross

According to the relationship between the solubility of iron in 55Al-Zn-Si bath and temperature, the usual 0.46wt.% solubility found at 873K jumps up to 2.15wt.% at 1073K [10]. In order to ensure enough bottom dross to be detected, the amount of Fe addition was set to 1wt.%. Figure 1 shows the morphology of the main phase in the sample with 1wt.% Fe addition into the 55Al-Zn-Si bath. According to the XRD pattern, figure 2(a), the main phase in the galvalume bath is $\text{Fe}_4\text{Al}_{13}$ (also called FeAl_3). The chemical composition of the $\text{Fe}_4\text{Al}_{13}$ is Al=79.57at.%, Fe=15.54at.%, Si=3.97at.%, Zn=0.92at.%, containing some Zn and Si in it, which suggests that Zn and Si can be

dissolved in the $\text{Fe}_4\text{Al}_{13}$. This result is in consistence with the report of references [11, 12]. The density of $\text{Fe}_4\text{Al}_{13}$ is 3.850 g/cm^3 while the density of liquid bath is 3.327 g/cm^3 [12], therefore $\text{Fe}_4\text{Al}_{13}$ will sink to the bottom and become the bottom dross in the bath.

When 0.15wt.% Ti+1wt.%Fe was added into the galvalume bath, $\text{Fe}_4\text{Al}_{13}$ and TiAl_3 can be detected by the XRD pattern, as can be seen in figure 2(b). However, the morphology of the $\text{Fe}_4\text{Al}_{13}$ wasn't changed with extra 0.15wt.%Ti addition, as can be seen in figure 3. The chemical composition of the $\text{Fe}_4\text{Al}_{13}$ observed in the sample of 0.15wt.%Ti+1wt.%Fe addition is Al=79.32at.%, Fe=16.17at.%, Si=3.44at.%, Zn=1.07at.%, which is almost identical with the composition of $\text{Fe}_4\text{Al}_{13}$ in the sample of 1wt.%Fe addition. Since there was no other Fe-containing phase detected by the XRD and the morphology of $\text{Fe}_4\text{Al}_{13}$ wasn't change with extra 0.15wt.%Ti addition. Therefore, it can be concluded that the addition of Ti in the galvalume bath cannot change the major bottom dross in the galvalume bath.

However, when 1wt.%Fe was added into the 0.1wt.%La-containing bath, the major dross precipitated in the bath was change into $\text{Fe}_4\text{Al}_{13}$ and τ_5 ($\text{Fe}_2\text{Al}_8\text{Si}$ or $\alpha\text{-AlFeSi}$), as can be seen in figure 2(c). The composition of τ_5 is Al=70.33at.%, Fe=17.55 at.%, Si=8.17at.% and Zn=3.95 at.%, whose Si content is higher than the $\text{Fe}_4\text{Al}_{13}$. The morphology of $\text{Fe}_4\text{Al}_{13}$ and τ_5 is shown in figure 4. Wu et al [6] studied the effects of 0.2wt.% rare earth addition on the microstructure and thickness of galvalume coating. It was suggested that La substitution in the Fe_2Al_5 and FeAl_3 phase could grab electronic charges from Al atoms and weaken the formation of the Fe-Al compounds [6]. In other words, the formation of $\text{Fe}_4\text{Al}_{13}$ was hindered by the existence of La in the bath. In the study of Lai et al [5], they investigate the effect of La on the microstructure and growth kinetics of the intermetallic layers at 600°C . They found that the addition of La made Si enriched in the intermetallic layer and promoted the growth of the τ_5 phase during the hot dipping. Therefore, it can be concluded that La in the bath can hinder the formation of Fe-Al phase and promote the enrichment of Si in it, which lead to the formation of τ_5 phase.

Therefore, when Ti and La exist in the galvalume bath, La is the element change the type of Fe-Al intermetallic phase in the bath instead of Ti.

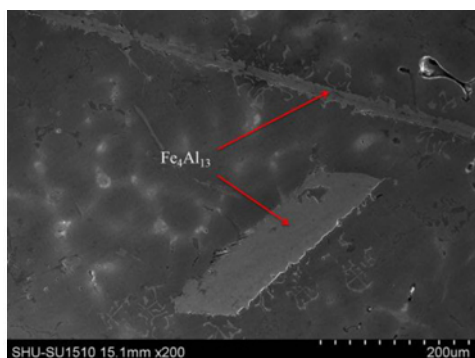


Figure 1. The BSE image of $\text{Fe}_4\text{Al}_{13}$ in the 55Al-Zn-Si bath with 1wt.%Fe addition

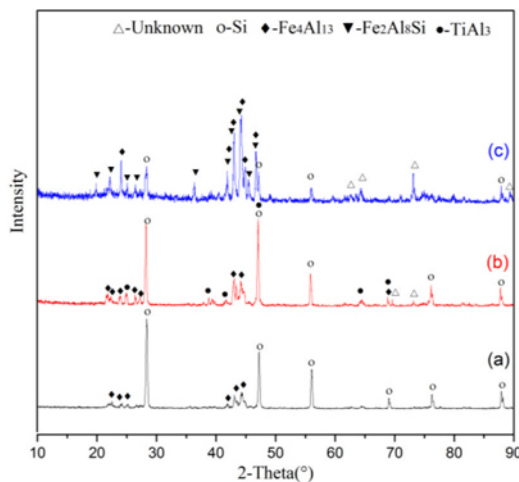


Figure 2. The XRD pattern of the extracted phase in the sample of (a) 55 wt.%Al-Zn-Si-1wt.%Fe (b) 55 wt.%Al-Zn-Si-1wt.%Fe-0.15wt.%Ti (c) 55 wt.%Al-Zn-Si-1wt.%Fe-0.10wt.%La

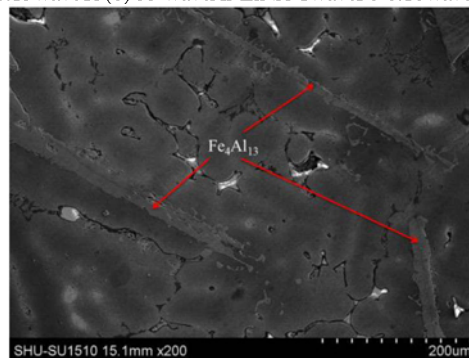


Figure 3. The BSE image of $\text{Fe}_4\text{Al}_{13}$ in the 55Al-Zn-Si bath with 1wt.%Fe+0.15wt.%Ti addition

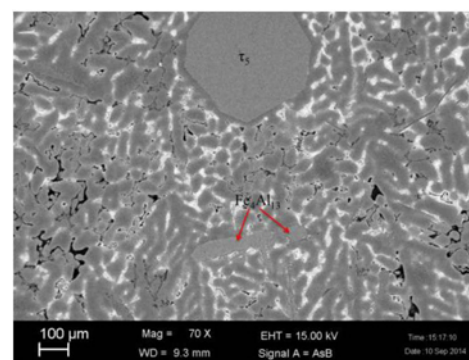


Figure 4. The BSE image of $\text{Fe}_4\text{Al}_{13}$ and τ_5 in the 55Al-Zn-Si-La bath with 1wt.%Fe addition

The Precipitation of Ti-containing Phase in the Galvalume Bath

The addition of 0.05, 0.10 and 0.15 wt.%Ti in the 55Al-Zn-Si bath would cause the precipitation of stripe-like phase, as shown in figure 5. The chemical composition of this phase is: Al=65.62at.%, Ti=19.27at.%, Si=14.24 at.%, Zn=0.86 at.%. Base on the composition of this phase, this phase is TiAl_3 . It is reported that the Si can replace some Al in the TiAl_3 . Bulanova et al [13] reported that the solubility of Si in the TiAl_3 is 13.29at.%. Zhu et al [14] adopted the first principles

method to calculate the site preference of Si in TiAl_3 and reported that the solubility of Si in TiAl_3 lies in the range between 12.5 at.% and 18.75 at.%. The Si content of TiAl_3 determined in this paper is in agreement with the reported references, therefore it can be also expressed as $\text{Ti}(\text{Al},\text{Si})_3$. Although the solubility of Ti in liquid aluminum is small, e.g. 0.15wt.% [15], the precipitation of TiAl_3 in the bath was not observed until the amount of Ti addition reached 0.15wt.%. In order to ensure the authenticity of this phenomenon, authors prepared three samples with the same experimental parameters in the addition of 0.10wt.%Ti. Still, no TiAl_3 was observed in these three samples. It is possible that 0.10wt.% of Ti didn't excess the solubility of Ti in the bath therefore TiAl_3 would not precipitate in the bath. However, due to the bath didn't reach the equilibrium state the Ti solubility was not measure in this paper.

Adding 0.05, 0.10 and 0.15 wt.%Ti into the 55Al-Zn-Si-La bath, two types of intermetallic phase precipitated in the bottom of the bath. The morphology of these phases is shown in the figure 6(a)-(c) and the chemical composition of these two phases is listed in table 1. The XRD pattern confirms that these two phases are $\text{Ti}_2\text{Al}_{20}\text{La}$ and TiAl_3 phase, as shown in figure 7.

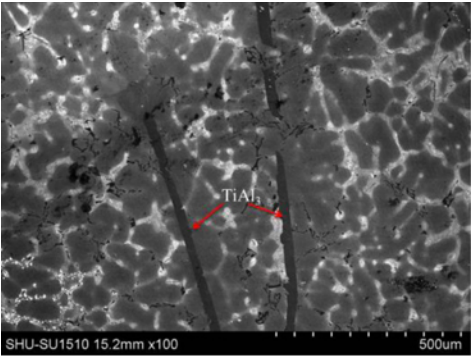


Figure 5. The BSE image of TiAl_3

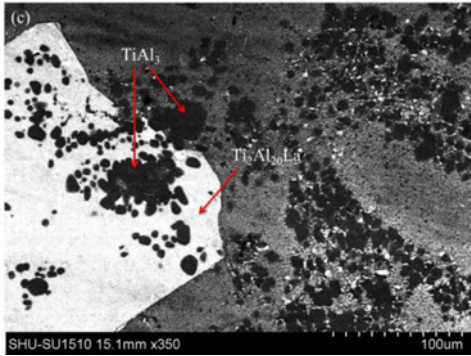
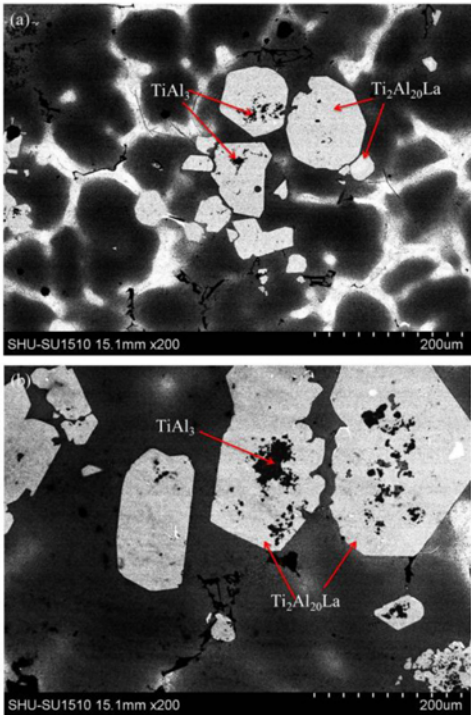


Figure 6 The BSE image of $\text{Ti}_2\text{Al}_{20}\text{La}$ and TiAl_3 in 55Al-Zn-Si-La bath with (a) 0.05wt.%Ti (b) 0.10 wt.%Ti (c) 0.15wt.%Ti addition

Table 1 The chemical composition of $\text{Ti}_2\text{Al}_{20}\text{La}$ and TiAl_3

Phase	Al (at.%)	Zn (at.%)	Ti (at.%)	La (at.%)	Si (at.%)
$\text{Ti}_2\text{Al}_{20}\text{La}$	65.32	22.20	7.96	4.52	-
TiAl_3	61.96	1.07	25.23	-	11.74

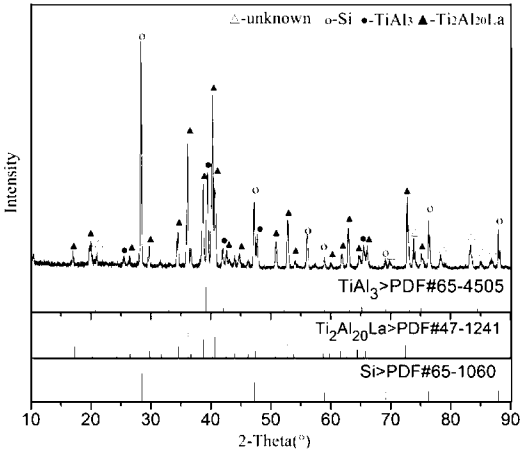


Figure 7 the extracted phase in the sample of 0.15wt.%Ti adding into 55Al-Zn-Si-La bath

As can be seen in figure 6 (a), the addition of 0.05wt.% Ti into the 55Al-Zn-Si-La bath can cause the precipitation of TiAl_3 , which suggests that La may decrease the solubility of Ti in the galvalume bath, leading to the precipitation of TiAl_3 phase with lower Ti addition. What's more, the morphology of TiAl_3 was changed from strip like shape to the cluster-like shape, as can be seen in figure 5 and 6. Li et al [16] pointed out that the surface-active element of rare earth enrich at the surface of TiAl_3 would inhibit the growth of strip-like TiAl_3 . Similarly, the inhibited effect of rare earth on the TiAl_3 also existed in the Al-Ti-B-RE master alloy [17]. Therefore, the morphology change of TiAl_3 in 55Al-Zn-Si-La bath is the result of growth inhibition effect of La on it. It can be proved by the phenomenon of TiAl_3 surrounded by $\text{Ti}_2\text{Al}_{20}\text{La}$, as shown in figure 6. According to the ICDD card 47-1241 and 01-1176, the lattice parameter of $\text{Ti}_2\text{Al}_{20}\text{La}$ is 1.47nm and $\alpha\text{-Al}$ is 0.404nm, which means that the mismatch of these two phases is 72.6%. Therefore, $\text{Ti}_2\text{Al}_{20}\text{La}$ is unsuitable for the heterogeneous nucleation for $\alpha\text{-Al}$ and the existence of $\text{Ti}_2\text{Al}_{20}\text{La}$ in the bath cannot serve as the grain refiner in the hot-dip coating process. As a result, $\text{Ti}_2\text{Al}_{20}\text{La}$ exists as dross in the bath, which will increase the amount of bottom dross. In the aluminum alloy, TiAl_3 is an effective grain refiner [18]. However, the formation of

Ti(Al,Si)₃ with Si solution in TiAl₃ will have negative impacts on the performance of grain refiner by altering the favorable lattice parameter of TiAl₃ [19]. Therefore, the grain refining effect TiAl₃ will also be decreased in the galvalume bath with Si solution. According to Easton et al [18], the grain refinement of aluminum by TiAl₃ is caused via the peritectic reaction on the primary particles of TiAl₃. However, as can be seen in the figure 5, the size of Ti(Al,Si)₃ is larger than the Al-rich dendrites, contradictory to the peritectic reaction, which suggests that the existence of Ti(Al,Si)₃ didn't serve as the grain refiner in the galvalume bath. Since it is insoluble and precipitate to the bottom, like Ti₂Al₂₀La, it becomes bottom dross and increase the amount of it in the bath.

In a nut shell, the coexistence of Ti and La in the galvalume bath will lead to the precipitation of TiAl₃ and Ti₂Al₂₀La, which increase the amount of bottom dross in it.

Conclusions

The dross formation in the 55Al-Zn-Si and 55Al-Zn-Si-La bath with Ti addition has been studied. The following conclusions can be drawn from this study.

- (1) La promotes the formation of Si-rich τ_5 phase in the bath while Ti has no influence on the Fe-Al phase.
- (2) Adding Ti into the 55Al-Zn-Si-La bath will lead to the precipitation of TiAl₃ and Ti₂Al₂₀La which become the bottom dross and increase the amount of it in the bath.

Acknowledgements

The authors thank Instrumental Analysis and Research Center of Shanghai University for their support of materials testing and research. This work was financially sponsored by the National Natural Science Foundation of China (51471103, 51404149)

References

- [1] A. R. Marder, "The Metallurgy of Zinc-Coated Steel", *Progress in Materials Science*, 2000, 45:191-271.
- [2] P. Perrot, G. Reumont, "Thermodynamic Description of Dross Formation When Galvanizing Silicon Steels in Zinc-nickel Baths", *Journal of Phase Equilibria*, 1994, 15(5):479-482.
- [3] G. Reumont, T. Gloriant, P. Perrot, "Titanium Solubility in the Fe-Zn Intermetallic Compounds When Galvanizing Iron Substrates in Zn-Ti Baths at 450 °C". *Journal of Materials Science Letters*, 1995, 14(10):752-754.
- [4] N. G. Cho, Method of Manufacturing a Coated Steel: US 5571566, 1999-11-05.
- [5] X. F. Lai, H. P. Peng, J. H. Wang, et al., "Effect of La on Intermetallic Layer of Galvalume", *Surface Engineering*, 2013, 29(5):390-395.
- [6] G. X. Wu, J. Y. Zhang, Q. Li, et al., "Microstructure and Thickness of 55 pct Al-Zn-1.6 pct Si-0.2 pct RE Hot-dip Coatings: Experiment, Thermodynamic, and First-principles Study", *Metallurgical and Materials Transactions B*, 2012, 43(1):198-205.
- [7] D. Yang, J. Chen, Q. Han, et al., "Effects of Lanthanum Addition on Corrosion Resistance of Hot-dipped Galvalume Coating", *Journal of Rare Earths*, 2009, 27(1):114-118.
- [8] P. J. Sippola. Method of Producing Hot-dip Zinc Coated Steel Sheet Free of Dross Pick-up Defects on Coating and Associated Apparatus: EP 1068369 B1, 2005-06-01.
- [9] A. Michalcová, D. Vojtěch, P. Novák, "Selective Aluminum Dissolution as a Means to Observe the Microstructure of Nanocrystalline Intermetallic Phases From Al-Fe-Cr-Ti-Ce Rapidly Solidified Alloy", *Micron*, 2013, 45:55-58.
- [10] C. M. Champan, F. C. Kaminski, N. H. S. Coni, Bottom Dross Removal and Control at CSN-PR: Inter ZAC, China, 2010.
- [11] S. Shawki, Z. A. Hamid, "Effect of Aluminium Content on the Coating Structure and Dross Formation in the Hot-dip Galvanizing Process", *Surface and Interface Analysis*, 2003, 35(12):943-947.
- [12] Q. Luo, F. Jin, Q. Li, et al., "The Mechanism of Dross Formation during Hot-dip Al-Zn Alloy Coating Process", *Journal for Manufacturing Science & Production*, 2013, 13(1-2):85-89.
- [13] M. Bulanova, L. Tretyachenko, M. Golovkova, et al., "Phase Equilibria in the α -Ti-Al-Si Region of the Ti-Si-Al System", *Journal of Phase Equilibria & Diffusion*, 2004, 25(3):209-229.
- [14] G. L. Zhu, D. Shu, Y. B. Dai, et al., "First Principles Study on Substitution Behaviour of Si in TiAl₃", *ACTA PHYSICA SINICA*, 2009, 58(z1):210-215. (in Chinese)
- [15] D. G. McCartney, "Grain Refining of Aluminium and its alloys Using Inoculants", *International Materials Reviews*, 1989, 34(1):247-260.
- [16] M. Li, Y. P. Kong, R. G. Guan, et al., "Effects of Rare Earth on Microstructure and Refining Performance of Al-3Ti-0.2C Refiner", *Foundry*, 2011, 60(05): 473-476. (in Chinese)
- [17] S.H. Zhang, H. Zhang, Y. Zhu, "Effect of rare earth element on Al-Ti-B-RE Master Alloys", *J.CENT.SOUTH UNIV. (SCIENCE AND TECHNOLOGY)*, 2005, 36(13):386-389.(in Chinese)
- [18] M. Easton, S. David, "Grain Refinement of Aluminum Alloys: Part I. the Nucleant and Solute Paradigms-a Review of the Literature", *Metallurgical and Materials Transactions A*, 1999, 30(6):1613-1623.
- [19] A. Hardman, E. Burhop, Characterisation of a New Generation of Grain Refiners for the Foundry Industry: TMS Light Metals, 2008.