Determination of the growth restriction factor and grain size for aluminum alloys by a quasi-binary equivalent method

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1. Introduction

The microstructural refinement of aluminium castings is highly desirable, fine and equiaxed grains are usually the “preferred” microstructures. This is because finer grains reduce the possibilities for hot tearing and promote a higher homogeneity and may improve mechanical properties and service characteristics [1]. A fine grain structure in aluminium alloys cast components can be produced by promoting heterogeneous nucleation. A larger number of crystals impinge on each other hindering grain growth. Different authors have distinct methods to assess the growth restriction factor (Q) or the amount of constitutional undercooling (P) for non-diluted or multi-component alloys [1–9].

The mechanism of grain refinement using chemical agents can be divided in two types. First type assumes that the nucleation particles are of ultimate importance while second type recognizes the solute essential to achieve finer microstructures [1,2,4,9,10]. The solute theory, formalized by suggests that both the nucleants and the segregation have influence in the grain refinement. Q was developed to determine the degree of segregation. Q is a measure of the growth restricting effect of solute elements on the growth of solid-liquid interface of the new grains as they coarsen into the liquid metal. Based on the binary Al–X system the Qf is defined as

\[ Q_f = \frac{m_f (1 - k) C_0}{k} \]

where \( m_f \) is the slope, \( k \) is the equilibrium partitioning coefficient and \( C_0 \) is the alloy composition.

The supercooling [11] and the growth restriction [12] parameters can be determined as follows:

\[ P = -\frac{m_f (1 - k) C_0}{k} \]

(1)

\[ Q = m (k - 1) C_0 = kP \]

(2)

where \( m \) is the liquidus slope, \( k \) is the equilibrium partitioning coefficient and \( C_0 \) is the alloy composition. The limitations of \( P \) is that this parameter is equal to the freezing range of the alloy assuming that both, the liquidus and solidus, lines are straight and the alloy solidifies as a solid solution. Therefore, \( P \) is the degree of undercooling induced by growth restriction.

Si is an example an element with dual function in the Al–Si system. In the Al–Si system the GS decrease first with additions of up to 1.5 wt% Si and tapers off at approximately 3 wt% Si; further additions have a poisoning effect resulting in grain growth [13–17]. An
Nomenclature

\[ Q \]  growth restricting factor \\
\[ GS \]  grain size \\
\[ R^2 \]  regression coefficient \\
\[ P \]  constitutional undercooling \\
\[ m_X \]  slope of the liquidus line \\
\[ C_0 \]  concentration of the solute in the melt \\
\[ k \]  equilibrium partitioning coefficient \\
\[ k_{p,i} \]  partition coefficient of individual element \\
\[ k_i \]  partition coefficient of all elements \\
\[ C_S \]  solute concentration in the solid \\
\[ C_L \]  solute concentration in the liquid \\
\[ d \]  grain size in diameter (Refs. [3,19,20]) \\
\[ T_{Liq} \]  liquidus temperature \\
\[ T_{DCP} \]  temperature at the dendrite coherency point \\
\[ (T_{E,NUC}, T_{AlSi}) \]  temperature at the Al–Si eutectic nucleation \\
\[ (T_{E,NUC}, T_{AlSiCu}) \]  temperature at the Al–Si–Cu eutectic nucleation \\
\[ T_{SOL} \]  solidus temperature \\
\[ \alpha-Al \]  primary Al grains \\
\[ d_f/dt \]  cooling rate \\
\[ Amount \ of \ Ti \]  wt% of Ti added to the melt \\
\[ Q_d \]  grain growth index for casting with minimal GS \\
\[ Q_b \]  grain growth index for original aluminum based material \\
\[ C_{Eq} \]  carbon equivalent \\
\[ Si_{Eq} \]  silicon equivalent \\
\[ X_{eq.i} \]  sum of the contribution of all elements expressed as the equivalent effect of individual element on the liquidus temperature \\
\[ a_X, b_Y, c_z \]  polynomial coefficients \\
\[ X_i \]  the concentration of the individual element in wt%

analysis of all the GS and thermal analysis data suggested that the GS in the above mentioned references was controlled by the rate of grain growth. The restriction effect of crystal growth by solute segregation increases with the partition coefficient \( k_i \) of all the elements. Therefore, the total \( Q \) should be given by Eq. (3).

\[
Q_{TOT} = \sum m(k - 1)C_0 \\
= \sum m_1(k_1 - 1)C_1 + \sum m_2(k_2 - 1)C_2 + \ldots
\]

Eq. (3) is valid for dilute alloying systems or alloys with elements that have limited or none interactions among the constitutional elements of the alloy. Therefore, this may result in an over or under-estimation of \( Q \) and prevents the accurate determination of GS.

Although, Eq. (3) has the advantages that it is accurate for dilute multi-component aluminum alloys and the approximation of \( Q \) and GS is conducted by a single function.

Easton et al. [3,13] and Lee et al. [14] developed empirical models (Eqs. (4) and (5), respectively) to determine the GS \( d \) as a function of \( Q \) and \( P \) for aluminum alloys. Eqs. (4) and (5) have been developed based on the effect of grain refiner (\( TiB_2 \)) for Al-alloys.

\[
d = \frac{32}{\sqrt{pct\ TiB_2}} + \frac{652}{Q}
\]

\[
d = \frac{43}{\sqrt{pct\ TiB_2}} + \frac{520}{Q}
\]

1.1. Utilization of thermal analysis in grain refinement

The thermal analysis methodology allows for the assessment of several thermal characteristic such as solidification temperatures (e.g. liquidus \( T_{Liq} \), dendrite coherency point \( T_{DCP} \), Al–Si eutectic nucleation \( T_{E,NUC}, T_{AlSi} \), Al–Si–Cu eutectic nucleation \( T_{E,NUC}, T_{AlSiCu} \) and solidus \( T_{SOL} \); as well as the Latent Heat of solidification and structural characteristics for multi-component 3XX Al alloys. In fact, the difference between the liquidus temperature and the undercooling for the nucleation of the \( \alpha-Al \) grains is proportional to the number of nuclei particles. The smaller the undercooling, the larger the number of solidified nuclei particles resulting in a finer microstructure, thus smaller grains [15]. A valid correlation based on the constitutional undercooling and the number of grains can be established.

Bäckerud et al. [18] developed an algorithm showing a detailed description and understanding of how the composition of aluminum alloys affects its self-refinement. Such algorithm can be used to calculate the desired level of grain refinement. The coherency point can be determined by thermal analysis based on the gradient temperature during solidification \( (d_f/dt) \) using a two thermocouples approach; one at the center of the sample and the other close to the wall [5,13,19]. The temperature gradient between both thermocouples is accumulative and increases during the initial stage of solidification. The maximum of this temperature gradient occurs at the coherency point, and then decreases after the gradient becomes lower. An alternative method using a single thermocouple approach is possible by analyzing the first derivative of the cooling history of a solidifying alloy as shown in Ref. [20].

An alternative method to determine the amount of Ti needed to reach a desired GS can be calculated with Eq. (6). Eq. (6) ignores the undercooling that takes place during the alloy solidification but considers the slope of the liquidus temperature \( (m_{Ti}) \) and the distribution coefficient of Ti \( (k_{Ti}) \) of the Al–Ti system [20].

\[
Amount \ of \ Ti = \frac{Q_d - Q_b}{(k_{Ti} - 1)m_{Ti}}[wt%]
\]

The “Amount of Ti” is the percentage by weight of Ti to be added to the melt, \( Q_d \) is the grain growth index resulting in aluminum castings with a minimal GS, \( Q_b \) is the grain growth index of the original aluminum base material.

1.2. Quasi-binary equivalent concept for grain refinement

To date, there are no comprehensive procedures for rapid prediction of structural properties of multi-component aluminum alloys in as-cast and/or heat treated conditions based on the alloy chemical composition. The equivalent concept proposed herein is similar to the well know carbon equivalent \( (C_{Eq}) \) concept used in ferrous alloys where carbon is the major alloying element [21,22]. Similar concept has been developed for the hypoeutectic and hypereutectic [5]. Similar concept has been developed for the hypoeutectic and hypereutectic [5,19] Al–Si alloy systems where...
Table 2

Polymer coefficients of the $S_{\text{AL}}$ for various binary Al–X alloys representing the most common major and minor elements of the 3XX aluminum alloys. Note that $a_0 = \theta$ for the elements presented in this table [5].

<table>
<thead>
<tr>
<th>Al–X alloy</th>
<th>$b_0$</th>
<th>$c_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–Cu</td>
<td>0.529</td>
<td>-0.027</td>
</tr>
<tr>
<td>Al–Mg</td>
<td>0.0258</td>
<td>-0.0088</td>
</tr>
<tr>
<td>Al–Mn</td>
<td>0.8221</td>
<td>-0.0349</td>
</tr>
<tr>
<td>Al–Sn</td>
<td>0.6495</td>
<td>0.0003</td>
</tr>
<tr>
<td>Al–Zn</td>
<td>0.1227</td>
<td>-0.0002</td>
</tr>
<tr>
<td>Al–Si</td>
<td>0.7849</td>
<td>-0.0313</td>
</tr>
<tr>
<td>Al–Bi</td>
<td>0.9076</td>
<td>-0.0092</td>
</tr>
<tr>
<td>Al–Pb</td>
<td>0.859</td>
<td>0.02976</td>
</tr>
<tr>
<td>Al–Ca</td>
<td>0.0594</td>
<td>0.00685</td>
</tr>
<tr>
<td>Al–Cu</td>
<td>0.8255</td>
<td>-0.0327</td>
</tr>
<tr>
<td>Al–Ni</td>
<td>0.5644</td>
<td>-0.0285</td>
</tr>
<tr>
<td>Al–Sr</td>
<td>0.7854</td>
<td>-0.0157</td>
</tr>
<tr>
<td>Al–Ti</td>
<td>-0.8159</td>
<td>0.009927</td>
</tr>
<tr>
<td>Al–B</td>
<td>-0.9977</td>
<td>0.00007506</td>
</tr>
</tbody>
</table>

Silicon is major alloying element and the respective methodology is known as silicon equivalent ($S_{\text{SiEq}}$). The equivalent ($C_{\text{SiEq}}$ and $S_{\text{SiEq}}$ respectively) is calculated as the sum of the contribution of the individual elements using as the addition or contribution of the equivalent effects of individual elements on the liquidus temperature ($\sum \delta S_{\text{SiEq}}$) for the Al–Si system as presented in Eq. (7). A detailed explanation of the development of the method can be consulted in Ref. [5]. The $S_{\text{SiEq}}$ concept covers all the family of Al–Si hypo and hypereutectic 3XX series of alloys.

$$S_{\text{SiEq}} = \text{Si} + \sum \delta S_{\text{SiEq}} \text{[wt%]}$$

Eq. (8) shows a mathematical model that relates the chemical composition for a particular alloy with the liquidus temperature for a quasi binary system (e.g. Al–Si). In order to determine the equivalent approach for any aluminum alloy Eq. (8) and Table 2 are needed [5] (wt%):

$$X_{\text{SiEq}} = a_0 X_{\text{Si}} + b_0 X_{\text{Si}} + c_0 X_{\text{Si}}^2$$

where: $a_0$, $b_0$, $c_0$ = polynomial coefficients (see Table 2), $X_{\text{Si}}$ = the concentration of the various elements present in the investigated alloys in wt%.

The results of the $X_{\text{SiEq}}$ algorithm as determined for every alloy composition can be directly used in Eq. (9) to determine the Q for Al alloys. Using the slope value of the liquidus line for the various Al–X binary systems, $m_{\text{K}}$, and its corresponding equilibrium partition coefficient, $k_{\text{X}}$, the Q for the pseudo binary Al–$X_{\text{SiEq}}$ alloy can be now express as:

$$Q = f(X_{\text{SiEq}}) = m_{\text{K}}(k_{\text{X}} - 1)X_{\text{SiEq}}$$

(9)

The traditional methods ignore the poisoning effect of individual alloying elements that is directly related to the changes in the liquidus temperature. In Eq. (9) the liquidus temperature slope is not ignored; further, this method is relatively simple. The bulk chemistry of the aluminum alloy, the slope of the liquidus line and partition coefficient of the Al–X quasi-binary system are the necessary input data to determine Q based on the equivalent approach.

This paper describes an alternative approach to determine the effect of solute elements in GS for the aluminum alloys that have been solidified in close to equilibrium conditions. In the work presented here in the samples were cooled at a rate of approximately 0.1 °C/s. It is expected that the equivalent concept can be applied to any Al sample cooled at a rate lower than one mentioned above. In the present work is proposed a simplified approach known as equivalent to reduce the effect of major alloying elements present in a multicomponent alloy into a binary system (e.g. Al–Si alloys or $S_{\text{SiEq}}$) [5]. Nonetheless, the $S_{\text{SiEq}}$ is just an example and its relative importance is due to the fact that the 3XX system of alloys is the most widely used family of aluminum alloys. Using the equivalent approach can be determined the values of Q and later the GS for various Al–X compositions. The results obtained in the present work are further compared with results of traditional (Eq. (3)), empirical (Eqs. (4) and (5)), thermal analysis (Eq. (6)) and the newly proposed equivalent concept presented in Eq. (11). The calculated values of GS are compared with actual GS values obtained experimentally for Al–X hypoeutectic alloys.

2. Alloys synthesis

Twelve 3XX alloys of different compositions were produced by melting charges of the 319 alloy, pure Al, Al–Si and Al–Cu master alloys. The nominal compositions of the twelve produced alloys have 5, 7, 9 and 11 wt% Si and 1, 2 and 4 wt% Cu with different amounts of Fe, Mn, Mg, Ni, Cu, Pb, etc. The actual chemical compositions of the resulting alloys, was determined using Optical Emission Spectroscopy (OES) and are provided in Table 3. In order to test the grain refining effect of the Al–5 wt% Ti–1 wt%B master alloy; the alloy identified as Al7Si4Cu in Table 3 was grain refined by adding 1.6 and 3.2 g of master alloy per kg Al7Si4Cu–Al–Si alloy.

The alloys were melted in a resistance furnace of 12 kg capacity. During the melting procedure the alloy was covered with a
chromatographic Argon protective atmosphere to prevent hydrogen and oxygen contamination. No grain refining agents were added to the melt except for the above-mentioned Al7Si4Cu alloy. The presence of Sr in levels above traces (Table 3) is attributed to residual Sr in the 319 Al-alloy that is a secondary alloy. A total of 42 specimens (three from each alloy and grain refining condition) with masses of 500 ± 10 g were poured into a low mass crucible. All samples were solidified under similar heat exchange conditions at a cooling rate of 0.1 °C/s that is similar to sand casting conditions and close to equilibrium conditions.

Specimens for light optical microstructure analysis were cut longitudinally from the thermal analysis sample close to the thermocouple. For metallography, samples were prepared following standard grinding and polishing procedures. The grain size was revealed by means of anodization using a 0.5% HBF₄ solution for 2 min and 20 V. The GS measurements were conducted using the linear intercepted method. This method was chosen due to the large range of GS observed (with ferret diameters between 1900 μm and 4000 μm) throughout the analytical samples.

3. Determination of grain growth restricting factor (Q) using equivalent method

Table 3 summarized the values of the Q for the 3XX series of aluminum alloys used in this research. Fig. 1 shows the comparison between GS for the 3XX Al alloys calculated using newly established equivalent method (Eq. (9)) and the traditional method (Eq. (3)). Fig. 1 as well as Fig. 2 show that Eq. (3) overestimates Q in comparison to these results obtained with the equivalent method. It is also evident that the scatter of the results with Eq. (3) is wider than using Eq. (9). The main reason for this difference is that Eq. (9) takes into account the exponential effect of the liquidus temperature slope; hence, some thermodynamic principles of solidification.

Using the multi-component effect of the slope of the various liquidus lines it is possible to identify potential interactions among elements that may result in the formation of stoichiometric compounds (intermetallics). Most stoichiometric compounds are identified in compositions that are beyond the level of additions used in commercial aluminum alloys; therefore, in the equivalent approach is contemplated the accumulative effect of the independent binary systems. This is usually enough to have an accurate determination of Q and GS. At higher levels of additions the interactions among elements results in a more evident and is typically known as poisoning effect (e.g. intermetallic formers).

From the elements present in the investigated alloys can be concluded that not all the elements form intermetallics. From the elements that form intermetallics, Mn is the one that requires the lowest concentration to start forming intermetallics (approximately 8.3 wt% Mn). It is important to clarify that the above statements do not have the intent to say that intermetallics are not present in commercial aluminum alloys; on the contrary, the intention of this work is to indicate that aluminum alloy solidifying at close to equilibrium conditions do not form intermetallics at the liquidus temperature. The intermetallics are usually formed at lower temperatures or under special circumstances such as solute enrichment. Some examples of intermetallics observed in the semi-solid state are: Mg₃Si, Al₃Ni, Al₃CuNi. Al-alloys with Cu additions have the tendency to form the well known Guinier–Preston zones (GP and GP’ zones) and θ phases that are intermetallics. Although, they have no effect on grain refining since they are formed during heat treatments, it means after the material is completely solid.

4. Statistical analysis

Fig. 2 shows the relationship between the chemistry of the 3XX series of aluminum alloys (expressed in as a function of the Siₑq) and their corresponding Q calculated using Eqs. (3) and (9). Statistical analysis revealed an almost perfect agreement between chemistry and the calculated values of Q by using the equivalent methodology (R² = 0.999). Using the traditional method of adding the individual factors (Eq. (3)) for each element the regression coefficient was R² = 0.86. Therefore, it can be concluded that the determination of the total Q for a multi-component alloy is more accurate using the equivalent methodology.

In Fig. 2 are presented the values for the Q calculated using the equivalent methodology (Eq. (9)) and traditional method involving equilibrium partition coefficient of all elements kᵢ (Eq. (3)). It is clear that the equivalent methodology is more accurate and simple. Moreover, Eq. (3) is limited to the determination of the Q; therefore, other algorithms are needed to calculate the grain size as presented in Fig. 2. The simplicity of the equivalent methodology is such that Table 1 and Eq. (8) are the only requirements to assess the Q and GS for any Al–Si alloy composition and have a regression coefficient of R² = 0.99.

Eq. (10) is a proposed method to estimate the GS as a function of the liquidus undercooling (ΔTₑq) for Al–Si–Cu alloy systems (Al–7 wt%Si–4 wt%Cu). The results of Eq. (10) are directly compared to the results of other methods previously reported in the literature (Eqs. (4)–(6)). It is important to mention that Eq. (10) is validated for the Al–7 wt%Si–4 wt%Cu alloy solidified at a 0.1 °C/s. Eq. (10) can be used to establish a more general algorithm by introducing parameters that correlate cooling rate and thermomechanical
processing (e.g. electromagnetic stirring). This will allow to use this model directly as an on-line quality control tool to predict the Q and the GS during solidification for any Al alloy composition and any casting plant or research facility. In this research the Al-Si system was used; however, this can be modified as needed to better fit to any casting requirements. Eq. (10) is quasi-empirical and relates constitutional undercooling of the Al–7 wt%Si–4 wt%Cu alloy chemically refined with Al–5 wt%Ti–1 wt%B master alloy with an $R^2 = 0.999$.

\[ GS_{Al–7\text{ wt}\%Si–4\text{ wt}\%Cu} = 0.0011 \Delta T_{LIQ} − 0.19(\text{mm}) \]  

(10)

4.1. Grain size (GS) determination using equivalent method

Eq. (11) is the relationship validated in this work for the Al–Si alloying system and may require slight modifications for other alloying systems.

\[ GS = 59.253(Q) + 0.664(\text{mm}) \]  

(11)

The GS for aluminum alloys can be determined by combining Eqs. (9), (10) and (11) and the equivalent methodology that is a function of the chemical composition. Eq. (12) is the results of this combination and in the present work has been validated against data obtained in samples of the 3XX Al–Si alloys solidified at a cooling rate of 0.1 °C/s. In Eq. (12), $X_i$ expresses Si equivalent that is the accumulative effect of each element present in the investigated alloy.

\[ GS = 59.253[mX_i(k_{X_i} – 1)X_{eq}] + 0.65 \]  

(12)

4.2. Algorithm for the grain refining effect of Ti

Fig. 3 shows a comparison between the empirical Eqs. (4) and (5), thermal analysis (Eq. (6)) and the equivalent method (Eq. (11)). From Fig. 3 can be concluded that most accurate method to determine GS is Eq. (11) with a regression coefficient of $R^2 = 0.986$. In contrast, Eqs. (4) and (5) have no clear correlation with GS ($R^2 = 0.034$ and 0.066, respectively). The analytical determination of GS for the Al–7 wt%Si–4 wt%Cu alloy refined with Ti is possible with Eqs. (6) and (11) and the results show a difference of approximately 10%. Therefore, the equivalent method proposed herein has a similar or higher level of accuracy to determine the grain refining effect of Ti.

5. Discussions

In the literature has been reported that the constitutional contributions from different elements can be additive [4] and the expression $\Sigma m_i(k_{X_i} – 1)X_{eq}$ can be used as an approximation to the total constitutional undercooling. However, the additive nature of the constitutional undercooling is still a controversial topic. Nonetheless, most authors agree that this is true for dilute solutions where in most cases the poisoning effects caused by the interactions among elements (i.e. Si and Zr) are minimized [13–7,14,19,22]. Such facts have been confirmed in the present work. Reliable values for solute diffusivities in liquid aluminum are difficult to obtain; thus Greer et al. recommend the determination of the growth restriction parameter by summing Q values [12].

In the present work are considered only the interactions among binary systems; nonetheless, the accuracy of this work to obtain the value of Q is relatively high ($R^2 > 0.96$). The main advantage of using the equivalent method ($X_{eq}$) to determine Q and GS is that in the present work is contemplated the poisoning effect of some elements for non-diluted and binary systems by using the exponential behavior of the liquidus line. The equivalent method consists on the introduction of the thermodynamics concept of the liquidus temperatures that is based on an exponential decay that assumes the typical, non-linear, grain restriction behavior observed by the additions. None of the elements investigated for the Al–Si system presented dual (positive and negative) contribution to the liquidus temperature. Therefore, the poisoning contribution in the investigated elements was not clearly observed in the determination of the GS as a function of the constitutional Q.

Qian et al. [24] made so far the most detailed model for grain size prediction on the micro level applicable for wide range of light metal alloys, describing different grain formation and initial growth mechanisms. Model was tested on reproduced data for wrought Al and Mg alloys [25]. Results showed high similarity to previously recognized linear correlation between GS and 1/Q. At the macro level the model suggests results similar to those obtained with Eqs. (4) and (5). Nevertheless, if alloy thermo-physical parameter (such as diffusion coefficient, growth velocity, number of stable inclusions, initial grain size and density) are known in initial stages of solidification suggested model will give actual GS instead relative grain size.

The analysis of Eq. (12) confirms that the constitutional undercooling decreases the dissolution of the solute promoting the growth of crystals allowing the survival of the new grains in the casting. Eq. (12) is a semi-empirical model that combines well known methods such as the $\Sigma m_i k X_{eq}$ and the constitutional undercooling with Eq. (11) that is proposed in the present work. Eq. (11) is the regression equation of the results presented in Fig. 3. This in turns allows the development simple of maps (Fig. 4) that relate the effect of other elements into the growth restriction factor. The maps shown in Fig. 4 can add significant value to an industrial setup where the GS determination can be assessed by looking at the effect of different elements on microstructure. The same type of maps can be developed for GS and constitutional undercooling. The results from Fig. 4 can be easily implemented as an on-line tool to determine Q and extrapolate it directly to Figs. 1 and 2 to assess the GS for ternary systems. The same figures can be produced for any quaternary or higher multi component alloys of any aluminum composition. Further thermomechanical processing and cooling rate effects can also be included or added to the maps presented in Fig. 4.

Eq. (12) can be modified by determining the relationship among the parameters that have effect on GS such as solidification range, superheat temperature, latent heat of solidification, cooling rate and thermomechanical processing. However, the contribution of the solidification range, increase superheating and latent heat
Fig. 4. Presents the effect of the main alloying (Cu, Ni and Zn), impurity (Fe, Mn, Bi and Pb), grain refiner (Ti and B) and Si modifier (Sr) elements on the growth restriction factor (Q) for the Al–Si binary system in function of the silicon equivalent (SiEq). Pb and Bi are plotted together because these they have similar effects on the Al–Si system, while Ti and B are used together as grain refiners.
of solidification is negligible and their determination required complex procedures and experiments. In addition, Eq. (12) has a \( R^2 = 0.99 \). For the same chemical composition, and solidification conditions a reduction in undercooling correspond to a structure with smaller GS and the larger the undercooling the larger the GS. The effect of cooling rate and thermomechanical treatments can be added to Eq. (12) by determining the respective effect to the \( \Delta T_{\text{eq}} \).

The determination of the GS using Eqs. (4) and (5) \cite{13,14} underestimates the GS in approximately 3000%. This is due to the significant difference in cooling rate for which Eqs. (4) and (5) were design. In addition, using the above equations and Eq. (12) an underestimation of 350% was obtained. On the other hand, using Eq. (6) can be observed that the level of accuracy is comparable to Eq. (12). However, Eq. (6) is limited to determine GS for Al–Si alloy grain refined with Ti; therefore, in Fig. 3 the GS is plotted only for three samples, but it is clear that there is a good agreement among the results of both research investigations. The intention of the equivalent methodology has as a main objective to develop a universal mathematical model to assess the GS for any aluminum alloy under any solidification conditions.

Optical emission spectroscopy (OES) chemical analysis is conducted routinely for ingots and melts. However, this information is used with the sole purpose of controlling additions or the presence of individual elements. In the present research OES is used to assess the effect of chemistry in the accurate prediction of GS. Therefore, the use of the thermal analysis and the equivalent methodology has a quite can be easily implemented industrially.

6. Conclusions

The newly proposed, equivalent, method to determine \( Q \) for aluminum alloys allows an accurate determination of the constitutional undercooling (\( Q \)) and GS of any (dilute and non-dilute) aluminum composition. This equivalent methodology incorporates the thermodynamic behavior of the alloying additions. The use of the equivalent method allows a relatively simple determination of \( Q \) and requires only the thermodynamic data from the Al–X binary diagrams. This methodology can, but not necessarily, be further simplified to assume a binary system where the contribution of the individual elements is added to that of the major alloying element in the system. For instance for the 3XX family of alloys the equivalent method can be simplified to the Si_eq approach. The equivalent methodology can be used for multi-component (e.g. commercial) alloys, but most importantly for non-dilute alloying systems. The elements with the highest grain refinement effect are Ti and B that are added in parts per million. Nonetheless, their effect in constitutional undercooling is significant enough that their grain refining effects can be accurately determined by the equivalent methodology. The \( Q \) and GS values have been validated herein for Al–Si alloys with a satisfactory level of accuracy (\( R^2 = 0.999 \)).

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