# Effect of Inoculant Composition on Grain Refining Process in Aluminum Casting Alloys

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**Abstract.** Grain refinement plays a crucial role in improving characteristics and properties of cast and wrought aluminum alloys. Generally Al–Ti and Al–Ti–B master alloys are added to the aluminum alloys to grain refine the solidified product. The mechanism of grain refinement is of considerable controversy in the scientific literatures and has been the subject of intensive research. There is common question for all producer of aluminum castings that how they can be sure about the quality of nucleation. Thermal analysis is an important tool to answer this question. In this research, different types of inoculants were used to investigation of nucleation in A356 aluminum alloy. The cooling curve of each sample was recorded and by using a special computer program, the first derivative was calculated. By calculating zero curve and analyzing the cooling curve, it is possible to predict the quality of nucleation and calculation fraction of solids, latent heat and other information. The result of this research have shown that if maximum undercooling of nucleation was approximately 3.8 C, the quality of nucleation process will be more reliable.

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**Key words:** Thermal Analysis, Grain Refining, Nucleation, A-356 Aluminum.

## 1. Introduction

Among aluminum alloys with high mechanical properties the various grades of Al-Si7Mg (A-356 ) occupy a position of growing importance . The alloy in fact has interesting technological characteristics, satisfactory castability, low tendency to hot tear , good corrosion resistance , and no susceptibility to stress corrosion [Centre Technique1989]. Grain refinement plays a vital role in aluminum alloys. It improves the casting quality by reducing shrinkage and gas porosities, uniform distribution of intermetllic phases, improvement of mechanical properties and pressure tightness [Shivakumar, Wang, Apelian, 1991], [Apelian, Sighworth, Wahler 1984] . Interest in the grain refinement of aluminum dates back with the work of Rosenhain et al [1930] Sicha and Bohem [1948] were the first to show that grain refinement improve markedly tensile strength and elongation in an Al- 4.5% Cu alloy casting. During the past 70 years, there are hundreds of academic and industrial researches who try to describe the mechanisms and technologies of grain refinement in aluminum alloys.

Titanium and Boron are main grain refiners in aluminum industry which may be added to molten metal in the form of salt fluxes, such as $K_2$ Ti $F_6$ and K B $F_4$ , or in the form of master alloys such as Al- Ti or Al – Ti – B or Al – B . Salt fluxes, react with molten metal and reduce efficiency of refiners and produce corrosive fume , increase hydrogen content and inclusions in the melt and not recommended for production of engineering parts [Sighworth,G.K.1986], [Sighworth, Guzowski, 1985]

## 2. Mechanisms of grain refinement

There are various theories who describe the mechanism of grain refinement in aluminum alloys. Peritectic theory proposed by Crossley and Mondolfo [1951], and Marcantonio, Mondolfo, [1970] and Davis, Dennis, Hellawell [1970] found particles of $TiAl_3$ at the center of aluminum grains and orientation relationships between these particles and the surrounding aluminum .

The Carbide theory assumed by Cibula [1950] established that the Titanium Carbide (Ti C) nuclies are main nucleant particles in aluminum alloys. Recent researches by Mohanty et al [1994] have demonstrated that TiC particles are not effective nucleants due to their thermodynamic instability, and also there are not enough atomic carbons in molten aluminum to produce enough TiC nucleation sites. Boride theory [Cibula 1952], Peritectic Hulk theory [1991], metastable phase of (AL – Ti) $B_2$, which is formed by a range of solid solutions of $ALB_2$ and $TiB_2$ and Hyper nucleation theory assumed by Jones[1976] and Pearson[1987] are part of studies to describe the mechanisms of nucleation, but neither of these have been proven conclusively. Table 1 present summary of the mechanisms of grain refinement in aluminum with the main observations for each of the different master alloys.

## 3. Grain refinement in Al – Si casting alloys

Most of researches on grain refinement in Al casting alloys, concentrate on the mechanism of nucleation by adding Ti, Ti – B or B content master alloys or fluxes. There are limited studies about the effect of chemical composition of aluminum alloy on grain refinement. Backerud, Yidong, [1991] and Bakerud, Johnson [1996] established that the alloying element such as Zn, Mg and Si added constitutional undercooling causes dendritic tips to become finer and coarser grains result. St John et al [1999] have shown of two nucleation mechanisms in Al – Si alloys. One involves at the mold wall nucleation, while the other impiles the activation of substrates in melt by constitutional under cooling resulting from Si content. Figure 1 show grain sizes relating to Si content of molten metal. Presence of Si is accompaniment with constitutional under cooling in Al - Si systems, which leading to reducing in grain size, followed by an increase associated with a change in the growth mode of the interface. [Ibarra,1999]

Table1: Summary of grain refinement mechanisms in Al-Si casting alloys.

| | Al-Si Casting Alloys | |
|---|---|---|
| **Master Alloy** | **Effect** | **Mechanism** |
| **Al-Ti** | Poor | Drop in Peritectic formation of $Ti_xSi_yAl_{t-(x+y)}$ to below liquidus of alloy |
| **Al-Ti-B Ti/B > 2.2** | Reasonable | $\alpha$ (Al) nucleates of $Ti_xSi_yAl_{t-(x+y)}$ Which forms peritectically on TiB2 |
| **Al-B** | Excellent | Eutectic Formation of $\alpha$ (Al) L $\rightarrow$ $\alpha$ (Al)+AlB2 |
| **Al-Ti-B** | Good, Better than if Ti/B > 2.2 | Eutectic Formation of $\alpha$ (Al) At TiB2 interface due to solute B |

Refinement limited by drop in peritectic temperature by Si.

## 4. Experimental procedure

A-356 aluminum primary ingots with following chemical composition used as casting alloy:

| % Si | % Mg | %Cu | |
|---|---|---|---|
| 6.8–7.3 | 0.25-0.3 | <0/1 | |
| %Sn | % Zn | %Fe | %Al |
| <0/1 | <0/1 | <0/15 | Reminder |

Tower shaft melting and holding furnace with 2 tones per hour melting rate and 6 tons holding capacity, was used as melting and holding unit.

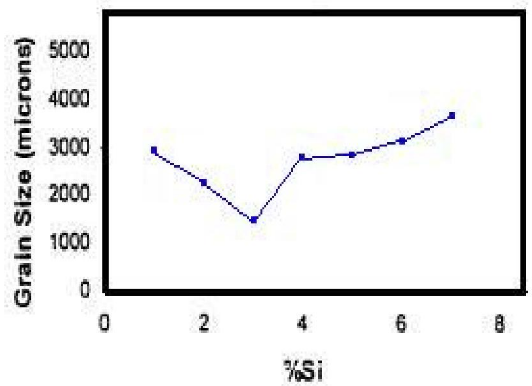


Figure 1- Effect of Si addition on refinement of aluminum alloys [Ibarra, 1999].

Cylindrical steel mold with 50 mm diameter and 75 mm height, preheated to 250°C and coated with zircon base diecoat, was used to casting the samples. To recording temperature changed versus time cooling curves, a k type thermocouple (Chromel – Alumel) was adjusted in center of mold. The molten metal at 760°C was poured in a 500 kg capacity ladle. Rotary degassing system was used to degassing and inclusion removal of molten aluminum with argon neutral gas, for 6 minutes.

To inoculation of molten aluminum, the 10 kg capacity crucible was used which preheated to 500°c. The required amount of each inoculant was placed in crucible and molten metal from 500 kg ladle poured on it. 4 samples from each type of inoculants and totally 20 samples were poured in cylindrical steel dies with 100 grams capacity at 705°C. In the case of salt flux, it is added by a plunger to molten metal. To recording the cooling curve, it is necessary to record the several thousands measurements for each test. A measurement rate of 60–80 per second by a thermo analyzer type MW- 100 which connected to P5 personal computer was used to ensure stabilization of measurements and provide the require accuracy for analysis of the solidification curve. The Tac-Plote 10 Computer Program was used to plot the cooling curves from experimental data. To measuring the grain size of castings, computer aided image analyzer system was used. For metallographic study of samples, the etchant solution with (60%HCL, 30%$HNO_3$, 5%HF, 5%$H_2O$) was used. To measuring the Ti and B content in cast specimens, spectrometery analysis was done on all samples. To analysis cooling curves and calculation its first derivative, solid percent, latent heat, and nucleation efficiency, a computer program in Turbo C++ language was written.

## 5. Cooling curve and thermal analysis

A precise recording of the solidification and the differential analysis, i.e. determination of all influences involved, is the fundamental condition for proper assessment of grain refinement. Thermal analysis monitors the temperature changes in a sample as it solidify, and resulting plot is a curve of temperature versus time, Figure 2.

The grain size of castings has been related to differences in temperatures between a minimum. $T_U$ occurring immediately after the beginning of solidification and the maximum temperature, $T_R$, reached due to recalescence of the sample. This quantity has been called recalescence undercooling $\Delta T_{R-U}$ [Tuttle,1984] .This parameter has been used to monitor the grain refinement of castings. By adding the grain refiners to the molten aluminum alloy the amount of the recalescence would be change. By monitoring these changes in casting, it is possible to predict the nucleation phenomena in castings [Tuttle,1984].

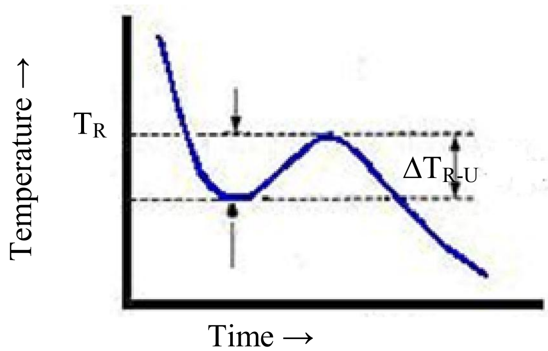


Figure 3- Cooling curve parameters.

## 6. Calculation of zero curve

Zero curve is the first derivative of cooling curve. To calculation of zero curve, it is assuming that there is no transformation or reaction in molten metal during solidification. Fourier and Newtonian methods could be use to analysis, and description the cooling curve once the zero curve is calculated. But the Fourier Method analysis is more reliable than Newtonian method [Emadi, et al. 2005] [Ihsan et al. 2004]. If the thermocouple was off-center in die. In this research the thermocouple fixed in center of die and Newtonian method selected to calculation of Zero Curve. In Newtonian method, thermal gradients across the sample can be considered to be zero and heat transfer take places by convection to the die at a constant temperature $T_\circ$. As the enthalpy decrease in metal is equal to the heat transferred to the die, the mathematical form of the Newtonian analysis is given as [Ihsan et. al. 2004]

$$L\rho V\frac{dfs}{dt} - V\rho C_P\frac{dT}{dt} = hA(T - T_0)$$

or :

$$\left(\frac{dT}{dt}\right)_{CC} = \frac{1}{V\rho C_p}\left[L\rho V\frac{dfs}{dt} - hA(T - T_0)\right]$$

In which ρ is density, V is the volume of sample, and Cρ is the specific heat. If there was no phase transformation, and by integration from equation, [D. Emadi, et. al. 2005]:

$$L = C_P\int_0^{ts}\left[\left(\frac{dT}{dt}\right)_{CC} - \left(\frac{dT}{dt}\right)_{ZC}\right]dt$$

This equation was used to calculation of Zero Curve.

## 7. Results and discussion

Figure 4 illustrates undercooling curves, first derivations and zero curves for sample no. 4. Variations of solid fraction with solidification time is illustrates in figures 5. Figures 6 and figures 7 illustrates grain structures for samples no.1 and 4 respectively.

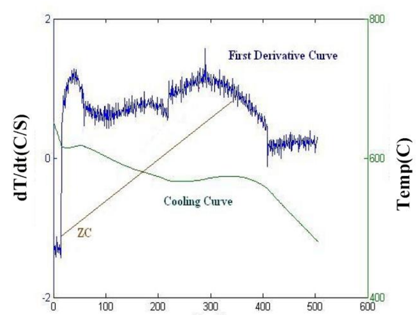


Figure 4- Cooling curve, first derivation and zero curve for sample no 4.

As the temperature decrease to eutectic, the nucleation of eutectic cells of Al-Si take place in molten metal. Latent heat release by nucleation, increase undercooling temperature to $T_U$. Hunt [1984] shows that the nucleation rate at a given undercooling can be calculate as:

$$\frac{dN}{dt} = K_1 (N_S - N) \exp\left(\frac{K_2}{(\Delta T_{R-U})^2}\right) \quad (6)$$

$N_S$ : Density of initial nucleation sites

$K_1$ : Collision frequency of atoms of the melt with Nucleation sites of the heterogeneous particles

$K_2$ : Interfacial energy balance between the nucleus, liquid and the foreign substrates on which nucleation occurs.

$\Delta T_{R-U}$ : Nucleation Undercooling

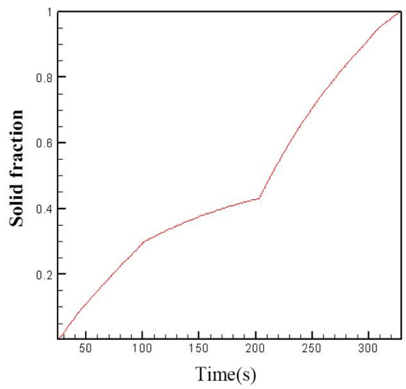


Figure 5- Solid fraction for sample no

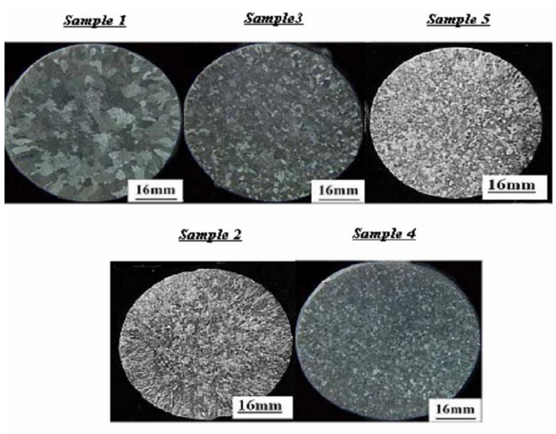


Figure 6- Macrostructure of Al–Si (A-356) alloy
Sample 1- Without grain refiner
Sample 2 - Al-5%Ti-1B grain refiner
Sample 3- Pressed powder Nucleant 2
Sample 4- Al-1.6%Ti-1.4%B grain refiner
Sample 5 - Al-10%Ti grain refiner

Table 2- Thermal analysis results

| Al Alloy A356 | Thermal Analysis Parameters | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Type of Inoculant | Amount of inoculant added to molten metal | Ti and B content of molten metal | Solidification Start Temperature (C) | Eutectic Solidification start time (S) | Eutectic Start Temp (°C) | Eutectic Finalize time( S) | Maximum Eutectic Undercooling (°C) | Latent Heat (J/gr) |
| Sample 1 | ----- | 0 | - | 615.7 | 18 | 568.8 | 216 | 7.9 | 215 |
| Sample 2 | Al-5Ti-1B | 200 gr | 0.2% Ti .038 % B | 615.8 | 25 | 565.6 | 330 | 3.125 | 352 |
| Sample 3 | Pressed Powder Nucleant 2 | 20 gr | 0.15 % Ti 0.035 % B | 614.8 | 26 | 568.4 | 327 | 2.69 | 387 |
| Sample 4 | Al-1.6%Ti-1.4%B | 320 gr | 0.1% Ti 0.08 % B | 614 | 17 | 556.7 | 338 | 3.8 | 350 |
| Sample 5 | Al-10Ti | 100 gr | 0.18 % Ti | 603 | 16 | 548 | 337 | 2.8 | 373 |

Addition of inoculants base on producer recommendation

The nucleation rate may be affected by density of nucleation sites and maximum undercooling. Table 2 Summaries the results of thermal analysis. In samples without inoculant, the maximum undercooling is 7.9 °C. Concerning equation (6), the nucleation rate is high and it is expected to have reduced grain size and well grain refinement in castings. But metallography test of casting in figure 6 show coarse grain structure in samples without inoculants addition. This is attributed to recalescence where, at high nucleation rates, evolution of latent heat of crystallization is enough to re-melt nucleation sites and increase grain sizes.

Adding the inoculants to molten metal, is accompanied by increasing the nucleation sites but decrease in eutectic undercooling and decrease of nucleation rate according to equation (6). But Influence of inoculants to increase of nucleation sites is more than its effect on reducing eutectic undercooling. In fact, there is a competitive behavior between nucleation sites and rate of nucleation [25]. Both factors affect grain refining process, and for maximum refining, it is necessary to use both effects. In inoculated samples, the maximum undercooling was less than 3.8°C. Metallography tests of samples indicate maximum grain refinement in sample no. 4 by Al-1.6%Ti-1.4%B inoculant with 3.8°C maximum undercooling. The second powerful inoculant is Al-5%Ti-1%B with 3.1°C maximum undercooling. Nucleant 2 with 2.7°C undercooling is the less efficient inoculant in this research. Metallography tests of samples confirm these results Standard test method ASTM A247 was used to determine grain size in samples. The results of measurements are shown in table 3.

Table 3 – Grain size measurment

| sample No. | grain size(µm) |
|---|---|
| 1 | 2095 |
| 2 | 483 |
| 3 | 950 |
| 4 | 327 |
| 5 | 680 |

These results indicate that inoculation process increase nucleation sites in molten metal but reduce maximum undercooling and nucleation rate. Among the different inoculants, each one with less effect on maximum undercooling, will have more effect on grain refining process. Concerning the results in tables 2 and 3, the TiBloy inoculant with maximum undercooling 3.8 °C have the most effect on grain refining process in comparison with others.

## 8. Conclusion

1- In samples without inoculation, the maximum under cooling is high resulting coarse grain structures. Adding inoculant to molten metal is accompanied by increasing nucleation sites, but decrease maximum undercooling. Both items, appointment the efficiency of grain refining process. This mechanism described by Arab, Varahram, and Davami [1997].

2- Inoculation of molten aluminum, decrease maximum undercooling to 3.8°C or less. Whatever the undercooling was near to 3.8 °C, the grain structure will be finer and whatever less than 3.8 °C, the grain structure will be coarser.

3- The results of this research indicate that Al-1.6%Ti-1.4%B have greatest effect on grain refining process than the others. Afterwards, Al-5%Ti-1%B, and Al-10% Ti are effective inoculants respectively. At last, there is Nucleant 2.

4- It is interesting that the best grain refining will be available on 3.8°C maximum undercooling. The mechanism of grain refining in this condition will be an interesting research course for researchers.

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