ARCHIVES
of
FOUNDRY ENGINEERING
DOI: 10.1515/afe-2016-0093
Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences
DE GRUYTER OPEN
ISSN (2299-2944)
Volume 16
Issue 4/2016
109 – 112

The Study of Phase Transformations of AlSi9Cu3 Alloy by DSC Method

J. Piątkowski [a,*], **R. Przeliorz** [a], **A. Gontarczyk** [b]
[a] Silesian University of Technology, Faculty of Materials Science, Krasińskiego 8, 40-019 Katowice, Poland
[b] Magna Modern Production Technologies S.A., Szkolna 15, 47-225 Kędzierzyn-Koźle, Poland
*Corresponding author. E-mail address: jaroslaw.piatkowski@polsl.pl

Received 04.04.2016; accepted in revised form 06.05.2016

Abstract

With the use of differential scanning calorimetry (DSC), the characteristic temperatures and enthalpy of phase transformations were defined for commercial AlSi9Cu3 cast alloy (EN AC-46000) that is being used for example for pressurized castings for automotive industry. During the heating with the speed of 10^{o}C·min^{-1} two endothermic effects has been observed. The first appears at the temperature between 495 ^{o}C and 534 ^{o}C, and the other between 555 ^{o}C and 631 ^{o}C. With these reactions the phase transformation enthalpy comes up as +6 J g^{-1} and +327 J g^{-1}. During the cooling with the same speed, three endothermic reactions were observed at the temperatures between 584 ^{o}C and 471 ^{o}C. The total enthalpy of the transitions is – 348 J g^{-1}.
Complimentary to the calorimetric research, the structural tests (SEM and EDX) were conducted on light microscope Reichert and on scanning microscope Hitachi S-4200. As it comes out of that, there are dendrites in the structure of α(Al) solution, as well as the eutectic (β) silicon crystals, and two types of eutectic mixture: double eutectic α(Al)+β(Si) and compound eutectic α+Al_2Cu+β.

Keywords: Al-Si cast alloys, Differential scanning calorimetry (DSC), Thermal analysis (ATD), Phase transformations, Enthalpy

1. Introduction

The phase transitions decides about the primary structure and how the alloys are being worn off in the exploitation conditions. These phenomenon are being accompanied by thermal reactions, which may be measured with e.g.: thermo analysis (ATD) and differential scanning calorimetry (DSC) [1÷4]. With differential scanning calorimetry the heating power is being measured for the changes of thermo flow, between sample that is being tested and the reference one. During the defined process the heating effects are being defined for chemical reactions and phase transitions during the heating and cooling processes. The analysis of the phenomenon taking place during the solidification and the possibility of defining the crystallization heat of the structure components allows the prognosis of the final use properties and definition of the usability area for newly developed metallic alloys. Especially crucial is the evaluation of the thermo durability of the alloys, which, through the specific heat capacity, entropy, and enthalpy of the system allows the calculation of thermodynamic Gibs potential [5]. The consequence of knowing mentioned above properties is - between other - the ability to define the spontaneous phase transitions, that are the base of the technology used for production of the final product [6, 7].

2. Scope and purpose of research

The goal of the dissertation is the analysis of the phase transitions with the use of differential scanning calorimetry (DSC) with the use of high temperature calorimeter Multi HTC and thermo analysis ATD of AlSi9Cu3 alloy. The scope of the work includes, between other:

- calorimetric tests DSC,
- thermo analysis ATD,
- structural tests.

3. Material and research method

The AlSi9Cu3 alloy (EN AC-46000), used – between other – for pressure casts of combustion motor heads and other elements in machining industry, was chosen for the research. The chosen silumin was heated out of the EN AM-AlSi20 alloy (as per PN-EN 575) and pure Al (PN-EN 576) being steel industry molds and hardener AlCu50. The alloy was melted in a SiC crucible of $600cm^3$ capacity in the vacuum induction furnace VSG 02/631.

The modification as 0,05% wt was done with the AlSr10 hardener, and refining was implemented with Rafglin3 solution. The alloy was casted to the sampler ATD Heareus Elektro Nite of 200g mass, registering the ATD curve. Out of the place of temperature measurement the samples were cut for scanning calorimetry and structural tests. The research over the phase transitions with differential scanning calorimetry DSC were conducted in the argon atmosphere of 99,9999 purity, temperature range 20-800^{o}C. The temperature measurement was done with thermo element Pt-Rh10 Pt. As a reference substance, high purity Al_2O_3 was used. Since the range of transition temperatures of the alloy is 500 – 800^{o}C, the calibration was conducted with the use of high purity Al. The heating and cooling speed was $10^oC \cdot min^{-1}$. The calorimetric sample, of 110 mg was in a roll shape of 3 mm diameter. After degreasing in ethyl alcohol the sample was placed in Al_2O_3 crucible of $0,45cm^3$ capacity. The calorimetric tests stand is shown on Figure 1.

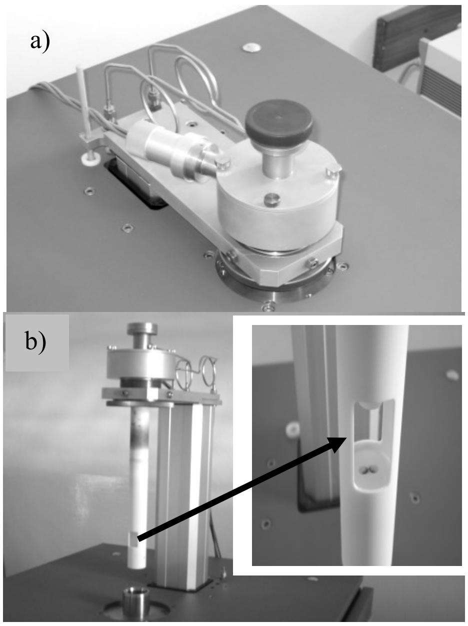

Fig. 1. High-temperature scanning calorimeter Multi HTC of Setaram: a) measurement head; b) calorimeter's crucible

The metallographic sections were done as per the standard procedure. The metallographic tests were conducted on light microscope MeF-2 Reichert. The quality phase analysis has been done on scanning microscope Hitachi S-4200, coupled with X-Ray spectrometer EDS Voyager of Noran.
The phase identification was implemented with the use of ICDD catalogue. The calibration of the calorimeter has been done with master sample Al (>99,998, $T_{top.}$=660,3^{o}C, ΔH= 401 J/g). The calibration conditions were the same as those during the experiment. The reversible transitions temperature was defined on the basis of DSC curve, being the result from heating and cooling process. The liquidus temperature was defined by local endothermic minimum of heating effect during the heating. The "onset" temperature was defined during the cooling process. This method is being used with DSC and ATD methods. The permanent eutectic temperature was defined as T_{onset} temperature.

4. Research results and analysis

The chemical content of the tested alloy, is shown in Table 1.

Table 1.
Chemical content of the AlSi9Cu3 alloy (EN AC-46000)

Alloy	Si	Cu	Mg	Ni	Cr	Mn	Fe	Al.
AlSi	10,16	3,18	0,32	0,09	0,11	0,31	0,51	rest

The DSC curves of AlSi9Cu3 alloy during the heating and cooling are shown on the Figures 2 and 3.

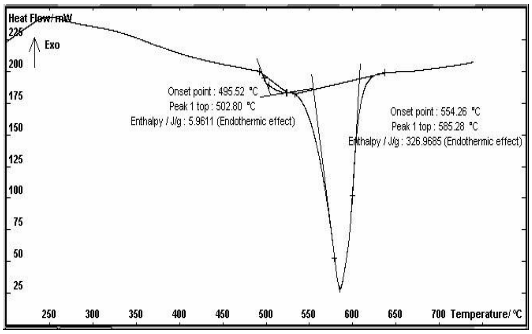

Fig. 2. The DSC curve of a heating process of AlSi9Cu3 alloy. Heating speed $10^oC \cdot min^{-1}$, atmosphere: argon

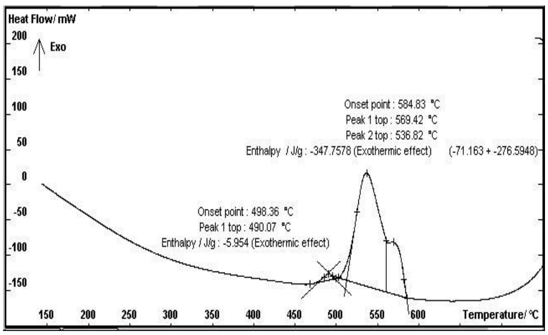

Fig. 3. The DSC curve after cooling process of AlSi9Cu3 alloy. Cooling speed $10^oC \cdot min^{-1}$, atmosphere: argon

On DSC curve during the heating, are two endothermic heating effects (Fig. 2.). First in the temperature range 495 – 525°C, and the second between 554 – 630°C. First heating effect is probably combined with melting of the β' (Al_2Cu) phase. The β' phase is a complex compound of the chemical content: α–Al_2Cu–β–$Al_5Cu_2Si_6$. The melting enthalpy is around +6 J g^{-1}.
Endothermic reaction in the temperature range 554 - 630°C is the result of the α–β eutectic: αAl–Si–Al_9Fe_2Si (β phase) melting [8]. The eutectic melting enthalpy is +327 J g^{-1}. The solidus temperature of AlSi9Cu3 alloy is T_{sol} = 495°C.
Three exothermic effects shows on DSC curve during the cooling (Fig.3). In the temperature of 585 °C (liquidus temperature) the α(Al) phase starts to sprout. The eutectic crystallization starts at 562 °C. The total heating effect of the exothermic α(Al) seeds sprouting and eutectic secretion is around –348 J g^{-1}. The third exothermic effect at temperature 498 °C corresponds with secretion of β' phase. Heat combined with β' compound secretion is around – 6 J g^{-1} and is equal to melting heat of this phase.

Complementing the phase transition tests with differential scanning calorimetry DSC were the ATD thermal analysis tests. Exemplary curve of modified with AlSr10 master alloy AlSi9Cu3 alloy solidification is shown on Figure 4.

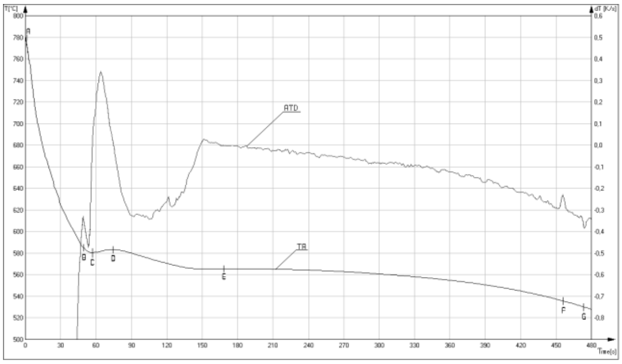

Fig. 4. TA and ATD thermo-analysis chart for AlSi9Cu3 alloy

The summary of the characteristic temperatures read out of the ATD chart is shown in Table 2.

Table 2.
Characteristic temperatures read out of the ATD diagram

Point	A	B	C	D	E	F	G
Temp.	T_{start}	$T_{p.liq.}$	$T_{liq.}$	$T_{k.liq.}$	T_E	$T_{E(Cu)}$	$T_{sol.}$
°C	760	585	580	584	562	536	529

where:
T_{start} – the temperature of registered solidification beginning, °C
$T_{p.liq.}$ – the temperature of α dendrites crystallization beginning, °C
$T_{liq.}$ – the temperature of α dendrites crystallization, °C
$T_{k.liq.}$ – the temperature of α dendrites crystallization end, °C
T_E – the temperature of α(Al)–β(Si) eutectic dendrites crystallization, °C
$T_{E(Cu)}$– the temperature of eutectic that includes AlCu crystallization, °C
$T_{p.liq.}$ – the temperature of alloy crystallization end, °C
As it comes of Table 2 and the calorimetric results (Fig 3 and 4), the phase transition temperatures are close one to other and are:
liquidus temperature 585°C (DSC) 585°C (ATD)
α–β eutectics temperature 554-630°C (DSC) 562°C (ATD)
α–AlCu–β eutectics temperature 495-525°C (DSC) 536°C (ATD)
solidus temperature 495°C (DSC) 529°C (ATD).

It should be noted, that the temperature differences in weight of the samples. The sample taken for calorimetric tests was of 110 mg, and the one for thermal analysis was 200g. Another difference comes from different cooling speed: 10°C·min^{-1} – for DSC and 1°C·min^{-1} – for ATD. The structural tests were the complementary ones to the calorimetric tests and thermo analysis. Exemplary microstructure of AlSi9Cu3 alloy, casted to the ATD mold is shown on Figure 5.

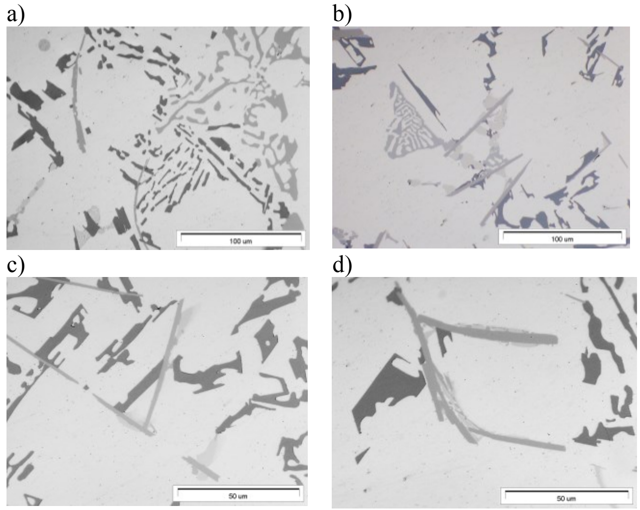

Fig. 5. The AlSi9Cu3 alloy microstructure:
a, b) magnification: 100 x; c, d) magnification 200 x

Since in both: calorimetric analysis DSC and thermal analysis ATD, the additional exothermic effect was observed at the end of crystallization of AlSi9Cu3 alloy for the crystallization of complex eutectic, that includes the intermetallic phase Al_xCu_y, the X-Ray phase analysis test was conducted. Exemplary diffraction pattern of the tested alloy is shown on Figure 6.

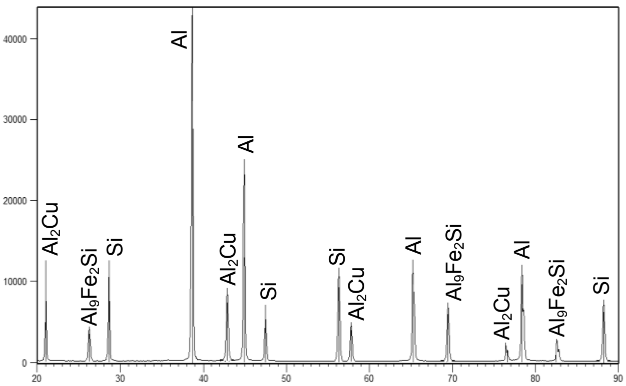

Fig. 6. Diffractograph of the AlSi9Cu3 alloy

The characteristic of network parameters of the components of AlSi9Cu3 alloy structure is shown in Table 3.

Table 3.
The result of network parameters of AlSi9Cu3 alloy calculation

Component	Spatial group	Network parameter, Å		% wt.
Al	F m – 3 m (225)	a0	4,050	58,4
Si	F d – 3 m (227)	a0	5,431	17,7
Al_2Cu	I 4/m c m (140)	a0	6,063	12,6
		c0	4,872	
Al_9Fe_2Si	R – 3 c (167)	a0	4,757	3,6
		c0	12,988	

The phase content research with XRD method, lead to repeated microstructure tests for AlSi9Cu3 alloy. Exemplary pictures of complex eutectics, that includes three phases Al_2Cu and Al_9Fe_2Si are shown on Figure 7. Identified intermetallic phases are compliant with triple balance system of phase equilibrium Al-Si-Cu, that is shown on Figure 8.

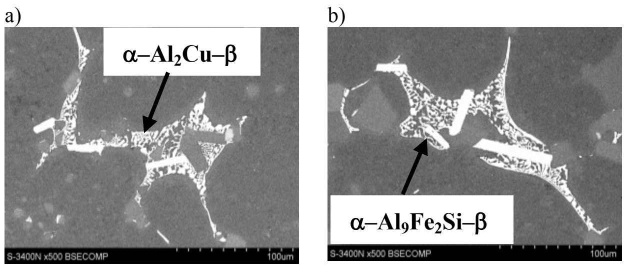

Fig. 7. Microstructure of AlSi9Cu3 alloy with visible eutectics secretions, that includes Al_2Cu and Al_9Fe_2Si phases

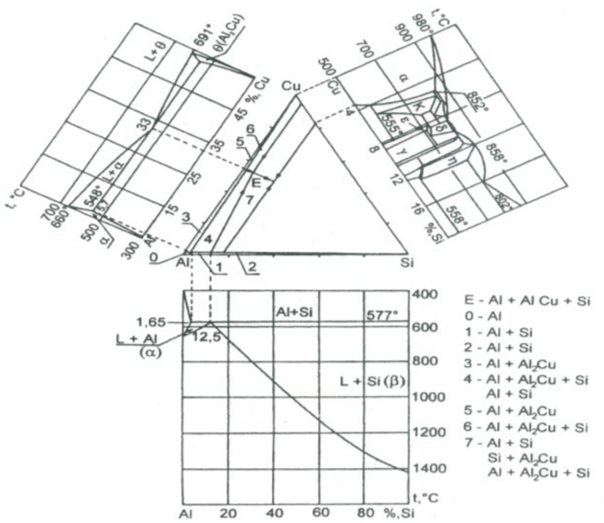

Fig. 8. Triple balance system of phase equilibrium Al-Si-Cu [9]

As it come from the microstructures of the tested alloy, that are shown on the Figure 5, the modification with AlSr10 mortar caused the change of the disadvantageous (irregular) eutectic of plate type, into the "ennobled" eutectic of fibrous structure. The modification causes also substantial fragmentation of the α(Al) solution dendrites.

5. Summary

Out of the conducted tests it comes, that in both methods, differential scanning calorimetry DSC and thermal analysis ATD the liquidus temperature T_{liq} is the same and equals to 585 °C. On the DSC curve, resulted from AlSi9Cu3 alloy heating, are two endothermic heat effects. Those are the result of melting of the complex β' phase and double eutectic α–β in the temperature range T_E = 554-630°C (for DSC) and 562 °C (for ATD). The solidus temperature T_{sil} = 495°C.

During the cooling, on DSC curve there are three exothermic effects. Additional heat reaction is combined with α(Al) solid solution secretion. The eutectics α–AlCu–β temperature is in the range 495-525°C (for DSC) and 536°C (for ATD). As it come from Table 2 and calorimetric results (Figures 3 and 4), the phase transitions temperatures are close one to the other, and the temperature differences may be coming from different mass of the samples and different cooling speed.

Both for heating and cooling the enthalpy combined with secretion of β' phase is +6 J g^{-1}. The enthalpy during the melting of double eutectic α–β is +327 J g^{-1}, and during the cooling the enthalpy comes to around –348 J g^{-1}.

With the use of XRD tests the eutectics consisting the intermetallic phases Al_2Cu and Al_9Fe_2Si were found (Figures 6 and 7), where the network parameters, as per the ICDD catalogue, are shown in Table 3.

References

[1] Piątkowski, J. & Gajdzik, B. (2013). Testing Phase Changes in Al-Si Cast Alloys with Application of Thermal Analysis and Differential Calorimetric Analysis. *Metalurgija. 52*, 469-472.

[2] Pezda, J. & Jarco, A. (2015). Influence of Natural Ageing on Impact Strength of the ENAC-AlSi9Cu3(Fe) Alloy. *Archives of Foundry Engineering*. 15(spec.1), 81-84.

[3] Piątkowski, J. & Formanek, B. (2011). Cast AlSi9Cu4 alloy with Hybride Strenghtened by Fe_xAl_y-Al_2O_3 Composite Powder. *Materials Science and Engineering*. 22. DOI: 012020.

[4] Heusler, L. & Schneider, W. (2001). Influence of Alloying Elements on the Thermal Analysis Results of Al-Si Cast Alloys. *Journal of Light Metals*. 2, 17-26.

[5] Kędzierski, Z. (1999). *Thermodynamics of Alloy*. Cracow: Publishing Science and Educational. (in Polish).

[6] Piątkowski, J. (2013). Physical and Chemical Phenomena Affecting Structure, Mechanical Properties and Technological Stability of Hypereutectic Al-Si Alloys After Overheating. Gliwice: Silesian University of Technology. (in Polish).

[7] Hatch, J.E. (1984). *Aluminum: Properties and Physical Metallurgy*. Ohio: American Society for Metals, Metals Park.

[8] Molina, R., Amalberto, P., Rosso, M. (2011). *Mechanical Characterization of Aluminum Alloys for High Temperature Applications*. Part1: Al-Si-Cu alloys, Metallurgical Science and Technology 29-1.

[9] Ashby, M., Jones, D. (1993). *Materials Engineering*. Warsaw: Publishing Science and Technical. (in Polish).