Analysis of the solidification path of Al-Si9-Cu(1-4) alloys using thermal analysis technique

M. B. Djurdjević, Z. Odanović

The present work displays the potential of cooling curve analysis to characterize the solidification path of Al-Si9-Cu(1-4) alloys. In additions the possibility of quantifying the Cu enriched phases in these alloys by using thermal analysis (TA) technique has been investigated. The proposed methodology is based on the following procedure: a total amount of the Cu enriched phases is defined as the ratio of the area between the first derivative of the cooling curve and the hypothetical solidification path of the Al-Si-Cu eutectic to the total area between the first derivative of the cooling curve and the base line. These calculations based on the cooling curve analyses are compared with Image Analysis (IA) and chemical analysis results in order to verify the proposed method. There is a good correlation between measured and calculated values for the area of Cu rich phase of the Al-Si9-Cu(1-4) alloys.

Keywords: Al alloys - Cu rich phase - Thermal analysis - Thermal freezing range

INTRODUCTION

The interest in better understanding in aluminum casting industry has extended significantly in the last few decades. Among many reasons following three from our point of view are very important: (i) the necessity to improve productivity and quality of cast products (ii) to speed up the design process and (iii) to improve the accuracy of simulation. The accuracy of casting simulation depends in great deal on the quality of the available physical and thermophysical material properties provided by the software's database. Available databases presently used by commercial simulation software packages for the casting industry usually come with material properties for only a few selected standard alloys. In the case of more sophisticated alloys with different chemical compositions, refinement and/or modification treatments, thermal analysis can be a very useful tool in order to collect the missing parameters or more accurate thermo physical data for investigated alloys. Thermal (cooling curve) analysis method is useful for commercial applications for a number of reasons: it is simple, inexpensive and provides consistent results. This technique is a good choice for drawing fundamental relationships between cooling curve characteristics and melts. A state–of-the-art thermal analysis system should be able to quantify parameters such as: grain size, dendrite coherency point, level of silicon modification, low melting point of secondary eutectic(s), fraction solid and other characteristic solidification temperatures. In this paper the cooling curve analysis has been used to describe the solidification path of AlSi9Cu(1-4) alloys.

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The Al-Si9-Cu(1-4) alloys have been characterized by the presence of two Al-Si and Al-Si-Cu eutectics, which are primarily responsible for defining the microstructure and mechanical properties of these alloys [1-4]. Both of these eutectics can be detected on a TA cooling curve, or more precisely on its first derivative. Metallographic analysis of the TA test samples has confirmed the presence of these phases. Their formation temperatures can help to define the maximum temperature at which castings can be exposed to during solution treatment i.e. by defining the temperature at which incipient melting will take place. Unfortunately, the total amount of Cu enriched phases presented in an alloy can thus only be measured using metallographic analysis. This information is critical as these phases play a role in the precipitation phenomena during artificial aging and can have a negative influence on the mechanical properties of the alloy. The investigation results presented in this paper tends to demonstrate the ability of cooling curve analysis to characterize the solidification path of Al-Si9-Cu(1-4) alloys as well as to quantify and to depict the development of Cu rich phases in the Al-Si-Cu alloys using the Thermal Analysis (TA) system. This estimation is verified using quantitative metallography (Image Analysis) and chemical analysis (Optical Emission Spectroscopy).

EXPERIMENTAL PROCEDURES

Materials

Three Al-Si-Cu alloys with the chemical compositions as presented in Table 1 were produced. Their chemical compositions have been determined using Optical Emission Spectroscopy (OES).

Alloy	Si	Cu	Fe	Mg	Mn	Zn	Ni	Al
Al-9Si-1Cu	8.92	1.05	0.12	0.31	0.01	0.01	0.007	rest
Al-9Si-2Cu	8.95	2.04	0.12	0.31	0.01	0.01	0.007	rest
Al-9Si-4Cu	8.85	4.38	0.14	0.27	0.01	0.01	0.009	rest

Table 1 - Chemical compositions (wt %) of the synthetic alloys.

Tabella 1 – Composizione chimica (peso %) delle leghe sintetiche.

Melting procedure

The alloys were melted in a furnace under protective nitrogen gas atmosphere to prevent hydrogen and oxygen contamination. No grain refining and modifier agents were added to the melt.

Thermal analysis procedure

Samples with masses of approximately 300g were poured into thermal analysis steel test cups. The test cup had conical shape with bottom diameter of 45 mm and top diameter of 55 mm. The height of the cup was 60 mm and the thickness of the wall 1.5 mm. Temperature was measured by the K type thermocouple which was inserted into the melt and temperatures between 750 - 400°C were recorded. The data for TA was collected using a high-speed data acquisition system linked to a personal computer. The cooling conditions were kept constant during all experiments and were approximately 0.1°C/s. The cooling rate has been calculated as the ratio of the temperature difference between liquidus and solidus temperature to the total solidification time between these two temperatures. Each TA trial was repeated four times. Consequently, a total of twelve samples were gathered. In all cases, the masses of the thermal analysis test samples were virtually identical.

Metallography and image analysis

Samples for microstructural analysis were cut from the TA test samples, close to the tips of the thermocouples. The cross sections of the specimens were ground and polished on an automatic polisher using standard metallographic procedures. The samples were observed under a Scanning Electron Microscope (SEM) using magnifications between X200 and X5000. Qualitative and quantitative assessments of the chemical compositions of the Cu enriched phases were done using an Energy Dispersive Spectrometer (EDS). The area fractions of the Cu enriched phases were calculated using Image Analysis software linked to a microscope, under a magnification of X500. Twenty-five analytical fields were measured for each sample and the final volume fraction was expressed as a mean value.

RESULTS AND DISCUSSION

Thermal analysis results

Three representative TA cooling curves obtained for alloys Al-9Si-1Cu, Al-9Si-2Cu and Al-9Si-4Cu alloys have been presented in Figure 1. The cooling rate in all three curves was approximately 6°C/minute. Results presented in figure 2 shows that increasing the Cu content in the investigated alloys, depresses all characteristic solidification temperatures as: T liquidus, T coherency, T Al-Si eutectic, T Al-Si-Cu eutectic and T solidus. All previously mentioned characteristic solidification temperatures except dendrite coherency temperature are very well understood. Therefore, only the dendrite coherency temperature will be here briefly highlight as well as its importance for better understanding of solidification process of AlSiCu alloys. During the solidification of any aluminum hypoeutectic alloys dendritic network of primary α - aluminum crystals will be developed. In the early stage of solidification dendritic crystals are separate and move freely in the melt. However, as the melt cools, the dendrite tips of the growing crystals begin to impinge upon one another until a coherent dendritic network is formed. The temperature at which this occurs is called Dendrite Coherency Temperature (DCT) and is very important feature of the solidification process. This temperature marked the moment when the "mass" feeding transferred to interdendritic feeding. Casting defects such as macrosegregation, shrinkage porosity and hot tearing begin to develop after the DCT. Therefore, a thorough understanding of the solidification behavior at the DCT and the factors that influence it are crucial for the engineering of a new alloys and the development of related manufacturing process (es).

The first derivatives of the cooling curves are presented in Figure 3. It is apparent that the shapes of the first derivative curves are strongly dependent on the amount of Cu in the melt. Specially, the Cu rich area is affected by different content of Cu [5].

The number and shape of the peaks visible in the Cu enriched region of the first derivative curves show a strong relationship with the amount of Cu present in the alloy. It can also be observed in Figure 4, that an increase in the Cu content increases the solidification time of the Cu rich eutectic phase. The precipitation temperature of the Cu enriched phases decreases when Cu increases from 1 to 4 wt%. The Cu enriched phase represented by the first peak on the cooling curve in Figure 4 (9 wt% Si, 1 wt% Cu alloy) began to precipitate at 528.7°C and the Cu enriched phase represented by the second peak precipitated at 505.3 °C. For alloy with 9 wt% Si, 2 wt% Cu alloy three peaks can be observed (although two of them are partly „convoluted"). One peak is dominant and the Cu phase represented by this peak began to precipitate at 509.4°C. Increasing the amount of Cu to 4 wt% (9 wt% Si) further changes the shape of the Cu enriched phase peaks (Figure 4). The precipitation temperatures are also altered. The Cu enriched phase represented by the first peak begins to precipitate at 507.7°C. Increasing the Cu content from

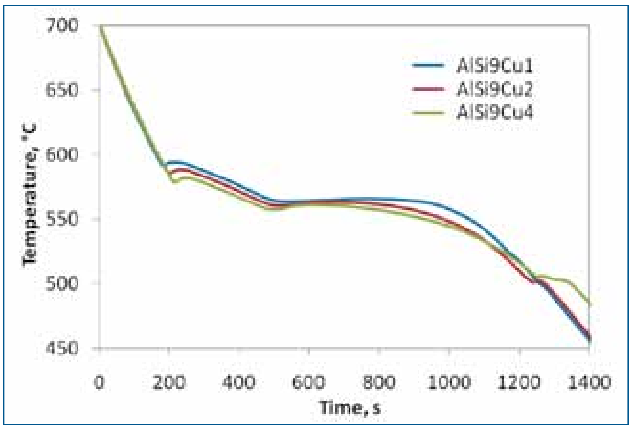

Figure 1 - Cooling curves of alloys with nominal 9 wt% silicon content (Table 1)

Figura 1 – Curve di raffreddamento delle leghe con contenuto nominale di silicio 9% in peso (Tabella 1)

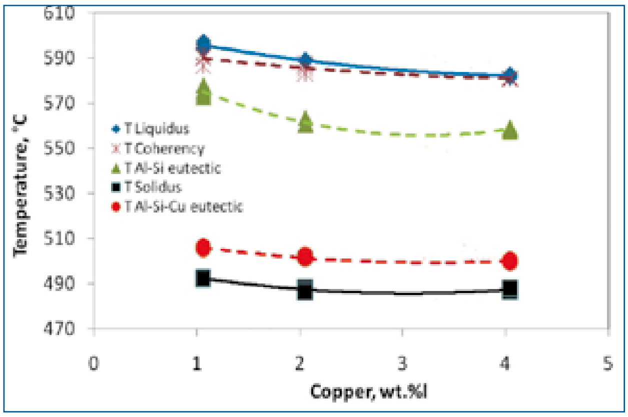

Figure 2 - Impact of various content of Cu on characteristic temperatures by Al-Si9-Cu alloys

Figura 2 - Impatto dei diversi contenuti di Cu sulle temperature caratteristiche per leghe Al-Si9-Cu

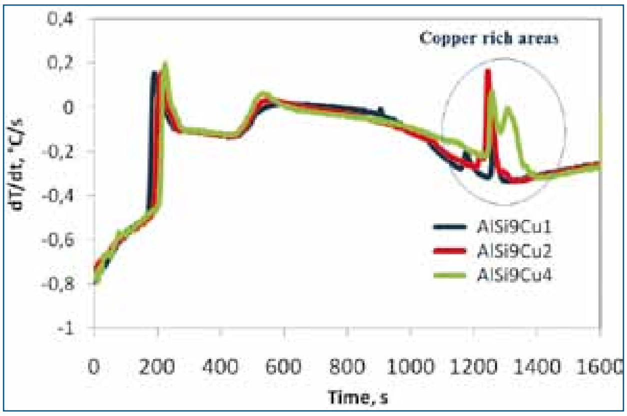

Figure 3 - First derivative of the Al-Si9-Cu(1-4) cooling curves

Figure 3 –delle Derivata prima delle curve di raffreddamento delle leghe Al-Si9-Cu(1-4)

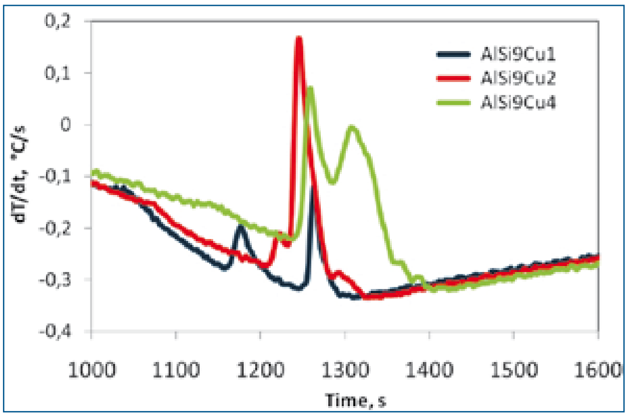

Figure 4 - First derivative of the Al-Si9-Cu(1-4) cooling curves related to Cu enriched region

Figura 4 – Curve delle derivate prime di raffreddamento delle leghe Al-Si9-Cu(1-4) in relazione alla regione arricchita in Cu

1 wt% to 4 wt% increased the total solidification time from 1290 seconds (in alloy Al-9Si-1Cu) to 1400 seconds (in alloy Al-9Si-4Cu), increasing also the total solidification interval of Cu rich phase(s) from 36.6°C (for Al-Si9-Cu1 alloy) to 48.2°C (by Al-Si9-Cu4 alloy).

The nucleation temperature of the Cu enriched phases can be accurately read from the first derivatives of the cooling curves and used to define the maximum temperatures that the castings can be exposed to during the conventional solution treatment process. However, before solution treatment routines can be "tailored" to specific alloys and applications, it is also necessary that the volume fractions of the Cu enriched phases be known. This will enable researchers to predict the mechanical properties of the castings and to design components according to predetermined specifications and requirements. To date, volume fraction assessment has only been possible through metallographic analysis.

Metallography, cooling curve and image analysis results

Light Optical Microscopy (LOM) observations combined with Image Analysis (IA) showed that the area fractions of the Cu enriched phases increased with additions of Cu. Cu addition from 1 to 4 wt% caused the area fraction of the Cu enriched phases to increase from about 0.6% to about 2.02%, as presented in Table 2.

Determination of the total Cu enriched phase area fraction by metallography is a time consuming and laborious procedure; therefore, it cannot be used as an on-line measurement tool, or as a method of controlling casting quality in a foundry environment.

For determination the area fraction of individual phases that precipitate during solidification of Al-Si-Cu alloys it has been used in this work the TA approach developed by Kierkus and Sokolowski [6]. In their work, the integrated area of the Cu enriched phases is defined as the ratio of the area

Alloy	Area. % of Cu-rich phases, (TA)	Area Fraction % of Cu-rich phases, (IAS)	Cu, wt.%
Al-9Si-1Cu	1.70	0.60	1.05
Al-9Si-2Cu	3.41	1.32	2.44
Al-9Si-4Cu	5.96	2.02	4.38

Table 2 - Comparison of Cu enriched phase area fraction detected by the IA system and determined using thermal analysis.

Tabella 2 – Confronto fra la frazione di area di fase arricchita in Cu rilevata col sistema IA e determinata utilizzando l'analisi termica

between the first derivative (FD) of the cooling curve and the hypothetical solidification path of the Al-Si-Cu eutectic (hatched area on Figure 5) to the total area between the first derivative of the cooling curve and the Base Line (BL). The rationale of this assumption is based on [6]:

1. The IA results, which permit one to postulate that the solidification of the Al-Si eutectic continues until the solidus temperature is reached.
2. The total latent energy evolved during alloy solidification is the sum of the energy released by all of the phases involved in the process.

This concept is briefly demonstrated in Figures 5 and 6, which present the first derivative of the cooling curve (FD) and the Base Line curve (BL). The area between the two curves, from the liquidus state (Tliq) to the solidus state (Tsol) is proportional to the latent heat of solidification of the alloy. If the two aforementioned assumptions are correct, then the regression line between the arbitrarily selected state (T^{AlSiCu}_{NUC}) and the solidus state (Tsol) is a part of the solidification path of the Al-Si-Cu eutectic (hatched area). Therefore, it is evident that the area between path (T^{AlSiCu}_{NUC})-(Tsol) and the first derivative of the cooling curve (FD) should be proportional to the latent heat of solidification of the Cu enriched phases. The corresponding proportionality constant of the total latent heat of alloy solidification and the latent heat of the solidification of the Cu enriched phases, could be defined as the "apparent specific heat" of the alloy.

A comparison of the total area fraction of the Cu enriched phases determined using IA with a integrated area (hatched area on Figure 5 of the Cu enriched phases of each alloy tested shows that the two measurements are almost perfectly correlated (see Figure 7).

The imperfect agreement between these two measurements can be explained by two factors: First, the IA measurements do not take into account small Si crystals that cannot be resolved by the LOM or the Si that is dissolved in the aluminium matrix. Only TEM investigations under very high magnification should be able to reveal the presence of ultra fine Al-Cu eutectics. Second, because the cast samples are heterogeneous and because only a finite number of regions were evaluated using the IA, these measurements may not be precisely representative of the entire sample.

The results of the Cu enriched phase determinations are

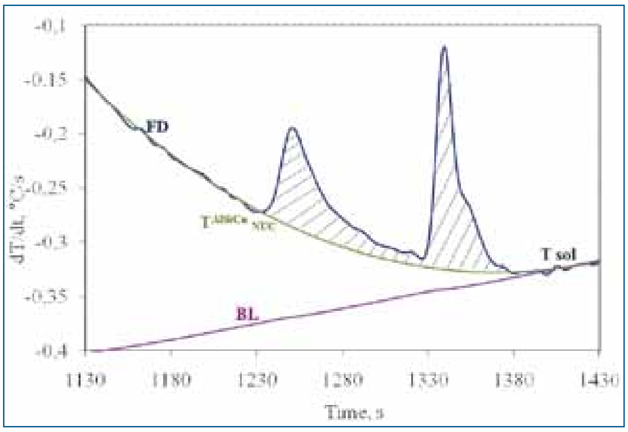

Figure 5 - The part of the first derivative curve related to Cu rich phase

Figure 5 – La parte della curva della derivata prima relativa alla fase ricca di Cu

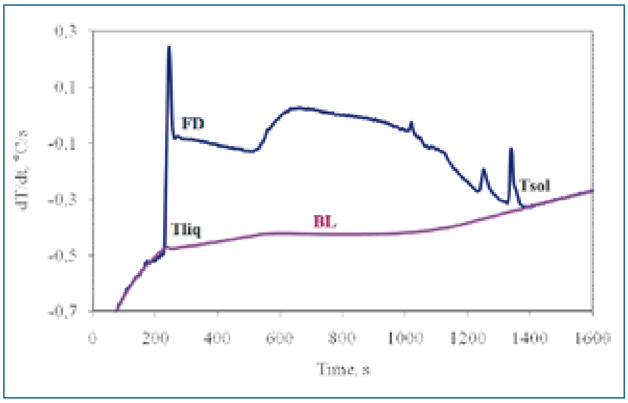

Figure 6 - The first derivative curve of the Al-Si9-Cu1 alloy (The base line has been calculated using Newtonian analysis)

Figure 6 - Curva della derivata prima della lega Al-Si9-Cu (la linea di base è stata calcolata mediante analisi Newtoniana)

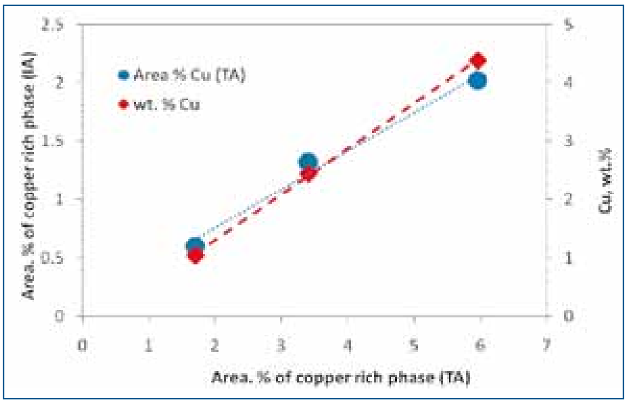

Figure 7 - Relationship between IA and TA measurements and the chemical compositions of the investigated alloys.

Figure 7 - Relazione fra misurazioni IA e TA e composizione chimica delle leghe analizzate.

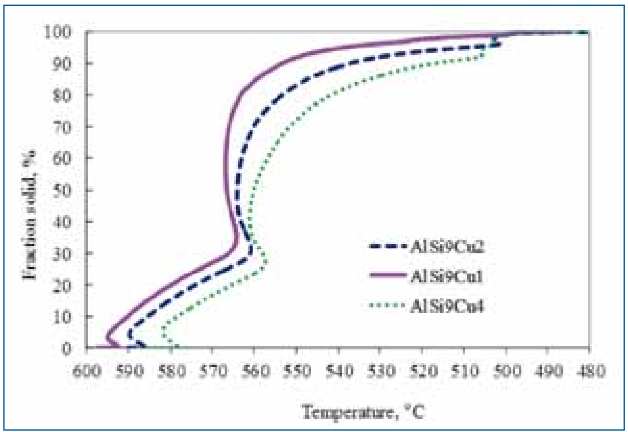

Figure 8 - Distribution of the fraction solid for Al-Si9-Cu(1-4) alloys calculated using cooling curve analysis

Figure 8 - Distribuzione della frazione solida per le leghe Al-Si9-Cu(1-4) calcolata usando l'analisi delle curve di raffreddamento

presented in Table 2 and in Figure 7. The high correlation observed on the regression plots (Figure 7) shows that it is possible to estimate the volume fraction of Cu enriched phases from the TA analysis experiments without resorting to IA.

Determination of solid fraction using cooling curve analysis

Beside characteristic solidification temperatures, the thermal analysis is often used to calculate solid fraction distribution between Tliq and Tsol temperatures. A critical requirement for the solid fraction calculation applying cooling curve analysis is determination of a base line [6, 7]. The base line is in principle the first derivative of the cooling curve measured by the thermocouple(s), inserted in the alloy test sample, assuming that the metal doesn't undergo any phase transformation during the solidification process. In other words the base line overlaps the first derivative of the cooling curve in single phase parts of the sample cooling process, for temperatures higher than T-liquidus and for temperatures lower than T-solidus. In the literature the Newtonian method [6-8] has been successfully used to calculate base line and solid fraction distribution using cooling curve analysis. Figure 8 shows the distribution of fraction solid for all investigated alloys.

Newtonian analysis

The Newtonian analysis of the metal solidification process is based on the following assumptions:

(a) the cooling behavior of the alloy test sample may be considered as "the lumped thermal system" where the Biot number is < 0.1. Lumped thermal system assumes a uniform temperature distribution throughout the thermal analysis test sample.
(b) the sensible specific heat for the alloy can be considered as temperature independent and constant in the freezing temperature range, and
(c) the heat transmission coefficient from the alloy test sample to its surrounding by convection, radiation and conduction can be characterized by the single unique temperature function for the given experimental conditions [6].

The heat balance equation for the solidifying thermal analysis sample - thermal analysis mould system can be written as [6, 8]:

$$\frac{dQ}{dt} - M\,C_P\,\frac{dT}{dt} = U\,A\,(T - T_0) \qquad (1)$$

where, M is the mass of the sample, C_P is specific heat of the metal, T is the metal temperature, t is time, U is overall heat transfer coefficient, A is sample surface area, T_0 is ambient temperature, and Q is latent heat of solidification. If no phase transformation occurs,
dQ/dt = 0, then the cooling rate of the test sample (first derivative of the cooling curve) can be written as:

$$\frac{dT}{dt} = -\frac{U\,A\,(T - T_0)}{M\,C_P} = BL_N \qquad (2)$$

The curve corresponding to Equation 2 represents the Newtonian base line (BL_N). The analysis starts by fitting a polynomial, usually of the order of 3 or higher, to the first derivative (FD) of the cooling curve versus recorded temperature in the single phase portion of the cooling curve (for $T > T_{LIQ}$ and $T < T_{SOL}$).
The solid fraction at time during solidification can be obtained by calculating the cumulative area between the first derivative curve and the base line as a fraction of total area between these two curves (Figure 6).

Terminal freezing range

Another useful criterion that can be extracted from the cooling curve analysis (exactly from the calculated fraction solid curve) is the non-equilibrium partial freezing range near termination of solidification that according to [9] has been abbreviated as terminal freezing range (TFR). The TFR has significant impact on the hot tearing formation. In general as the freezing range increases the hot tearing susceptibility also increases. The chemical composition is the main influencing factor on the freezing range. Unfortunately, it is not yet established a range in which this criterion has to be calculated. In this paper a range between 95 % and 99.5% fraction solid recently proposed by Schumacher et al [10] was applied. Beside this criterion in the literature there are others theoretical models [11-14] for the calculation of the hot cracking tendencies. The most commonly used is the cracking susceptibility coefficient (CSC) model from Clyne and Davies [11]. The CSC model correlates the susceptibility-composition relationship based on the consideration of the time during which processes related to crack production may take place and the structure is most vulnerable to cracking (critical time interval during solidification). The CSC is defined as = t_V/t_R; where t_V is the vulnerable time period and is calculated as the time difference between mass fraction

Alloy	Al-Si9-Cu1	Al-Si9-Cu2	Al-Si9-Cu4
CSC	0.4902	0.3691	0.2453
TFR (fS = 95 – 99.5 %)	40.76	11.50	7.02

Table 3 - CSC and TFR values for evaluated alloys calculated using cooling curve analysis (fraction solid curves calculated using Newtonian analysis)

Tabella 3 – Valori CSC e TFR per le leghe esaminate calcolati utilizzando l'analisi della curva di raffreddamento (curve di frazione solida calcolate mediante analisi Newtoniana)

of liquid 10% and mass fraction of liquid 1%. t_R is the time available for stress relief processes and is calculated as the time difference between mass fraction of liquid 60% and mass fraction of liquid 10%. In this work, the CSC was determined using fraction solid curves which have been calculated using data from cooling curve analysis.
Table 3 summarized terminal freezing range (TFR) and cracking susceptibility coefficient (CSC) values that have been calculated using data from fraction solid distribution curves of investigated alloys. From both results it is evident that Cu contents have significant impact on the hot tearing formation. Experimental evaluation of hot tearing tendency in aluminium alloys is very complex. With these two calculations it has been shown that cooling curve analysis has potential for quantifying vales of the terminal freezing range (TFR) and cracking susceptibility coefficient (CSC).

CONCLUSIONS

A comprehensive understanding of melt quality is of paramount importance for the control and prediction of actual casting characteristics. Thermal analysis is already used tool for melt quality control in aluminium casting plant. It has been used routinely for assessment the master alloys addition into aluminium melt. In addition, its application can be extended to quantify the total volume fraction of the Cu enriched phases in the Al-Si-Cu aluminium alloys.
Performed experiments indicated that the Cu enriched phases precipitate at different temperatures depending on the amount of Cu present in the particular Al-Si9-Cu(1-4) alloy. From the obtained results the nucleation temperature of the Cu enriched phases can be accurately read from the first derivatives of the cooling curves and used to define the maximum temperatures that the castings can be exposed to during the conventional solution treatment process. This will enable researchers to predict the mechanical properties of the castings and to design components according to predetermined specifications and requirements. To date, volume fraction assessment has only been possible through metallographic analysis.
Terminal freezing range (TFR) and cracking susceptibility coefficient (CSC) values were calculated using data from fraction solid distribution curves of investigated alloys. Both results have shown that Cu contents had significant impact on the hot tearing formation. With these two calculations it has been shown that cooling curve analysis has potential these criterions to quantify.
Future work should confirm that on-line quantitative control of the Cu enriched phases is possible by other series of Al-Si alloys using TA. The data collected using cooling curve analysis should be applied in existing simulation software in order to improve accuracy of simulation.

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Analisi del percorso di solidificazione delle leghe Al-Si9-Cu(1-4) mediante tecnica di analisi termica

Parole chiave: Alluminio e leghe - Solidificazione

Il presente lavoro mostra le potenzialità dell'analisi della curva di raffreddamento per caratterizzare il percorso di solidificazione delle leghe Al-Si9-Cu(1-4). Inoltre è stata investigata la possibilità di quantificare le fasi arricchite in Cu di queste leghe utilizzando la tecnica di analisi termica (TA). Il metodo proposto si basa sulla seguente procedura: una quantità totale della fase arricchita di Cu viene definita come il rapporto fra l'area, compresa tra la prima derivata della curva di raffreddamento e il percorso di solidificazione ipotetico dell' eutettico Al-Si-Cu, confrontata con l'area totale, compresa tra la derivata prima della curva di raffreddamento e la linea di base. Questi calcoli basati sull'analisi della curva di raffreddamento sono stati confrontati con l'Analisi dell'Immagine (IA) e con i risultati dell'analisi chimica, al fine di verificare il metodo proposto. Esiste una buona correlazione fra valori misurati e valori calcolati per l'area della fase arricchita di Cu delle leghe Al-Si9-Cu(1-4).