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QUANTIFICATION OF THE COPPER PHASE(S) IN Al-5Si-(1–4)Cu ALLOYS USING A COOLING CURVE ANALYSIS

UPORABA ANALIZE OHLAJEVALNE KRIVULJE ZA OCENO KOLIČINE BAKROVIH FAZ V ZLITINAH Al-5Si-(1-4)Cu

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The aim of this paper is to demonstrate that it is possible to characterize the development and quantify the area percentage of Cu-enriched phases in Al-5Si-(1-4)Cu alloys by applying a cooling-curve analysis. It is shown that several distinct Cu-enriched phases are manifested as peaks on the first derivative of the cooling curve. The total area percentage 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 the image-analysis and chemical-analysis results in order to verify the proposed method. There is a good correlation between the measured and calculated values for the area of the Cu-rich phase in Al-5Si-(1–4)Cu alloys.

Keywords: aluminum alloys, thermal analysis, cooling-curve analysis, image analysis

Namen tega članka je predstaviti možnost ocene nastanka in količinsko določiti področja s Cu bogatih faz v zlitinah Al-5Si-(1-4)Cu z analizo ohlajevalne krivulje. Pokazano je, da se več ločenih, s Cu bogatih faz kaže v obliki vrhov v prvem odvodu krivulje ohlajanja. Skupni delež območja s Cu bogatih faz je določen kot razmerje površin med prvim odvodom krivulje ohlajanja in hipotetične poti strjevanja Al-Si-Cu-evtektika ter celotno površino prvega odvoda krivulje ohlajanja in osnovno linijo. Izračuni, ki temeljijo na analizi ohlajevalnih krivulj, so bili primerjani z analizo slik in rezultati kemijske analize, da bi potrdili predlagano metodo. Obstaja dobra korelacija med izmerjenimi in izračunanimi vrednostmi področij s Cu bogatih faz v zlitini Al-5Si-(1–4)Cu.

Ključne besede: aluminijeve zlitine, termična analiza, analiza ohlajevalne krivulje, analiza slik

1 INTRODUCTION

The automotive industry makes frequent use of the Al-Si-Cu series of aluminum alloys. In order to ensure that cast components have good mechanical properties, their as-cast microstructures must be closely monitored. Two eutectic microconstituents are primarily responsible for defining the microstructures of Al-Si-Cu series alloys: Al-Si and Al-Cu. Both of these eutectics can be detected on a thermal-analysis (TA) cooling curve, or more precisely, on its first derivative. The solidification of Al-Si-Cu series alloys and the formation of Cu-enriched phases can be described, according to many authors, as follows:[1–4]

1. A primary α-aluminum dendritic network forms between 580–610 °C. The exact temperature depends mainly on the amounts of Si and Cu in an alloy. This leads to an increase in the concentration of Si and Cu in the remaining liquid.
2. Between 570–555 °C (the Al-Si eutectic temperature), a eutectic mixture of Si and α-Al forms, leading to a further localized increase in the Cu content of the remaining liquid.
3. At approximately 540 °C, Mg_2Si and $Al_8Mg_3FeSi_6$ phases begin to precipitate.
4. At approximately 525 °C, a "massive" or "blocky" Al_2Cu phase (containing approximately w = 40 % Cu) forms together with β-Al_5FeSi platelets.
5. At approximately 507 °C, a fine Al-Al_2Cu eutectic phase forms (containing mass fractions approximately 24 % Cu). If the melt contains more than 0.5 % Mg, an ultra-fine $Al_5Mg_8Cu_2Si_6$ eutectic phase also forms at this temperature. This phase grows from either of the two previously mentioned Al_2Cu phases.

A metallographic analysis of the TA test samples, presented in **Figure 1**, combined with an X-ray microanalysis has confirmed that Cu-enriched phases appear with three main morphologies: the blocky type, the eutectic type and the fine eutectic type.[3,5,6]

The Al-5Si-(1–4)Cu alloys are characterized by the presence of the two eutectics (Al-Si and Al-Si-Cu) that are primarily responsible for the mechanical properties of these alloys. Both eutectic temperatures can be detected on a TA cooling curve, or more precisely, on its first derivative. The eutectic-formation temperatures can

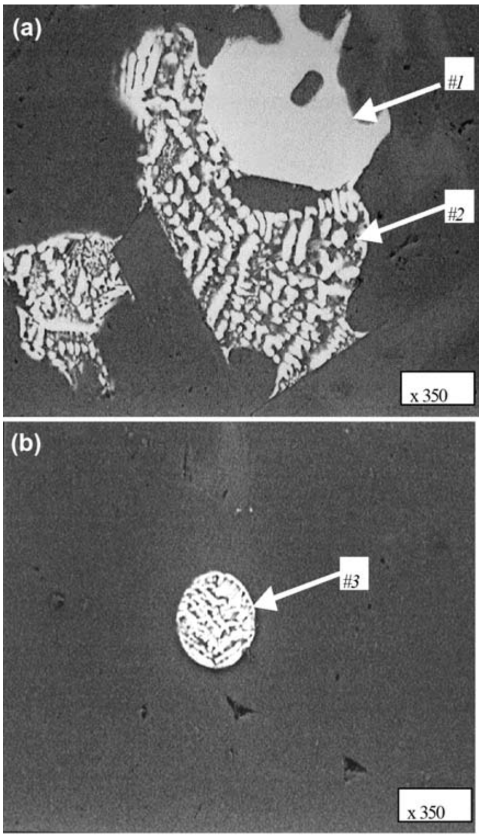

Figure 1: SEM micrographs (BSE images) with the characteristic morphologies of Cu-enriched phases found in the investigated alloys: a) the blocky (#1) and eutectic types (#2), b) the fine eutectic type (#3)[6]

Slika 1: SEM-posnetka (BSE-posnetka) z značilno morfologijo s Cu bogatih faz v preiskovih zlitinah: a) kockasta (#1), evtektik (#2), b) drobni evtektik (#3)[6]

help to define the maximum temperature, to which castings can be exposed during a solution treatment (i.e., by defining the temperature, at which incipient melting will take place). Unfortunately, the total amount of the Cu-enriched phases present in an as-cast part can, so far, only be measured using a metallographic analysis. This information is critical because these Cu-rich phases play a significant role in the heat-treatment process and can have a negative influence on the mechanical properties of the Al-5Si-(1–4)Cu alloys. The goal of this paper is to demonstrate that it is possible to quantify and characterize the development of the Cu-enriched phases in the Al-5Si-(1–4)Cu alloys using the TA system. This estimation is verified using quantitative metallography (an image analysis (IA)) and a chemical analysis (optical emission spectroscopy (OES)).

2 EXPERIMENTAL PROCEDURES

Three Al-Si-Cu alloys with the chemical compositions presented in **Table 1** were produced. Their chemical compositions were determined using the OES.

Liquid test samples with the masses of approximately 300 g were poured into thermal-analysis steel test cups. The weight of a steel test cup was 50 g. Two K-type thermocouples were inserted into the melt and the temperatures between 700–400 °C were recorded. The tip of a thermocouple was always kept at the constant height, 15 millimeters from the bottom of the crucible. The accuracy of a thermocouple was ± 0.5 °C. 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 the experiments and the cooling rate was approximately 6 K min^{-1}. The cooling rate was calculated as the ratio of the temperature difference between the liquidus and solidus temperatures to the total solidification time between these two temperatures. Each TA trial was repeated three times. Consequently, a total of nine samples were gathered. In all the cases, the masses of the thermal-analysis test samples were virtually identical.

The samples for the 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 with a scanning electron microscope (SEM) using the magnifications between 200-times and 5000-times. 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 500-times. Twenty-five analytical fields were measured for each sample and the final area fraction was expressed as the mean value.

3 RESULTS AND DISCUSSION

3.1 Thermal-analysis results

Three representative TA cooling curves obtained for the Al-5Si-1Cu, Al-5Si-2Cu and Al-5Si-4Cu alloys are presented in **Figure 2**. The cooling rate for all three curves was approximately 6 K min^{-1}. **Figure 3** shows that the increasing Cu amount of the melt lowers all the

Table 1: Chemical compositions (mass fractions, *w*/%) of the synthetic alloys
Tabela 1: Kemijska sestava (masni deleži, *w*/%) sintetičnih zlitin

Alloy	Si	Cu	Fe	Mg	Mn	Zn	Ni	Al
Al-5Si-1Cu	4.85	1.03	0.09	0.14	0.01	0.01	0.007	residual
Al-5Si-2Cu	5.01	2.06	0.10	0.26	0.01	0.01	0.007	residual
Al-5Si-4Cu	4.89	3.85	0.09	0.16	0.01	0.01	0.009	residual

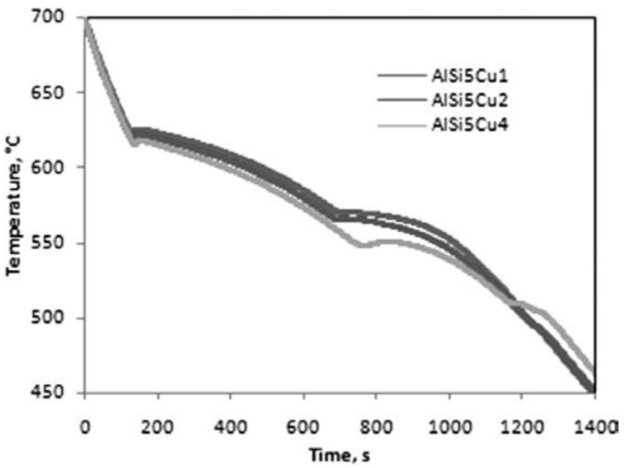

Figure 2: Cooling curves of the investigated Al-5Si-(1–4)Cu alloys
Slika 2: Ohlajevalne krivulje preiskovanih zlitin Al-5Si-(1-4)Cu

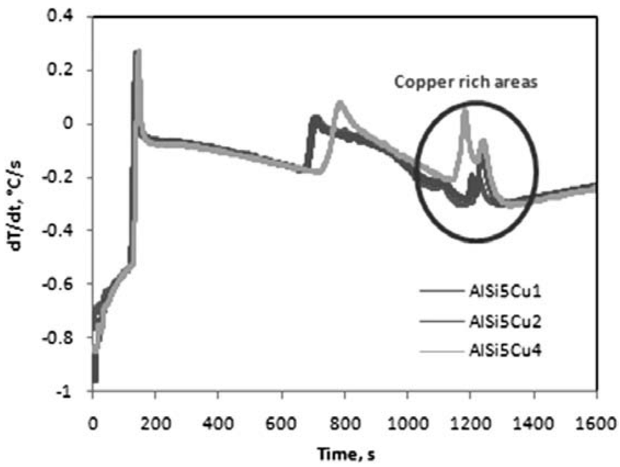

Figure 4: First derivatives of the Al-5Si-(1–4)Cu cooling curves
Slika 4: Prvi odvod ohlajevale krivulje zlitin Al-5Si-(1-4)Cu

characteristic solidification temperatures (T_{LIQ}, T_{COH}, T_{EUT}^{Al-Si} and $T_{EUT}^{Al-Si-Cu}$) except the solidus temperature that is almost constant for all the investigated alloys.

The first derivatives of the cooling curves are preented in **Figure 4**. It is apparent that the shapes of the first derivative curves strongly depend on the Cu amount in the melt. The Cu-rich area is particularly affected by different Cu amounts.

The numbers and shapes 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 5** that an increase in the Cu amount increases the solidification time of the Cu-rich eutectic phase. The precipitation temperature of the Cu-enriched phases decreases when Cu increases from mass fractions 1 % to 4 %. The Cu-enriched phase represented by the first peak on the cooling curve in **Figure 5** (5 % Si, 1 % Cu in the alloy) began to precipitate at 542.7 °C and the Cu-enriched phase represented by the second peak precipitated at 503.2 °C. For the alloy with 5 % Si and 2 % Cu, three peaks precipitated at various temperatures, (530.4, 505.4 and 498.1) °C, respectively. The increasing amount of Cu to 4 % (5 % Si) further changes the shapes of the Cu-enriched phase peaks (**Figure 5**). The precipitation temperatures were also altered. The Cu-enriched phase represented by the first peak of the Al-Si5-Cu4 alloy begins to precipitate at 514.4 °C, while the second peak appears at 507.2 °C. The increasing Cu amount from 1 % to 4 % slightly increased the total solidification time from 1167 s (for the Al-5Si-1Cu alloy) to 1211 seconds (for the Al-5Si-4Cu alloy), increasing also the total solidification temperature interval of the Cu-rich phase(s) from 31.4 °C (for the Al-5Si-1Cu alloy) to 65.4 °C (for the Al-5Si-4Cu alloy).

These results of the experiments (**Figures 2** to **5**) indicate that the Cu-enriched phases precipitate at different temperatures depending on the amount of Cu pre-

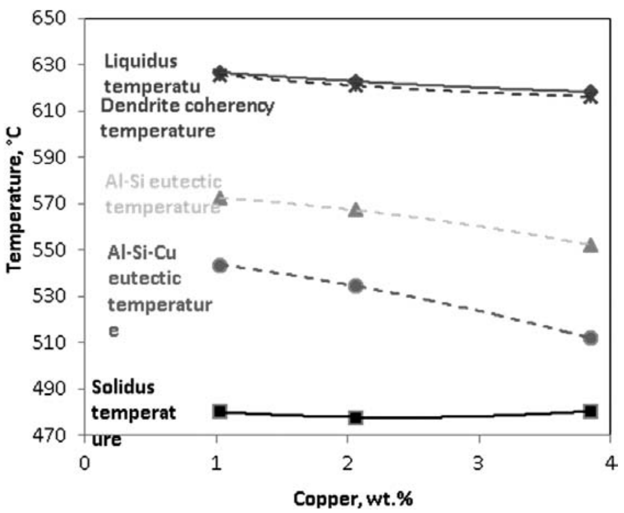

Figure 3: Impacts of different Cu amounts on the characteristic temperatures of Al-5Si-(1–4)Cu alloys
Slika 3: Vpliv različnih vsebnosti Cu na značilne temperature v zlitinah Al-5Si-(1-4)Cu

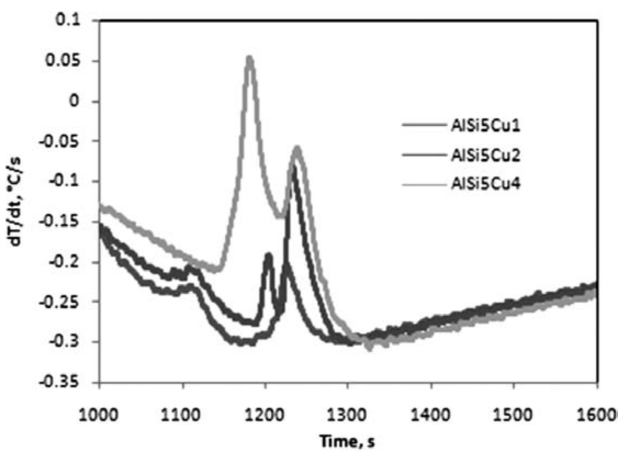

Figure 5: First derivatives of the Al-Si5-Cu(1–4) cooling curves related to the Cu-enriched region
Slika 5: Prvi odvod ohlajevalnih krivulj Al-5Si-Cu(1-4) glede na z bakrom bogato področje

sent in the particular Al-Si5-Cu(1-4) 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 the solution-treatment routines can be "tailored" to specific alloys and applications, it is also necessary that the volume fractions of the Cu-enriched phases are known. This data enables the researchers to predict the mechanical properties of the castings and design components according to the predetermined specifications and requirements. To date, a volume-fraction assessment has only been possible through a metallographic analysis.

3.2 Metallography, the cooling curve and image-analysis results

Light optical microscopy (LOM) observations combined with the IA showed that the area fractions of the Cu-enriched phases increased with additions of Cu. A Cu increase from 1 % to 4 % caused the area fraction of the Cu-enriched phases to increase from about 0.55 % to about 2.42 % (**Table 2**).

Table 2: Comparison of the Cu-enriched-phase area fractions detected by the IA system and determined with the TA
Tabela 2: Primerjava deleža področij s Cu bogatih faz, ugotovljenih z IA-sistemom in določenih s TA

Alloy	Area of Cu-rich phase, (TA) %	Area of Cu-rich phase, (IAS) %	*w*(Cu)/%
Al-5Si-1Cu	0.90	0.55	1.03
Al-5Si-2Cu	2.55	1.65	2.06
Al-5Si-4Cu	4.30	2.42	3.85

An additional SEM observation, combined with an X-ray spot microanalysis for the investigated alloy (Al-5Si-4Cu) was performed to identify the morphologies and stoichiometries of the observed Cu-enriched phases. This analysis confirmed the earlier assertion that Cu-enriched phases appear with three main morphologies: the blocky type, the eutectic type and the fine eutectic type (**Figure 6**). The quantitative X-ray microanalysis of the revealed stoichiometries of the Cu phases (**Table 2**) is presented in **Figure 6**.

It should be noted that a complete evaluation of the morphologies and the corresponding stoichiometries of the Cu-enriched phases is beyond the scope of the present paper. Quenching experiments will be necessary to establish the crystallization sequences of the Cu-enriched phases and the corresponding stoichiometries with respect to the TA results.

The imperfect agreement between these two measurements can be explained with two factors: First, the IA measurements do not take into account the small Si crystals that cannot be resolved with the LOM or the Si that is dissolved in the aluminum matrix. Second, because the cast samples are heterogeneous and due to the fact that only a finite number of regions were evaluated using the IA, these measurements may not be representative of all the test samples.

A determination of the total Cu-enriched-phase area fraction with 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 the casting quality in a foundry environment.

The TA approach developed by Kierkus and Sokolowski[5] was used in this work for determining the area fractions of individual phases that precipitate during

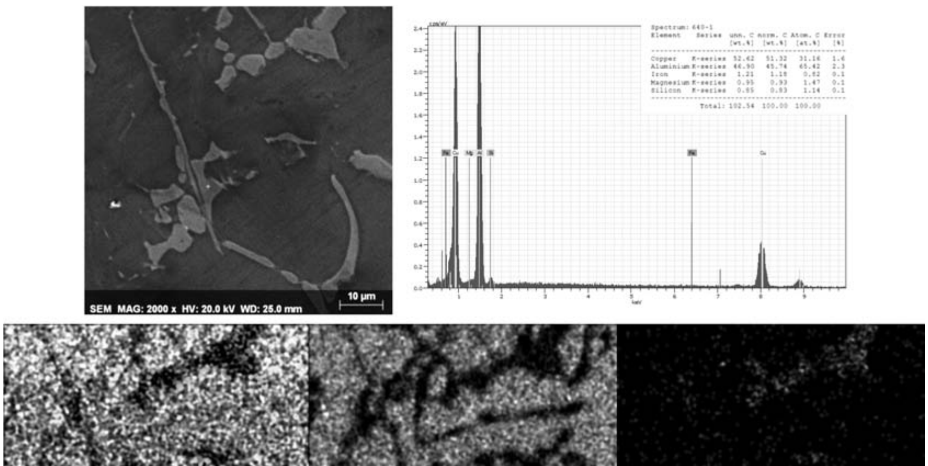

Figure 6: SEM micrographs of the characteristic morphologies of Cu-enriched phases and their EDX elemental maps
Slika 6: SEM-posnetki značilne morfologije s Cu bogatih faz in njihova elementna EDS-analiza

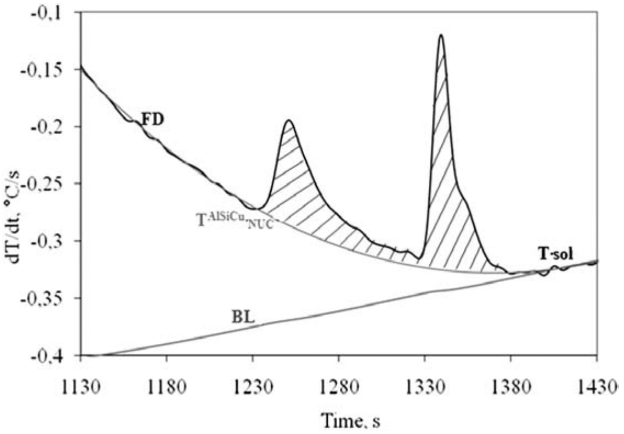

Figure 7: Part of the first-derivative curve (FD) related to the Cu-rich phase[5]
Slika 7: Del prvega odvoda krivulje (FD) glede na s Cu bogate faze[5]

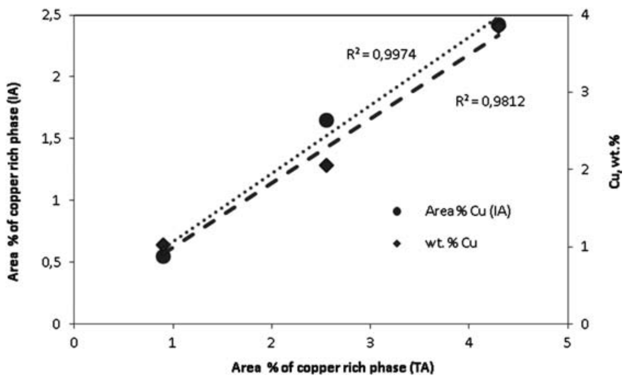

Figure 9: Relationship between IA and TA measurements and the chemical compositions of the investigated alloys
Slika 9: Odvisnost med IA- in TA-meritvami ter kemijsko sestavo preiskovanih zlitin

solidification of Al-Si-Cu alloys. In their work, the integrated area of the Cu-enriched phases is defined as the ratio of the area between the first derivative (FD) of the cooling curve and the hypothetical solidification path of the Al-Si-Cu eutectic (the hatched area in **Figure 7**) 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:[5]

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 the 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 7** and **8**, which present the FD of the cooling curve and the BL curve. The area between the two curves, from the liquidus state (T_{LIQ}) to the solidus state (T_{SOL}), is proportional to the latent heat of the solidification of the alloy. If the two aforementioned assumptions are correct,

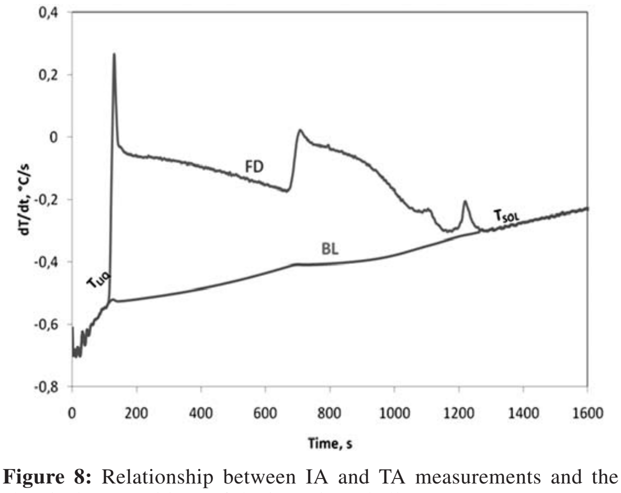

Figure 8: Relationship between IA and TA measurements and the chemical compositions of the investigated alloys
Slika 8: Odvisnost med IA- in TA-meritvami ter kemijsko sestavo preiskovanih zlitin

then the regression line between the arbitrarily selected state ($T_{NUC}^{Al-Si-Cu}$) and the solidus state (T_{SOL}) is a part of the solidification path of the Al-Si-Cu eutectic (the hatched area). Therefore, it is evident that the area between the path ($T_{NUC}^{Al-Si-Cu} - T_{SOL}$) and the FD of the cooling curve should be proportional to the latent heat of the solidification of the Cu-enriched phases. The proportionality is constant in both cases; the total latent heat of the alloy solidification and the latent heat of the solidification associated with the Cu-enriched phases are the "apparent specific heat" of the alloy.

A comparison of the total area fraction of the Cu-enriched phases determined using the IA with the integrated area (the hatched area in **Figure 7**) of the Cu-enriched phase of each alloy tested shows that the two measurements are almost perfectly correlated (**Figure 9**).

The imperfect agreement between these two measurements can be explained with two factors: First, the IA measurements do not take into account the small Si crystals that cannot be resolved with the LOM or the Si that is dissolved in the aluminum matrix. Only TEM investigations under a very high magnification would 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 all the samples.

The results of the Cu-enriched-phase determinations are presented in **Table 2** and in **Figure 9**. A high correlation observed on the regression plots (**Figure 9**) shows that it is possible to estimate the volume fraction of the Cu-enriched phases from the TA analysis experiments without resorting to the IA.

4 CONCLUSIONS

A comprehensive understanding of the melt quality is of a paramount importance for the control and prediction of actual casting characteristics. The thermal analysis is an already used tool for the melt-quality control in an aluminum casting plant. It has been used routinely for assessing the master-alloy additions to an aluminum melt. In addition, its application can be extended to quantify the total volume fraction of the Cu-enriched phases of the Al-Si-Cu aluminum alloys. Future work should confirm that an on-line quantitative control of the Cu-enriched phases is also possible for the other series of Al-Si alloys using TA.

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