Association of Metallurgical Engineers Serbia and Montenegro
AME *UDC:669.715.45.001.572=20*

MODELLING OF CASTING PROCESSES PARAMETERS FOR THE 3XX SERIES OF ALUMINUM ALLOYS USING THE SILICON EQUIVALENCY ALGORITHM

MODELOVANJE PARAMETARA LIVENJA KOD ALUMINIJUMSKIH LEGURA 3XXX KORIŠĆENJEM ALGORITMA SILICIJUMOVOG EKVIVALENTA

M. B. ĐURDJEVIĆ*, B. ĐURIĆ**,
A. MITRAŠINOVIĆ* AND J. H. SOKOLOWSKI*

**) NSERC / Ford-Nemak / University of Windsor Industrial Research Chair in Light Metals Casting Technology Mechanical, Automotive and Materials Engineering University of Windsor, Room 203, Essex Hall, 401 Sunset Avenue, Windsor, Ontario, Canada, N9B 3P4*
***) Vinca Institute of Nuclear Sciences, Belgrade, Yugoslavia*

Primljeno: 16. 04. 2003.

ABSTRACT

A novel algorithm for the modeling of casting processes is proposed. It utilizes information that has been derived from binary equilibrium phase diagrams in order to develop a silicon equivalency (Si_{EQ}) method. The new Si_{EQ} algorithm will express the chemical compositions of major and minor alloying elements in the aluminum melt through the value of the Si_{EQ}. This work will demonstrate how this algorithm can be used to calculate the characteristic temperatures of the equilibrium solidification of multi-component 3XX series aluminum alloys such as: the liquidus temperature T_{LIQ}, as well as the T^{AlSi} eutectic temperature. The authors will also verify that this algorithm can be used to estimate the latent heat of aluminum alloys (L_H). The above mentioned algorithm can then be implemented on the foundry floor for quality control of cast components.

INTRODUCTION

The modeling of casting processes has remained a topic of active interest for several decades, and with the availability of numerous software packages on the market, is a good indication of the interest that casting plants have in this field. Most of the input data used in these software packages are read or estimated from the binary or multi-component phase diagrams. Unfortunately, except for binary diagrams, many ternary or higher order phase diagrams are still not accurate enough. Keeping in mind that most aluminum binary systems are very well established [1-10], an attempt has been made to transfer multi-

component systems into one well known Al-X pseudo binary system. This type of system could be used to calculate several thermo-physical and solidification characteristics of multi component as cast aluminum alloys. This lends the model the ability to make predictions of the solidification characteristics for given cast section(s), where cooling rates are slow and the solidification process has to be investigated in greater detail in order to avoid problems in the casting. In this particular case the aluminum – silicon phase diagram was chosen as a reference one.

A new equivalent relationship developed for aluminum multicomponent alloys is called the silicon equivalent Si_{EQ}. The newly established Si_{EQ} algorithm should summarize the effect of all alloying elements present in the Al-ΣXi solution and express their influence on characteristic temperatures (T_{LIQ} and T^{AlSi}_{EU}). This paper will introduce the new algorithm and demonstrate its application, for 3XX series (aluminum-silicon) casting alloys. They are being widely used in many of the automotive components because of their good casting characteristics, reasonable mechanical properties and heat-treatability.

THEORETICAL HYPOTHESIS

Development of the Silicon Equivalent (Si_{EQ}) Algorithm

As can be seen in Figure 1, the liquidus and solidus temperatures (on the Al-rich side of the Al-Xi phase diagram) decreases uniformly, down to the eutectic concentration, while increases the amount of silicon up to its eutectic concentration.

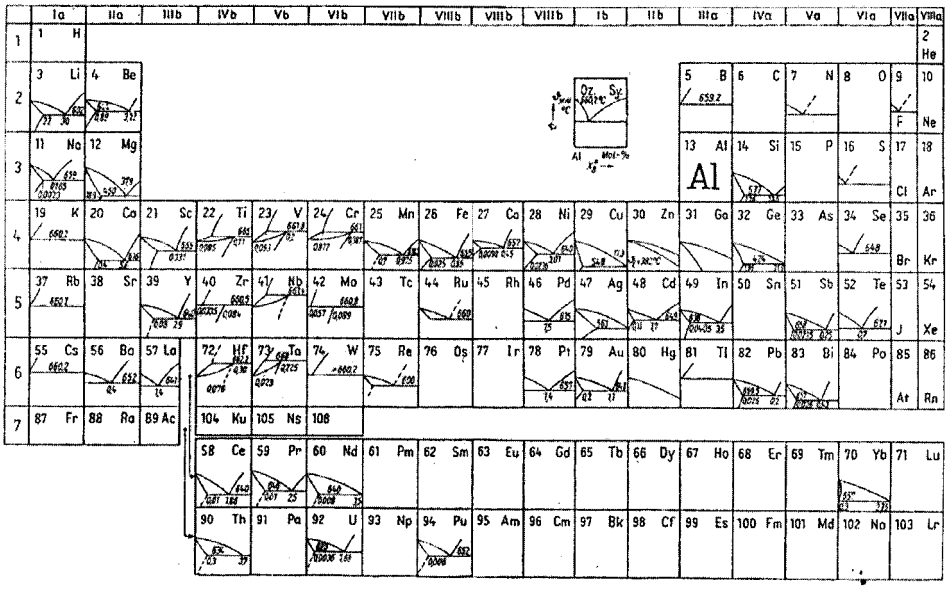

Figure 1 - Al-Xi binary phase diagram [3]

Mathematically, the liquidus and solidus lines of these binary systems can be approximated by linear equations or can be more accurately expressed in the second polynomial form as follows:

$$T^{Al\text{-}Xi}{}_{LIQ} = A - B \cdot Xi - C \cdot Xi^2 \qquad (1a)$$

$$T^{Al\text{-}Xi}{}_{SOL} = A - D \cdot Xi - E \cdot Xi^2 \qquad (1b)$$

where:

Xi is the content of the alloying element in wt.%

A is the melting point of pure aluminum 660.452°C.

B, C, D, and E are polynomial coefficients determined by the mathematical regression analysis using the Al-Si phase diagram.

Applying the numerical values for A,B,C and D, the coefficient equations for the liquidus and solidus line for the Al-Si binary system can be analytically expressed as follows:

$$T^{Al\text{-}Si}{}_{LIQ} = 660.452 - 6.11 \cdot Si - 0.057 \cdot Si^2 \qquad (2a)$$

$$T^{Al\text{-}Si}{}_{SOL} = 660.452 - 52.8 \cdot Si - 3.70 \cdot Si^2 \qquad (2b)$$

The analysis of the two binary phases diagrams, Al-Si and Al-Cu presented in Figure 2, shows that a high degree of similarity exists between these two diagrams.

- Both are of the eutectic type.
- In both diagrams the melting point of pure aluminum is at the same temperature, 660.452°C.
- The addition of an alloying element decreases the liquidus temperature of the alloy down to its corresponding eutectic temperature.
- The main difference is recognized in the slope of the liquidus line, Al-Si being steeper than Al-Cu.

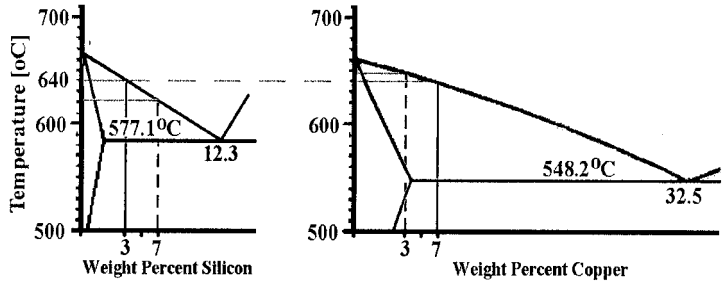

Figure 2 - Al-Si and Al-Cu binary phase diagrams

Figure 2 shows that the equivalent depression of the melting point of the aluminum alloys in both binary phase diagrams is obtained by adding a different concentration of alloying element. The depression of the melting point of the Al-Si or Al-Cu alloy to 640°C is reached by alloying aluminum either with 3 wt.% of Si or 7 wt.% of Cu. The isothermal concentration difference between these two alloying elements can be mathematically expressed as follows:

$$Si^{Cu}{}_{EQ,T=CONST} = Si(wt.\%) - Cu(wt.\%) \qquad (3)$$

Silicon as the major alloying element for this type of aluminum alloy was chosen as the reference element. It has the most significant influence on the casting properties of the 3XX series alloys (e.g. fluidity and shrinkage).

For the temperature range between the melting point of pure aluminum (660.452°C) and the eutectic temperature of the Al-Si and Al-Xi binary systems, at any isotherm, the value of the isothermal concentration difference, $Si^{Xi}{}_{EQ,T=CONST,}$ can be calculated.

Because the isothermal concentrations of Si are usually smaller than the corresponding concentrations of the observed Xi element, the values of $Si^{Xi}{}_{EQ,T=CONST}$ in Equation 3, are given as absolute values.

Applying the regression analysis, the relationship between isothermal concentration differences, for at least three isothermal temperatures, and the concentrations of the considered alloying element, Xi can be established as:

$$Si^{Xi}{}_{EQ} = a_0{}^{Xi} + b_0{}^{Xi} \cdot Xi + c_0{}^{Xi} \cdot Xi^2 \qquad (4)$$

where,

$a_0{}^{Xi}$, $b_0{}^{Xi}$ and $c_0{}^{Xi}$ are polynomial coefficients.

Xi is the concentration of alloying element in wt.%

Table I summarizes all necessary coefficients derived from the binary phase diagram(s) that must be used to calculate the value of the silicon equivalent for a multi-component system.

The above mentioned coefficients are valid up to a particular Al-Xi eutectic concentration.

The Si_{EQ} for major and minor alloying elements as well as for some impurity elements can be determined as the sum of the individual contributors ($\Sigma Si^{Xi}{}_{EQ}$) plus the effect of silicon itself.

$$Si_{EQ} = Si + \Sigma Si^{Xi}{}_{EQ} \qquad (5)$$

The liquidus temperature for the multi component aluminum system can be calculated using the following equation:

$$T^{Al\text{-}Si\text{-}\Sigma i}_{LIQ} = 660.452 - 6.11 \cdot Si_{EQ} - 0.057 \cdot Si_{EQ}^2 \qquad (6)$$

Table I - Polynomial coefficients for different binary Al-Xi alloys

Al-Xi Alloy	a_o	b_o	c_o
Al-Cu	0	0.350	-0.027
Al-Mg	0	0.0258	-0.0088
Al-Mn	0	0.8221	-0.0349
Al-Fe	0	0.6495	0.0003
Al-Zn	0	0.1227	-0.0002
Al-Sn	0	0.7849	-0.0313
Al-Bi	0	0.9076	-0.0092
Al-Pb	0	0.859	0.02976
Al-Ca	0	0.0594	0.00685
Al-Sb	0	0.8255	-0.0327
Al-Ni	0	0.5644	-0.0285
Al-Sr	0	0.7854	-0.0157
Al-Ti	0	-0.8159	0.009927
Al-B	0	-0.9977	0.00007506

CALCULATION OF LIQUIDUS TEMPERATURE

Unfortunately, there are only two published equations for calculation of liquidus temperature, related to multi component aluminum alloys. These equations will be shown and later compared with the newly developed equation.

The best known equation for calculating liquidus temperature of aluminum alloys (T_{LIQ}), based on their known chemical compositions, was developed by Drossel [5] using multiple regression analysis of the experimental data:

$$T_{LIQ} = 661 - 4.97\,Si - 0.15\,(Si)^2 - 6.13\,Cu - \\ - 17.4\,Mg + 2.72\,Zn + 5.08\,CuMg,\ (C^o) \qquad (7)$$

A second equation for predicting T_{LIQ} of aluminum alloys was recently developed by Vijayaraghavan et al.[6]. This equation was derived from the aluminum-silicon copper (Al-Si-Cu) ternary phase diagram through the use of multiple regression analysis:

$$T_{LIQ} = 664 - 6.9\,Si - 2.5\,Cu\ (^oC) \qquad (8)$$

EXPERIMENTAL PROCEDURE

Materials

Twelve synthetic 3XX compositions were made by melting a charge of Al-5wt.% Si, Al-7wt.% Si, Al-9wt.% Si or Al-11 wt.% Si base alloys and adding 1, 2 or 4 wt.% Cu. The chemical compositions of the resulting alloys, as determined using Optical Emission Spectroscopy (OES) are presented in Table II.

Table II - Chemical compositions (wt.%) of the synthetic alloys and their corresponding T_{LIQ} and $T^{AlSi}{}_{E}$ temperatures measured by using the Thermal Analysis technique

Alloy	Si	Cu	Fe	Mg	Mn	Zn	Ti	T_{LIQ}	$T^{AlSi}{}_{E}$
5/1	4.85	1.03	0.09	0.14	0.01	0.01	0.057	627.06	575.77
5/2	5.01	2.06	0.10	0.15	0.01	0.01	0.062	624.11	571.25
5/4	4.89	3.85	0.09	0.16	0.01	0.01	0.057	622.63	565.34
7/1	7.13	0.96	0.12	0.28	0.01	0.01	0.098	611.70	576.35
7/2	7.05	1.98	0.13	0.28	0.01	0.01	0.094	610.26	572.89
7/4	6.75	4.38	0.12	0.29	0.01	0.01	0.091	609.39	567.42
9/1	9.17	1.05	0.12	0.31	0.01	0.01	0.100	597.39	575.46
9/2	9.02	2.44	0.12	0.31	0.01	0.01	0.096	595.41	571.86
9/4	9.85	4.38	0.14	0.27	0.01	0.01	0.090	587.05	568.80
11/1	10.84	0.94	0.11	0.19	0.01	0.01	0.062	584.98	574.81
11/2	10.67	1.95	0.10	0.16	0.01	0.01	0.060	584.23	572.60
11/4	10.55	4.36	0.13	0.17	0.01	0.01	0.056	581.75	568.70

Melting Procedure

The alloys were melted in a reverberatory furnace. During processing, the melt was covered with a protective nitrogen gas atmosphere to prevent hydrogen and oxygen contamination. No grain refining agents were added to the melt. The ingots used were pre-modified with Sr.

Thermal Analysis (TA) Procedure

Samples with masses of approximately 300g ± 10g were poured into specially manufactured, ultra light, stainless steel (SS 304) cups, (mass = 2.5 ± 0.2g). Two specially designed supersensitive K type thermocouples (with extra low thermal time constants) were inserted into the melt and temperatures between 750 – 400 °C were recorded. The data for TA was collected using a high-speed National Instruments Data Acquisition System linked to a personal computer. Each TA trial was repeated three times. Consequently, a total of 36 samples were gathered.

Differential Scanning Calorimetry (DSC) Experiments

The liberated heat for all tested DSC specimens was measured using a NETZSCH DSC 404 C Pegasus Differential Scanning Calorimeter. The DSC experiments were performed at the same heating and cooling rate of 6^0C/min. Argon as a protective gas was used during the experiments. The DSC Thermal Analysis (TA) equipment was calibrated using a sapphire standard test sample. Starting at room temperature (25^0C) the DSC samples were heated to 800^0C held at this temperature for 10 minutes and cooled down to room temperature. Each DSC experiment for each particular alloy was repeated four times and an average value for latent heat was taken for further consideration.

RESULTS AND DISCUSSIONS

In order to statistically evaluate the accuracy of the newly developed equations, an additional twelve alloys (see Table III) were chosen from the literature [7-11]. The main purpose for taking into consideration all 24 alloys (literature plus experimental data, see Table II and III) was to statistically prove the reliability of the newly developed concept of silicon equivalency. In addition, the accuracy of the equations developed for the estimation of the characteristic solidification temperatures of the aluminum 3XX series of alloys over a wide chemical range was verified. All calculated liquidus and AlSi eutectic temperatures were compared with measured temperatures, and the corresponding statistical analysis parameters of this data are presented in Table IV.

Table III - Chemical compositions (wt.%) of the 3XX aluminum alloys and their corresponding T_{LIQ} and $T^{AlSi}{}_E$ temperatures measured by using the Thermal Analysis technique.

Lit	Si	Cu	Fe	Mg	Mn	Zn	Ti	T_{LIQ}	$T^{AlSi}{}_E$
[7]	6.867	0.005	0.14	0.477	0	0	0.144	616	578.4
[7]	6.990	0.211	0.10	0.466	0	0.01	0.143	617.7	573.74
[7]	6.946	0.666	0.08	0.444	0	0.01	0.145	617	573
[7]	6.823	1.562	0.10	0.458	0	0.01	0.143	613.6	569
[7]	7.034	2.325	0.08	0.503	0	0.01	0.139	610.8	567
[7]	7.362	3.693	0.10	0.491	0	0.02	0.15	606.7	564.8
[1]	5.10	2.91	0.30	0.27	0.05	0.03	0.10	622.8	567.2
[1]	5.75	3	0.31	0.30	0.05	0.04	0.07	615.7	-
[8]	12	3.39	0.20	1.55	0.01	0.03	0.01	565.7	-
[9]	7	0	0	0.51	0	0.01	0.143	580	-
[10]	5.10	2.91	0	0.27	0	0.03	0.10	614	-
[11]	7	0.003	0.05	0.35	0.01	0.02	0.05	612.81	-

Table IV summarizes the following statistical parameters: multiple regression coefficients – R^2, standard deviation - σ, average values, minimum and maximum differences between calculated and measured temperatures.

Table IV shows that all three equations used to calculate the liquidus temperatures of the 3XX series of aluminum alloys according to the R^2 criteria are very accurate. Further statistical analysis (standard deviation, average value...) revealed that the application of Drosseel's equation and Vijayaraghavan's equation provided less accurate data in comparison to the measured data, then by applying the newly developed equation (6).

Table IV - Regression Coefficients, Standard Deviations and Average Values of the Liquidus Temperature Calculated Using the Method of Silicon Equivalency and Methods Developed by Other Authors

Statistical Data	Si_{EQ} Method	Drossel Method	Vijayaraghavan Method
R^2	0.98	0.92	0.95
Standard Deviations	2.70	4.75	3.22
Average Value	-1.24	6.17	-1.21
Maximum	3	15.62	4.85
Minimum	-6.6	-3.12	-7.09

Equation (7) developed by Drossel is less accurate than the other two equations. One of the reasons for this lies in the fact that this equation is valid only for the following ranges of chemical alloy compositions (expressed in weight percent of the elements):

$$Si \leq 9.30;\ Cu \leq 2.50;\ Mg \leq 0.60;\ Fe \leq 1.15;$$
$$Mn \leq 0.40;\ Zn \leq 0.63;\ Ni \leq 0.43;\ Ti \leq 0.05$$

Therefore, the applicability is limited to alloys that have chemical compositions falling inside these ranges.

Vijayaraghavan's equation (8), which shows statistically better results than Drossel's equation (7) is limited because it applies only to those alloys for which T_{LIQ} can be estimated using only Al, Si and Cu concentrations as independent variables. It fails to account for the potentially important influence of other components (e.g. Mg, Mn, Fe, Zn and Ti). Therefore, substantial error is created in its estimate of liquidus temperature in those cases where the components mentioned above have a considerable influence. This is evident from the fact that the equation's constant (664°C) is considerably higher than the known and widely accepted melting point of pure aluminum (660.452°C).

The liquidus temperature calculated using the newly established Si_{EQ} method according to statistical analysis shows more accurate results in

comparison to the measured results. The accuracy of the calculated liquidus temperature is dependent solely on the accuracy of the polynomial coefficients, (Table I) outline the means by which the corresponding alloy content is converted into an equivalent silicon weight percent. However, these coefficients are derived from the silicon liquidus lines in the respective binary systems, and their reliability is closely related to the accuracy with which the liquidus curves are experimentally determined and numerically fitted. Therefore, some inaccuracy is also observed by applying this method. In order to exclude this source of error a re-examination of the liquidus lines on the silicon rich side of the respective binary systems or even better the ternary Al-Si-Xi systems would be necessary.

Application of Si_{EQ} in order to calculate the AlSi Eutectic Temperature of Al Alloys

Another advantage of the new Si_{EQ} method is its application to calculate the temperature of the AlSi eutectic in the 3XX series of aluminum alloys. Potentially, a similar approach could be used to develop an equation for calculation of the solidus temperature of aluminum multi component alloys.

The available literature provides one equation [12] that can be used to calculate the aluminum-silicon eutectic growth temperature of the 3XX series of aluminum alloys. This equation is based on the effect of the chemical composition of the melt on the depression of aluminum-silicon eutectic temperature. The effect of each particular element has been derived using literature data and the authors own experimental data. The equation reads as follows:

$$T^{AlSi}{}_{,E} = 660.452 - (6.11\,Si + 0.057\,Si^2)\,(12.6/Si) -$$

$$- (3.4\,Cu + 1.34\,Fe + 6.3\,Mg + 1218.9\,Sr - 32965\,Sr^2 -$$

$$- 4.293\,Sb + 186.3\,Sb^2 - 495.5\,Sb^2),\ (^oC) \qquad (9)$$

- all the element contents are given in weight percent.

The aluminum-silicon binary system has a eutectic temperature of 577°C. From the literature and from the experimental data any addition of alloying elements to the aluminum-silicon melt decreases this temperature. In the case of the 319 alloy the aluminum-silicon eutectic temperature for standard chemical composition at this temperature is in the range between 561 and 563°C. The Si_{EQ} method can be used to calculate the temperature of the aluminum-silicon eutectic, $T^{AlSi}{}_{,E}$ based on the chemical composition of the aluminum melt. The $T^{AlSi}{}_{,E}$ is calculated as follows:

$$T^{AlSi}{}_{,E} = 660.452 - ((6.11 \cdot Si_{EQ} + 0.057 \cdot Si_{EQ}{}^2) \cdot (12.3/Si,\ wt.5) \qquad (10)$$

Table II and III summarize values of calculated $T^{AlSi}_{,E}$ versus their experimentally determined counterparts using equations (9) and (10).

The corresponding value of the multiple regression coefficient R^2 show that equation (10) can calculate the $T^{AlSi}_{,E}$ temperature more accurately than equation (9).

Due to the nature of the interaction between atoms of different alloying elements into liquid (short-range order of atoms) and solid (long-range order of atoms) solutions, more significant errors in the calculation of the characteristic temperatures of solidification will be observed in temperatures under the liquidus temperature. In a high alloyed aluminum system these effects may be much more prominent. Therefore, in the literature no attempt has been made to develop equations that can be used to predict the solidification temperature of aluminum alloys below their Al-Si eutectic temperatures.

Application of Si_{EQ} in order to calculate Latent Heat of 3XX Aluminum Alloys

The latent heat of solidification is a thermo physical property of the material. During the solidification process every substance releases a certain amount of heat that characterizes this substance. For an alloy that has a zero degree of freedom (i.e., an alloy with an invariant reaction; eutectic or compounds with a congruent melting point), or for pure metal, it is not difficult to experimentally determine the value of the latent heat. However, there is no easy way to get the value for latent heat of solidification of multi-component alloys that solidify in a temperature range (mushy zone), either using measuring techniques or calculation procedures. For any alloy which solidifies in a given temperature range, the evolution of the latent heat begins at the liquidus temperature. The release of the latent heat continues until the alloy reaches its solidus temperature. In the mushy zone (the region between the liquidus and the solidus temperature), the substance is a mixture containing a fractional amount of both liquid and solid. Several models of latent heat released have already been proposed for modelling of casting solidification. These models include the linear and quadratic releases of latent heat between liquidus and solidus temperatures, as well as the use of the Lever Rule and Scheil's equation [12,13]. Each of these models assumes that the amount of latent heat released is proportional to the fraction solid in the casting.

The solidification path for multi-component 3XX alloys, under cooling rates close to equilibrium conditions, can be roughly described as follows [14,15]:

1. A primary α aluminum network forms between 620-580^{0}C. The exact temperature depends mainly on the amount of Si and Cu in the alloy.

2. Between 570-555^{0}C (the AlSi eutectic temperature) the eutectic mixture of Si and α-aluminum forms, leading to a further localized increase in the Cu content of the remaining liquid.

3. At approximately 540^{0}C the Mg_2Si and $Al_8Mg_3FeSi_6$ phases begin to precipitate. A reduction in the temperature allows for precipitation of $A_{l2}Cu$ and $A_{l5}Mg_8Cu_2Si_6$ phases between 530-490^{0}C.

Applying the method of silicon equivalency, the multi-component 3XX series of aluminum alloys can be considered as pseudo binary Al-Si_{EQ} alloys. In this case the solidification path can be described through formation of a primary α-Al solid solution and later on precipitation of the Al-Si eutectic (secondary aluminum and primary silicon). Applying the Si_{EQ} method, the multi-component 3XX series of aluminum alloys are transferred into a well understood Al-Si_{EQ} pseudo binary system. Applying the Lever Rule (Equation 11) the amount of primary α-aluminum can be calculated, assuming that the precipitated α-aluminum solid solution has the same value for latent heat of solidification as pure aluminum.

$$f^{\alpha\text{-}Al}{}_{PRIMARY} = (C_E - C_0)/(C_E - C_{\alpha\text{-}E}) \qquad (11)$$

where:

C_E- is the eutectic concentration at 12.3wt.% Si.

C_0- is the content of the Si constituent in the Al-Si binary alloy at the eutectic temperature.

$C_{\alpha\text{-}E}$ – is the maximum solubility of Si in the α-Al solid solution at the eutectic temperature, (1.6 wt.% Si).

Using Equations (12) and (13) the amount of secondary aluminum present in the remaining eutectic as well as the amount of primary silicon has been calculated.

$$f^{Al}{}_{SECUNDARY} = ((C_{\beta\text{-}E} - C_E)/(C_{\beta\text{-}E} - C_{\alpha\text{-}E})) * f^{AlSi}{}_E \qquad (12)$$

where,

$C_{\beta\text{-}E}$ – is the concentration of Silicon, which corresponds to the maximum solubility of aluminum in the β solid solution at the eutectic temperature, (0.015 wt.% Al).

$$f^{Si}{}_E = ((C_E - C_{\alpha\text{-}E})/(C_{\beta\text{-}E} - C_{\alpha\text{-}E})) * f^{AlSi}{}_E \qquad (13)$$

By knowing the value for latent heat of solidification for pure silicon (1800 J/g) and pure aluminum (390 J/g) and by applying Equation (14), the total latent heat for the equilibrium solidification of the Al-Si_{EQ} alloy can be calculated.

$$L^{Al\text{-}Si}{}_{HEAT\ of\ SOLIDIFICATION} = f^{\alpha\text{-}Al}{}_{PRIMARY} * L_{HEAT\ of\ PURE\ Al} +$$

$$+ f^{Al}{}_{SECUNDARY} * L_{HEAT\ of\ PURE\ Al} + f^{Si}{}_{E} * L_{HEAT\ of\ PURE\ Si} \qquad (14)$$

For non-equilibrium solidification conditions Scheil's equation can be used to calculate the amount of fraction solid of primary and eutectic phases. Alternatively, Computer Cooling Curve Analysis (CCA) may also be used to calculate fraction solid and latent heat released during non-equilibrium solidification [16,17].

Non-equilibrium solidification is characterized as no diffusion in the solid and complete diffusion in the liquid (the liquid has a uniform composition). The freezing of the alloy starts at T_{LIQ} but does not end at the T_{SOL} temperature as in equilibrium freezing, and may proceed to much lower temperatures due to the enrichment of the liquid with the solute during solidification. In a eutectic system, the liquid may reach the eutectic composition due to solute enrichment, and subsequently, the alloy freezes as a eutectic. In this case, the fraction solid of the primary α-Al solid solution is calculated using Scheil's equation until the eutectic temperature and the rest of the liquid solidifies as a eutectic. The latent heat evolved in rapid solidification has not yet been determined exactly, and it is very difficult to immediately determine the latent heat actually released during rapid solidification [17, 18].

Cooling Curve Analysis (CCA) is primarily used for process control in the metal casting industry, usually to predict alloy composition, control the grain size and the level of silicon modification i.e., to allow production of sound casting(s). The Thermal Analysis (TA) cooling curve technique can also be used to calculate the amount of primary and eutectic phases precipitated during solidification of the alloy under equilibrium and non-equilibrium conditions. The rate by which the fraction solid is formed during solidification is proportional to the amount of latent heat released during liquid/solid transformation. The main problem in applying this method is how accurately the amount of fraction solid can be estimated from the Cooling Curve Analysis (CCA). It has been proven by many authors that accurate calculation of fraction solid heavily depends on the evaluation of the zero curve [17,19].

In the DSC curves the reaction peaks reflect the specific phase changes and the peak area is proportional to the heat of reaction associated with the phase transformations. There are at least three peaks appearing in this type of 3XX series of aluminum alloys for both heating and cooling curves, see Figure 3. Peak 1 corresponds to the development of primary aluminum dendrites; Peak 2 represents mainly the binary eutectic reactions, Peak 3 is associated with the formation of minor copper rich eutectic phases.

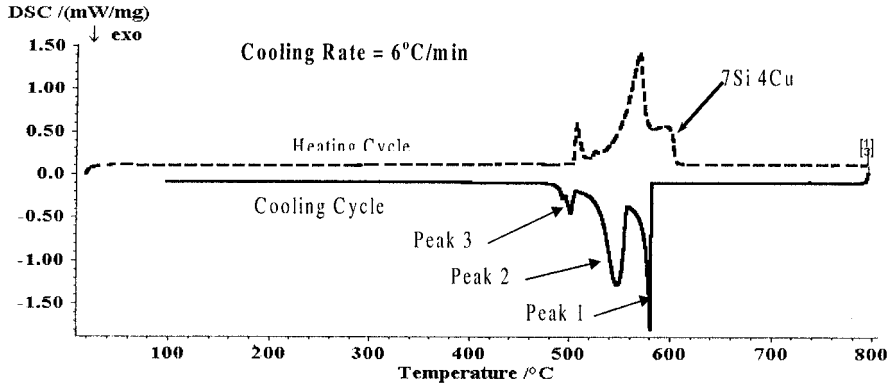

Figure 3 - Heating and cooling traces of the DSC curves for the Al 7wt.%Si 4wt.%Cu aluminum alloy.

It is apparent that the shapes of the DSC curves are strongly dependent on the amount of silicon and copper content in the 3XX aluminum melt. The increasing content of silicon has a significant effect on the beginning and duration of the primary solidification of the α-Al dendrites and on the precipitation of the Al-Si eutectic. It appears that silicon does not substantially influence the shape and number of copper enriched eutectic peaks. It can also be observed that an increase in the copper content decreases the primary solidification time of the α-Al dendrites although not to the same extent as silicon. This also means that elements, such as silicon and copper control the fraction solid of the primary and eutectic phases, and have an influence on the amount of released latent heat during solidification.

The DSC curves have been used to measure the values of latent heat for each particular chemical composition of alloys as presented in Table 2. The latent heat of solidification has been measured taking into consideration the area between the DSC curve and the base line. This area is proportional to the latent heat energy released during solidification. For the same chemical composition the value of latent heat has also been calculated using the novel method proposed in this work.

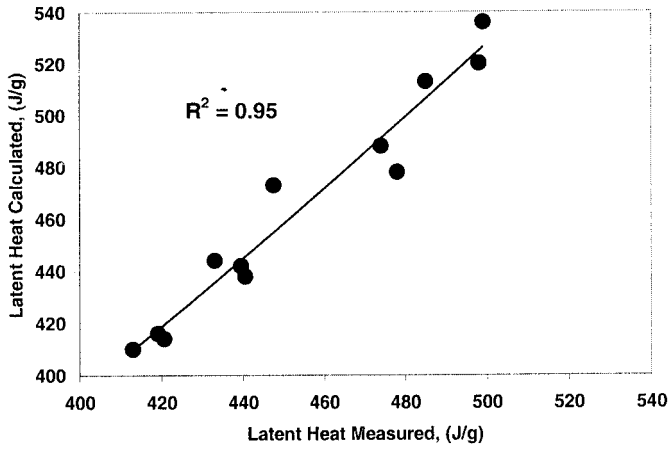

Figure 4 - Comparison between the measured and calculated value of latent heat for the 3XX series of Al alloys.

Figure 4 shows the comparison between the measured values of latent heat of solidification and the calculated values obtained by applying the novel algorithm for calculation of the latent heat.

The results presented in Figure 4 show a close agreement between calculated and experimental values for latent heat without taking the above mentioned factors into consideration. The high standard correlation ($R^2 = 0.95$) confirms that it is possible to estimate the latent heat of solidification of the 3XX series of alloys that solidified under equilibrium conditions using the novel method based on the Si_{EQ} algorithm.

CONCLUSIONS

A novel Si_{EQ} method has been developed for the multi component 3XX series of aluminum alloys. The Si_{EQ} algorithm has summarized the effect of all alloying elements present in the Al-ΣX_i solution and has expressed the influence on characteristic temperatures such as T_{LIQ}, $T^{AlSi}_{E,G}$, $T^{AlCu}_{E,G}$ and T_{SOL}. The calculation procedure presented here is more accurate than those found in the literature. It has been shown that the Si_{EQ} can be used to calculate the latent heat of solidification of the 3XX series of Al alloys. Multi-component aluminum alloys have been analyzed as pseudo binary by applying the already developed method of silicon equivalency. The results of these calculations were found to be very accurate in comparison to measured values.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to the Natural Sciences and Engineering Research Council of Canada (NSERC) and to the Nemak of Canada Corporation for their sponsorship. Special thanks to Ms. E. Moosberger for her assistance with the preparation of this manuscript.

LITERATURE REVIEW

[1] Mondolfo, L. F., "Aluminum Alloys, Structure and Properties", Butterworths, London, 1979, pp. 213/614.

[2] Kissing, R. J. and Wallace, J. F., Refinement of Aluminum-Silicon Alloys, Foundry, 1963, pp. 74-79.

[3] Wang, O. G., and Davidson, J. C., "Solidification and Precipitation Behavior of Al-Si-Mg Casting Alloys'; Journal of Materials Science 36, 2001, pp. 739-750.

[4] ASM Specialty Handbook, Aluminum and Aluminum Alloys; Edited by J. R. Davis, ASM International The Materials Information Society: May 1994.

[5] G. Drossel, "Der Einfluss von Schmelzebehandlungen auf die Dichtheit von Gusskoerpern aus Al-Si Gusslegierungen", Giessereitechnique, Vol.27, No.1, p.7-12, (1981).

[6] R. Vijayaraghavan, N. Pelle, J. Boileau, J. Zindel, R. Beals; "A Micro Model for Al-Si Alloys", Scripta Materialia, Vol.35, No 7, pp. 861-867 (1996).

[7] NSERC/FORD/University of Windsor Industrial Research Chair, " Experimental Evaluation of Fraction Solid, Dendrite Coherency Point and Latent Heat for Aluminum Alloys". Report dated June 5, 1996.

[8] B. Closset, K. Pivie, and J. E. Gruzleski, "Comparison of thermal analysis and electrical resistivity in microstructure evaluation of Al-Si foundry alloys", AFS Transactions, 84-27, 1984, p.123/133.

[9] Li B. Q., Liu J. C., and Brock J. A., The Minerals, Metals and Materials Society (1992), p. 841/857.

[10] L. Arnberg, A.K.Dahle, C.J.Paradies and F. Syveertsen " Feeding Mechanisms in Aluminum Foundry Alloys" 99th Casting Congress, Kansas City, Missouri, April 23-26, 1995.

[11] M. Djurdjevic, W. Kierkus, G. Byczynski and J. Sokolowski, "Calculation of Liquidus Temperature for the Aluminum 3XX Series of Alloys" AFS Trans. 1998, v. 47, 143-147.

[12] Djurdjevic, M. B., Kierkus W. T., Byczynski, G., Stockwell, T., and Sokolowski, J. H., "Modeling of Fraction Solid for 319 Aluminum Alloy", AFS Transactions 99-14, 1999, p.173-179.

[13] Bennon, W. D and Incropera F. P. " A Continuum Model for Momentum, Heat and Species Transport in Binary Solid-Liquid Phase Change Systems" Int. J. Heat Mass Transfer, 30, 1987, pp. 2161-2187.

[14] Backerud, L. "Solidification Characteristics of Aluminum Alloys", Vol. 2, AFS, Skanaluminium, 1991.

[15] Caceres, C. H., Djurdjevic, M. B., Stockwell, T. J, and Sokolowski, J. H., " The Effect of Cu Content on the Level of Microporosity in Al-Si-Cu-Mg Casting Alloys", Scripta Materialia Vol. 40, No. 5, 1999, pp. 631-637.

[16] Barlow, J.and Stefanescu, D. "Computer Aided Cooling Curve Analysis Revisited", unpublished, 1996.

[17] Emadi, D., and Whiting, L., "Determination of Solidification Characteristics of Al-Si Alloys by Thermal Analysis, AFS Transactions 02-033, pp. 1-12, 2002.

[18] Zhang, Y., "Enthalpy Estimation of the Non-Equilibrium State in As Melt Spun Al-Si and Al-Mn Alloys and Crystal Growth As a Non-Equilibrium Crystallization During Rapid Unidirectional Solidification" Thermochimica Acta, 286, 1996, pp. 139-159.

[19] Kierkus, W. T. and Sokolowski, J. H. "Recent Advances in CCA: A New Method of Determining the 'Baseline' Equation", AFS Transactions, v. 66, 1999, 161-167.