The Effect of Primary Phase Grain Refinement of Al-Si alloys on heat cracking

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Abstract. In this research thermal analysis was carried out for different alloys which use for gravity die cast cylinder heads. The experiments were implemented under industrial conditions. The aim was to examine the effect of the small amount of supplementary grain refining pre-alloy on primary crystallization for hot-crackings. Different evaluating methods of thermal analysis were tested and compared. Results proved that the dosing small amount of grain refining alloy is favorable in the foundry production practice.

1. Introduction
In the foundry practice, the amount of titanium (Ti) grain refinement is prescribed which is checked by spectrometric analysis. The necessary amount of titanium is set by the supplier of the alloy-block and there is no additional dosing. The aim of the performed tests is to investigate the achievable changes by adding a small amount of grain refining pre-alloy. The starting material for the tests was AlSi7MgCu0,5 (356Cu), AlSi9Cu1 (226L) alloy melt. The thermal analysis of the melt was examined from various foundry casting alloys by gravity mold casting. The effect of the auxiliary small amount of added AlTi5B1, 750 (g/ton) to 800 (kg) of liquid metal, grain refining pre-alloy on primary solidification was investigated. Moreover, various evaluating methods of thermal analysis have applied and compared.

The changing of the charge material, the high ratio alloy/recycled waste, or the charging of scrap castings will result in the change in the state of the grain at the primary solidification of the melt on account of the coarsening of titanium-containing grain forming particles. These effects on primary crystallization can be only detected by thermal analysis. The evaluation and comparison of the characteristics have done, based on the literature survey. The performed tests justify that the qualification of the grain refinement with several parameters together gives a reliable result.

2. The application of thermal analysis to qualify grain refining
In thermal analysis (TA) the temperature of the cooling alloy is detected and analyzed vs. the time. In practice, the simplest method is when we take the cooling curve of a melt which is cooling down in a mold or in a test cup. The evaluation process is based on the fact that all processes occurring during crystallization are influences the shape of the cooling curve. In the case of cast aluminium alloys, the efficiency of grain refinement and the modification of the eutectic can be examined. The shape of the cooling curve is determined by the amount of the latent heat released during solidification and the heat which is given to the environment. Also, the pouring temperature and the amount of the cast melt are determinative [1, 2].
Thermal analysis is the only well-known melt rating method that can effectively characterize the potential of the nucleation of a given alloy, so the efficiency of grain refinement. It is important to emphasize that the parameters determined by thermal analysis are strictly valid only at the cooling rate characteristic of the test. For a given casting, the cooling conditions may be significantly different in a casting part, so the size of the created particles/grains may be different locally than we would be expected from the results of the thermal analysis. However, it can be said that the greater potential of the nucleation in thermal analysis results, the more likely it is that the grain refinement is successful in all parts of the casting [3].

The efficiency of chemical grain refinement can be investigated near the range of liquidus temperature on the cooling curve. Based on the cooling curve and its first-time derivative, the characteristic temperature and the connected time values of the primary $\alpha$-Al crystallization can be determined (Fig. 1.). $T_{\text{NUC}}^{\alpha-Al}$ is the nucleation temperature at which the nucleation of primary $\alpha$-Al particles begins. At $T_{\text{MIN}}^{\alpha-Al}$ temperature, the latent heat released during primary crystallization, and the heat which is released from the mold are come to balance so the measured value of the cooling rate in this point (so the first derivative) is 0 (°C/s). $T_{G}^{\alpha-Al}$ is the temperature which connects to the maximum of warming back which is caused by the released latent heat during crystallization (in literature is named as growth temperature), after which the value of the first derivative is going to be negative again [4].

![Figure 1. Determining the characteristic temperature of the primary $\alpha$-Al crystallization](image)

The value of $T_{\text{NUC}}^{\alpha-Al}$ the nucleation temperature significantly depends on the efficiency of grain refinement. The more potential heterogeneous nucleating phases are introduced into the melt, the process of nucleation is easier. Thus, the reason for effective chemical grain refinement the nucleation begins at a higher temperature, so the temperature of nucleation is also grown [5]. This is illustrated in Fig. 2., which shows the cooling curves of a grain refined and an unrefined alloy.
Figure 2. The effect of the grain refinement on nucleation temperature [5]

In Fig. 2, \( T_N \) is the (nucleation) temperature of the creation of dendritic nucleation; \( T_G \) is the beginner temperature (connecting to the maximum after overcooling) of dendritic crystallization.

It is important to note that the small overcooling is necessary, but not a satisfactory criterion for the creation of the properly grain refined structure. Namely, the grain size significantly depends on the particle growth process and on the available time during the growth can happen [6].

Currently, there is no generally accepted evaluating method of the qualification of the grain refinement efficiency by thermal analysis. There are many different opinions in the literature that which parameter describes the best efficiency of the chemical grain refinement. According to Charbonnier [7], the knowledge of two important parameters is necessary for the qualification (Fig. 3.). One is the apparent overcooling which is the difference between the minimum and the maximum temperatures (\( \Delta T \)) of primary crystallization. The other parameter is the passed time (\( t_4 \)) between the overcooling and the warming back which is defined by the time between the minimum and maximum temperatures. According to Bekaeert and Wetinck [8], the most important qualifying characteristic is the value of \( t_4 \) is shown in Figure 3., which with increasing the average grain size is also increasing.

The efficiency of grain refinement can be qualified at AlSi7Mg alloys as follows:

- fine grain structure: if \( t_4 < 12.5 \) (s),
- medium-sized grains: if \( 12.5 \) (s) < \( t_4 < 18.8 \) (s),
- rough grains: if \( t_4 > 18.8 \) (s).

The qualitative parameters for grain refining, which can be determined by thermal analysis are summarized in Fig. 4. Fig. 4./a) shows only the temperature and in Fig. 4./b) time parameters are displayed. Fig. 4./c) shows qualifying characteristics that are widely used in industrial-scale as part of an automated quick-rating process. KF16 is measured at 2 \(^\circ\)C/s cooling rate and connecting to the 16. seconds temperature values difference which calculated from the minimum temperature of overcooling. \( t_{f,Th-AI} \) is the time from the minimum overcooling temperature to the moment when the temperature reaches again the temperature value connecting to the overcooling minimum point after heating back [9].

Figure 4. a) Temperature, b) time, c) other parameters which can be determined by thermal analysis of grain refining [9]
With the improving of grain refinement efficiency $\Delta T_{N-R}$ and KF16 are increased, while $\Delta T_{R-U}$, $t_1$, $t_3$, $t_{f,TR-AL}$ are reduced. According to recent researches, the time parameters and the connecting KF16 values characterize better the efficiency of grain refinement than the temperature-related characteristics, because of their values dependent more from the energy of primary crystallization [9].

According to R. Döpp et al. [10], the value of KF16 is the temperature in the prevent cooling section of liquidus-transition at the point of 2 ($°C/s$) cooling rate and this is given by the difference of the temperatures connecting to the followers 16 seconds. An effective qualification can also be provided by the method presented by Bäckerud [11]. It is important to note that similarly to the KF16 described above this method is also based on temperature and time parameters. So it determines the efficiency of the grain refinement based on several measurement results. In the case of time parameters classification, the identity of the tested samples’ weight is important. Therefore, the method described by Bäckerud and the results obtained by KF16 can be considered more accurate than the rating methods based on only time or temperature parameters described above [11].

3. The relationship between grain refinement and strength properties
Grain refinement significantly improves the strength properties of castings based on that first the finer microstructure causes a consistent dispersion of secondary phases (intermetallic compounds and porosity) in the material structure [5]. On the other hand, with the increasing grain number, the specific quantity of grain boundaries is also increasing in the metallic matrix which moves dislocations more difficult [12]. The latter effect can be expressed by Hall-Petch correlation [13]. During and after crystallization the occurring mechanical strains are distributed on the grain boundaries in the castings. The smaller average grain size, specifically the greater surface area of the grain boundaries on which strains are dispersed. So grain refinement reduces the stress concentration values within the casting. As a result, with finer grain size the casting is more resistant to mechanical strains, so the hot crack sensitivity will be smaller and the tensile strength will be higher [14].

The finer grain particles do not only have higher tensile strength but result in a higher elongation at rupture, too.

With the help of tensile strength and elongation at rupture, values can be determined by the so-called Quality Index which makes the quality of castings quantitative and comparable based on their strength properties. Calculation of Quality Index [15]:

$$Q = R_m + 150 \cdot \lg A_5 \text{ (MPa)} \quad (1)$$

where Q is the quality index (Mpa), $R_m$ is the tensile strength (Mpa) and $A_5$ is the elongation (%).

4. Experimental conditions
The basic material of the investigations was AlSi7MgCu0,5 (356Cu), AlSi9Cu1 (226L) alloys, where L means low iron content. The chemical composition is given in Table 1. After melting in the gas-fired Striko furnace during tapping the prescribed amount of AlSr10 auxiliary alloy added to the metal bath in the forwarder ladle to provide the strontium concentration about 200 (ppm) (alloy 1. in Table 1.). In the next step, the melt was poured into an 800 (kg) capacity heat furnace where 750 (g/t) experimental amount of AlTi5B1 pre-alloy is added to liquid metal.

| Table 1. Chemical composition of the investigated alloys (weight%) |
|-------------------|-------------|-------------|-------------|-------------|
| Element (%)       | 356Cu      | 356Cu+Ti   | 226L        | 226L+Ti     |
| Si                | 6,93       | 7,10       | 9,80        | 9,74        |
| Fe                | 0,091      | 0,097      | 0,110       | 0,110       |
| Cu                | 0,468      | 0,491      | 0,967       | 0,958       |
| Mg                | 0,388      | 0,393      | 0,424       | 0,418       |
| Ti                | **0,1194** | **0,1229** | **0,1109**  | **0,1131**  |
| Sr                | 0,0235     | 0,0251     | 0,0239      | 0,0238      |
Before casting the melt was held for 1 hour at 730 ± 5 °C. The hydrogen content of the alloy was checked by the density-index method and thermal analysis was used/done for the melt before and after adding the pre-alloy. The investigations were performed on three doses per alloy.

5. Experimental results
The cooling curves of investigated alloys show differences in the chemical composition. In the primary crystallization phase of all two alloys, overcooling and heat back are occurred. Fig. 5-6. show the cooling curves of the effect of a small amount of grain refining pre-alloy addition.

![Figure 5. Effect of the grain refining pre-alloy added to melt of AlSi7MgCu (356Cu) alloy on the primary crystallization of the cooling curve](image)

![Figure 6. Effect of the grain refining pre-alloy added to melt of AlSi9Cu1 (226L) alloy on the primary crystallization of the cooling curve](image)
We examined the microstructure of the casting samples after Barker etching to count the grain numbers. The specimens were examined by optical light microscopy at 25X amplification. The results of before and after titanium addition were averaged and shown in Fig. 7. The results of the diagram show that the microstructure was refined after the titanium addition.

We have also selected those samples in which mechanical properties were the best. Results of samples without titanium addition and with titanium addition were shown in Table 2. The effect on the mechanical properties was not detectable due to other factors influencing the strength properties (melt inclusions, directional freezing, etc.) The standard deviation is significant.

![Figure 7](image_url)

**Figure 7.** The effect of the 750 (g/t) grain refining pre-alloy on the primary crystallization stage of the cooling curve which was added to the alloy melt, a) before pre-alloy addition, b) after pre-alloy addition

| Table 2. Average mechanical results of tensile rods machined out from experimental castings |
|---------------------------------------------|---------------------------------------------|
| Samples                                    | Experimental castings                       |
| Marking                                    | AISi7Mg - 356                               |
|                                             | AISi9Cu1 – 226L                             |
|                                             | Before Ti adding                            |
|                                             | After Ti adding                             |
| Rm (MPa)                                   | 237,2                                       |
|                                             | 236,1                                       |
|                                             | 321,6                                       |
|                                             | 314,8                                       |
| Rp0.2 (MPa)                                | 163,1                                       |
|                                             | 168,6                                       |
|                                             | 260,1                                       |
|                                             | 256,1                                       |
| A5 (%)                                     | 10,5                                        |
|                                             | 8,9                                         |
|                                             | 3,8                                         |
|                                             | 3,9                                         |
| Q (MPa)                                    | 390,4                                       |
|                                             | 378,5                                       |
|                                             | 408,6                                       |
|                                             | 403,5                                       |

We investigated with stereo microscopy the test bars and found different sized aluminium-oxide films and porosities on the fracture surfaces at both alloys which generate the decreasing values also before and after titanium additions (Fig. 8.).
Figure 8. Al-oxide films and porosities on the fracture surface of tensile test bars at both alloys

Significant differences are shown between the cooling curves and their first derivative curves (cooling rate) at all three alloys by the effect of a small amount AlTi5B1 grain refinement pre-alloy are added. Typical differences at the auxiliary titanium addition:

- primary crystallization initial temperatures, the liquidus maximum ($T_{LR}$) and liquidus minimum ($T_{LU}$) temperature values are higher,
- the temperature difference is lower ($\Delta T = T_{LR} - T_{LU}$) at heat back in the phase of primary crystallization,
- the grain refining rating number (KF16) is higher,
- the duration of the primary crystallization stay in the initial phase ($t_1$ and $t_2$) is shorter,
- in the initial phase of primary crystallization, the area of positive (above 0) values of the first derivative curve is smaller.

The rating indicators of primary crystallization at the tested alloys are determined based on the evaluation of cooling curves (Fig. 4., [9]). The rating data of prepared experimental doses are summarized in Table 3, with the addition of a small amount of AlTi5B1 grain refinement pre-alloy at the foundry and degassing treatment.

Table 3. Measured and calculated data for the thermal analysis of investigated alloys

| Rating     | AlSi7Mg | AlSi7Mg+Ti | AlSi9Cu1 | AlSi9Cu1+Ti |
|------------|---------|------------|----------|-------------|
| $T_{LU}$ (°C) | 612.3   | 615.6      | 590.1    | 595.9       |
| $\Delta T_{LR}$-$T_{LU}$ (°C) | 1.31    | 0.00       | 0.88     | 0.00         |
| KF16 [9] (°C) | 3.50    | 9.47       | 4.06     | 6.87         |
| KF16 [10] (°C) | 2.74    | 7.58       | 3.94     | 5.23         |
| $t_1$ [3] (s) | 7.0     | 0.0        | 12.0     | 0.0          |
| $t_4$ [9] (s) | 18.5    | 0.0        | 24.0     | 0.0          |
| $t_5$ [9] (s) | 16.0    | 0.0        | 21.5     | 0.0          |

The determination of characteristic temperature and time data with the grain refining of the foundry aluminium alloys allows the formation of multi-parameters rating methods which help reliably estimate the modification and the primary crystallization processing.

6. Conclusion

Thermal analysis of various foundry alloys is performed and the effect of the AlTi5B1 grain refining pre-alloy auxiliary addition is investigated.

In the foundry practice, thermal analysis is performed with a target device developed for this purpose. The rating of primary crystallization of the melt based on the defined parameters by the associated program connecting to the device.

The evaluation and comparison of characteristics in literature have done connecting to the thermal analysis of primary crystallization. The examinations prove that the rating of grain refinement gives a reliable result with the consideration of several parameters.
In the foundry practice, the change of the used deposit material, the high recyclable waste ratio, or the melting of scrap, the long term heat keeping of melting at primary crystallization induce the change of nucleation phase because of the roughness of titanium-containing nucleation forming compound particles. Their effect on primary crystallization can only be detected by thermal analysis.

The test results confirm the beneficial effect of using 0.75 kg/t AlTi5B1 grain refining pre-alloy for melt which meets the foundry requirements for titanium-content according to the regulations.

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