J. PIĄTKOWSKI, B. GAJDZIK

ISSN 0543-5846
METABK 52(4) 469-472 (2013)
UDC – UDK 65.012.2:669.013.5.004.8/65.01:669.013.5.009.04.502.5=111

TESTING PHASE CHANGES IN Al-Si ALLOYS WITH APPLICATION OF THERMAL ANALYSIS AND DIFFERENTIAL CALORIMETRIC ANALYSIS

Received – Prispjelo: 2012-11-05
Accepted – Prihvaćeno: 2013-03-30
Original Scientific Paper – Izvorni znanstveni rad

The paper presents enthalpy of melting and solidification of casting aluminium alloys AlSi6, AlSi12 and AlSi18 during heating and cooling. Calorimetric measurements preceded by tests of thermal analysis ATD were conducted on high-temperature scanning calorimeter multi HTC. A direct method was used for determining parameters of high-temperature processes and enthalpies occurring in phase changes. This method allowed for precise determining of endothermic and exothermic phase changes and, on their basis, the characteristic parameters of solidification necessary to assess the thermal endurance were marked.

Key words: Al-Si alloys, phase changes, thermal analysis, calorimetric analysis

INTRODUCTION

Phase changes influence the shaping of structure, physical and mechanical properties as well as behaviour of alloys in increased temperature. Such phenomena are accompanied by heat effects which may be measured with various methods: thermal analysis (automated *thermal desorption*) ATD, differential calorimetric analysis DSC thermo-gravimetric analysis TGA and thermo-mechanical analysis TMA [1]. In differential calorimetric scanning the heat power is measured of changes in the difference of heat flux which builds up between tested sample and reference sample during the given process. Thermal effects of chemical reactions are being marked together with effects of phase changes during processes of heating and cooling of clean substances and casting alloys. The explanation of phenomena which take place during solidification, particularly the possibility of determining the value of crystallization heat in each element of microstructure allows for predicting the final useful properties, especially of newly elaborated metal alloys. Knowledge about the thermal properties of solid bodies (proper thermal capacity, entropy and enthalpy of the system) enables the calculation of Gibbs thermodynamic potential and the thermal durability of metals and their alloys [2-6].

MATERIALS AND RESEARCH METHODOLOGY

The objects of research were characteristic alloys: AlSi6, AlSi12 and AlSi18 for creation of which the following elements were used: aluminium type AR1 (99,96 %Al) and silicon with purity of 98,8 % (the remaining parts were Fe and other elements). The melts were conducted in induction furnace Leybold-Heraeus IS5/III in crucible made of magnesite mix with capacity of 700 g under protection cover of NaF and KCl. After reaching the temperature of about 780 °C, the metal bath was refined with preparation Rafglin-3 in the amount of 0,3 % mas. and next it was modified with the use of strontium in the form of master alloy AlSr10 (for alloys AlSi6 and AlSi12) and alloy CuP10 (for silumin AlSi18). Temperature of casting was controlled by immersion in liquid bath of thermo-element NiCr-NiAl TP-202K-800-1. After waiting for about 10 minutes, silumins were poured into standard sampler ATD (Quick-Cup 4010), recording the course of solidification curve. Samples were taken from the achieved casts for chemical composition analysis, the results of which are presented in Table 1.

Characteristic values of crystallization temperature of solid solution α(Al), eutectic α(Al)+β(Si) and Si crystals were marked with the use of thermal analysis method. In order to perform it, the signals from thermo-element placed in the central part of sampler Quick-Cup were placed on microprocessor converter of analogue-

Table 1 **Chemical composition of Al-Si alloys /%mas.**

Content of alloy elements	Alloy		
	AlSi6	AlSi12	AlSi18
Si	5,87	11,67	17,66
Cu	0,002	0,005	0,003
Ni	0,003	0,008	0,001
Mg	0,001	0,002	0,001
Fe	0,161	0,472	0,638
Mn	0,028	0,042	0,088
Sn	0,003	0,003	0,001
Ti	0,002	0,004	0,001
Al	rest	rest	rest

J. Piątkowski, B. Gajdzik, The Silesian University of Technology, Faculty of Materials Science and Metallurgy, Katowice, Poland

digital MC201 type with the use of program Analdta the curves of: temperature in time function (TA) and its first derivative (DTA) were drawn.

Tests of phase changes were conducted with the use of differential scanning calorimetry DSC on high-temperature scanning calorimeter HTC in argon atmosphere N 50, in temperature range from 150 to 850 °C with fixed speed of heating and cooling 5 °C/min. Samples for calorimetric tests (with cylindrical shape ∅3×5 mm and mass of 95 mg) were placed in cavity of measuring head of calorimeter.

RESULTS OF TESTS AND THEIR ANALYSIS

Example graph of thermal analysis ATD of silumins AlSi6, after modification process are presented in Figure 1.

It can be read from the graphs of thermal analysis ATD for all experiments (both before and after the modification process) what characteristic solidification temperature values can be achieved. They are presented in Table 2.

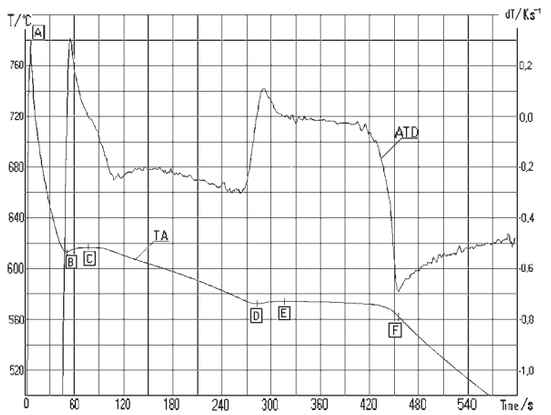

Figure 1 Thermal analysis of AlSi6m alloy after modification AlSr10 master

Table 2 **Results of thermal analysis of the Al-Si alloys /°C**

Alloy	Characteristic values of crystallization temperature					
	T_p	$T_{liq.min}$	$T_{liq.}$	$T_{E.min}$	T_E	$T_{sol.}$
AlSi6	775	620	622	572	573	562
AlSi6m	778	613	616	572	574	563
AlSi12	777	lack	lack	560	561	551
AlSi12m	775	lack	lack	558	564	555
AlSi18	772	681*	684**	561	565	541
AlSi18m	778	708*	709**	557	560	539

where: T_p – temperature of the beginning of registration of solidification process, $T_{liq.min}$–liquidus temperature – beginning of dendrites crystallization in solution α(Al), T_{liq}–liquidus temperature–crystallization of dendrites in α(Al), $T_{E.min}$–temperature of beginning of eutectic crystallization α+β, T_E–temperature eutectic crystallization α+β, $T_{sol.}$– solidus temperature, the end of crystallization, m – alloy after modification, * – temperature of crystallization beginning of primary crystals of silicon, ** – temperature of crystallization primary crystals of silicon.

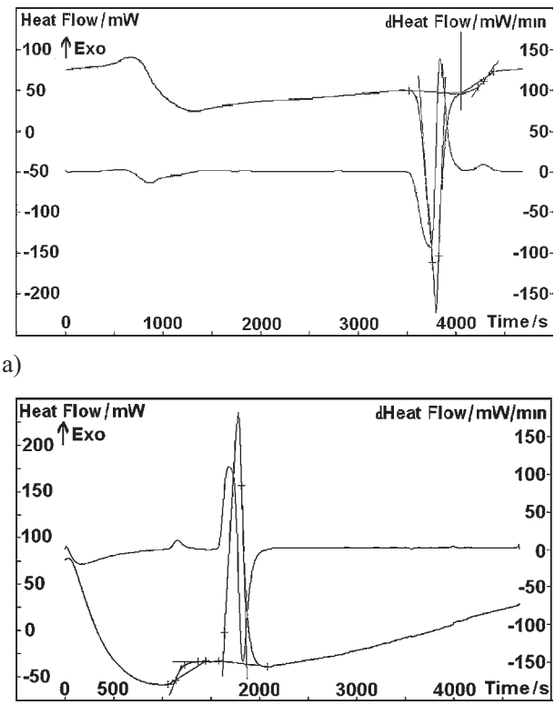

Figure 2 DSC diagram of AlSi18m alloy during: a) heating, b) cooling

On the basis of SetSoft program, DSC curves were drawn in coordinate system of heat flux and temperature in time function. Example DSC curves for AlSi18 alloy during heating and cooling are presented in Figure 2.

Because of the fact that the silumin structure before modification is very non-uniform the DSC curves were marked for tested alloys only after modification process. On such basis the characteristic values of temperature and enthalpy were marked for phase changes during heating and cooling of tested silumins. The results are presented in Table 3.

For alloy AlSi6 the graph DSC shows the registered two endothermic effects during melting and solidification. First endothermic effect comes from melting the eutectic (α+β→L) in temperature of about 574 °C. Next, there is annealing of silicon which ends in temperature of 586 °C. Next, the graph DSC shows second endothermic effect caused by melting of dendrites of solutionα, in temperature range from 611 °C to 634 °C. Total melting heat of silumin AlSi6 equals ΔH=375,2 J/g (176,1 J/g for eutectic and 199,1 J/g for Al).

During cooling, the first exothermic effect appears and is connected with aluminium dendrites solidification in temperature range from 619 °C to 611 °C. Second exothermic effect connected with eutectic solidification occurs in temperature range from 569 °C to 559 °C. Total value of solidification enthalpy for this alloy equals ΔH=-373,6 J/g (-234,3 for α and -139,3 J/g for eutectic

Table 3 **Temperature and enthalpy of phase transformations during heating and cooling alloys**

Alloy	Parameter	Melting			
		Dendrites	Eutectic	Silicon	Sum
AlSi6	T_p, /°C	611	575	–	–
	T_k, /°C	635	586	–	–
	ΔH, /J/g	199,1	176,1	–	375,2
AlSi12	T_p, /°C	–	578	–	–
	T_k, /°C	–	601	–	–
	ΔH, /J/g	–	468,2	–	468,2
AlSi18	T_p, /°C	–	578,3	645,9	–
	T_k, /°C	–	605,5	674,7	–
	ΔH, /J/g	–	443,4	9,6	453,1
		Solidification			
AlSi6	T_p, /°C	619	569	–	–
	T_k, /°C	611	559	–	–
	ΔH, /J/g	-234,3	-139,3	–	-373,6
AlSi12	T_p, /°C	–	562	–	–
	T_k, /°C	–	544	–	–
	ΔH, /J/g	–	-464,2	–	-464,2
AlSi18	T_p, /°C	–	565,0	657,4	–
	T_k, /°C	–	536,5	638,65	–
	ΔH, /J/g	–	-423,0	-18,6	-441,7

where: T_p – temperature of transformation beginning (onset point), °C; T_k – temperature of transformation end (peak 1 top), °C; ΔH – change of phase transformation enthalpy, J/g.

(α+β). For alloy AlSi12 the DSC graph shows one endothermic effect during heating and cooling. Melting the eutectic in this alloy occurs in temperature range from 578 °C to 601 °C, with enthalpy value of ΔH=468,2 J/g. Solidification of eutectic occurs in temperature range from 562 °C to 544 °C with enthalpy value of ΔH=-464,2 J/g. For hypereutectic silumin AlSi18 on DSC curves during heating two endothermic effects occur during melting and solidification. First endothermic effect comes from melting the eutectic (α+ß→L) in temperature range from about 578 °C to 605 °C. Next the second endothermic effect is observed, one connected with nucleation and growth of big, primary silicon crystals. It happens in temperature range from 646 °C to 675 °C. During heating, the total value of melting enthalpy for this silumin equals ΔH=453 J/g (443,4 J/g from crystallization of eutectic mixture and 9,6 J/g – from crystallisation of primary divisions of Si). During cooling of silumin AlSi18 there are also two exothermic effects observed. First is connected with crystallization of primary silicon divisions in temperature range from 657 to about 639 °C. Second effect refers to solidification of eutectic Al+Si which crystallises in temperature from 565 to 536 °C. Total value of solidification enthalpy for AlSi18 alloy ΔH=-441,7 J/g (-423 J/g from crystallization of eutectic mixture and -18,7 J/g from crystallization of primary divisions of Si). On the basis of calorimetric tests (Table 3), a phase composition of tested alloys was calculated. On DSC curves of alloy AlSi12 no thermal effects were found

Table 4 **List of results phase composition of the Al-Si alloys**

Phase contribution	Phase composition of silumins, / %		
	AlSi6	AlSi12	AlSi18
Phase α	62,4	5,7	lack
Eutectic	37,6	94,3	94,6
Phase β	lack	lack	5,4

from melting to solidification of phase α dendrites. Assuming that the total enthalpy of melting is marked for alloy AlSi12 and is the enthalpy of melting the eutectic (which equals 468,2 J/g), the contribution of eutectic in alloys AlSi6 and AlSi18 was calculated together with reference of such data to silumin AlSi12. Compilation of calculations for structure elements on the basis of results achieved during calorimetric analysis of tested silumins is presented in Table 4.

CONCLUSIONS

Crystallization of hypoeutectic AlSi6 alloy begins in liquidus temperature (T_{liq}=622 °C) after reaching the lowest temperature from nucleation to growth of dendrites of phase α. Crystallization is preceded by several degree value of overcooling ($T_{Lmin.}$=620 °C). Process of dendrites crystallization in aluminium lasts to the lowest temperature T_{Emin} (temperature of crystallization beginning of eutectic α+β). In temperature of 573 °C, as a result of solution treatment of the remaining liquid with silicon, the crystallization of eutectic mixture Al+Si begins. Crystallization of AlSi6 alloy ends in temperature T_{sol}=562 °C, which is equal to solidus temperature. Modification with the use of AlSr10 master alloy each time causes decrease in temperature value T_{liq}. As it is presented in literature [7, 8] an addition of Sr causes significant decrease of the value of this temperature even up to 20 °C. According to data presented in Table 2 the decrease is not as significant and liquidus temperature of silumin AlSi6 after modification equals 616 °C. Further course of the crystallisation process is similar to the one for alloy without modification. Crystallization of AlSi12 alloy has a slightly different course. After overcooling to the lowest temperature T_{Emin} which equals around 558 °C, nucleation and growth of Al dendrites begins. The liquid supersaturates with silicon which during crystallisation builds the basis for heterogeneous nucleation of phaseα. Value of temperature for eutectic crystallisation α(Al)+β(Si) with maintenance of slight degree of overcooling, is similar for all the experiments and equals about 564 °C. It is lower that the equilibrium temperature of eutectic crystallization (577 °C) by a few degrees which is caused by solidification in real conditions. Crystallization of silumin AlSi12 ends in temperature $T_{sol.}$ which equals 551 °C. Crystallization of hypereutectic silumin proceeds in a slightly different way. Maximum heat effect registered in temperature T_{liq} which equalled 684 °C is caused by crystallization of big primary divisions of silicon. Nucleation

and growth of those crystals begins after maximum overcooling of liquid to temperature $T_{liq.min}$ which equals 681 °C. As it results from DSC curves and conducted analysis of scanning calorimetry, the values of change enthalpy undergo changes together with the increase of percentage content of silicon. It is caused by the decrease of eutectic phase participation in favour of silicon phase.

Total, absolute value of solidification enthalpy (dendrites α+eutectic) is slightly lower than the enthalpy of melting. It is in accordance with thermodynamics rules [9, 10] and could also be caused by overlap of heat effects of dendrites melting in alloy AlSi12. Taking into consideration that the silicon content in this alloy equals 11,67 % (Table 1) it is still a slightly hypoeutectic alloy so dendrites of aluminium should be present in it. Perhaps due to their small amount the heat effect was not registered. It could also be caused by silicon segregation in mother mould (ATD tester) from where the sample was taken to test with calorimetric analysis method. The last one seems highly probable and that is why DSC curves were marked only for silumins after modification process. The analysis done by melting is more reliable because of big influence of cooling on solidification.

For alloy AlSi18 by melting the eutectic the enthalpy equals 443,44 J/g, and the heat of melting silicon is 9,67 J/g. During solidification those values are different and equal respectively for crystallization of Si -18,68 J/g and for crystallization of eutectic -423,01 J/g. It can be explained by different solidification speed of samples from thermal analysis and calorimetric analysis. During calorimetric tests the solidification of the sample occurs with constant, relatively small decrease of temperature (5 °C/min). Moreover the sample used for tests is small which makes the conditions more equivalent so during solidification more hypereutectic silicon solidifies than eutectic silicon. Moreover, it should be assumed that calculation results based on marked enthalpy values are more precise and sure because the sample for calorimetric tests was taken from the middle area of ATD tester. Small intensity of cooling of casting in crust form can be the reason of silicon segregation as a result of lack of its solubility in Al [11]. This can therefore signify that the sample for calorimetric tests could have been taken from cast area with slightly bigger silicon content than the chemical composition analysis of the whole cast has shown.

REFERENCES

[1] Górny Z., Sobczak J.: Non-ferrous metals based novel materials in foundry practice. ZA-PIS, Cracov 2005, p. 185-219.
[2] Moraczewski A. G.: Thermodynamics of liquid metals and salts. WNT, Warsaw 1993, p. 28-45.
[3] Guy A. G.: Introduction to materials science. PWN, Warsaw 1977, p. 18-51.
[4] Feest E. A., Tweed J. H.: Comparative viability of processing routes for intermetallic based materials. Mater. Science and Technology 8, (1992)4, 308-316.
[5] Naka S., Thomas M., Khan T.: Potential and prospects of some intermetallic compounds for structural applications. Mater. Science and Technology 8(1992) 4, 291-298.
[6] Nowacki K.: Possibility of Determining Steel Grain Size Using Ultrasonic Waves, Metalurgija, 48(2009) 4, 113-115.
[7] Pietrowski St.: Silumins. University of Technology, Łódź 2001, p. 38-150.
[8] Fraś E.: Crystallization of metals. WNT, Warsaw 2003, p. 446-460.
[9] Kędzierski Z.: Thermodynamics of alloys WND, Cracov 1999, p. 11-64.
[10] Balakin Yu., A., Gladkov M. I.: Thermodynamic analysis of high-temperature treatment of metallic melts: Part II. Theory of Metallurgical Processes 8, (2008), 730-733.
[11] Piątkowski J., Gajdzik B., Matuła T.: Crystallization and structure of cast A390.0 alloy with melt overheating temperature. Metalurgija 51(2012) 3, 321-324.

Note: The responsible translator for English language is D. Grachal, Katowice, Poland