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Application of calorimetry in evaluation of phase transformations in the selected hypoeutectic silumins

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Abstract
The investigations of phase transformations described in this study were carried out on hypoeutectic alloys from the Al-Si during heating and cooling. The determination and analysis of characteristic temperature values from the solidification range was made by the DSC method in calorimetric investigations carried out on a high-temperature multi HTC Setaram scanning calorimeter. Applying the lever rule, the phase composition of the examined slumins was calculated and compared with the results of DSC calorimetry.

Keywords: Calorimetric analysis, Enthalpy of melting and solidification, Hypoeutectic silumins

1. Introduction

Phase transformations are combined with thermal effects which can be measured by various methods of thermal analysis, e.g. differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) [1]. The calorimetric method measures the thermal power of changes in the difference of heat flux formed between the examined sample and reference sample using a computer program. The thermal effects of chemical reactions, phase transformations, processes of dissolution and heating of pure substances and cast alloys used for various applications are also determined.

Moreover, an additional thermal effect, related most probably with pre-eutectic crystallization of primary silicon, was observed and confirmed by calorimetric examinations [2] and mechanical properties [3] casting alloys.

2. Methods of investigation

For investigations, the silumins from AlSi3, AlSi6 and AlSi9 family modified with AlSr10 were selected. The above mentioned alloys were fabricated from aluminium, grade AR1 (99,96% Al) and silicon of 98,5% purity (the rest was Fe and other alloying elements). Alloys were melted in induction furnace, model IS5/III, made by Leybold-Heraeus, in a 0,7kg capacity crucible made of magnesite composition under the protective cover of 2NaF and KCl. Upon reaching the furnace temperature of ~ 820^{o}C, the melt was subjected to a refining treatment with Rafglin-3, added in an amount of 0,3 wt.% and to modification with AlSr (~10 % Sr). The temperature of pouring was controlled by a NiCr-NiAl TP-202K-800-1 thermocouple immersed in liquid melt. From the ready castings, samples were taken for analysis of the chemical composition. An additional advantage was development of appropriate software called „SETSOFT", owing

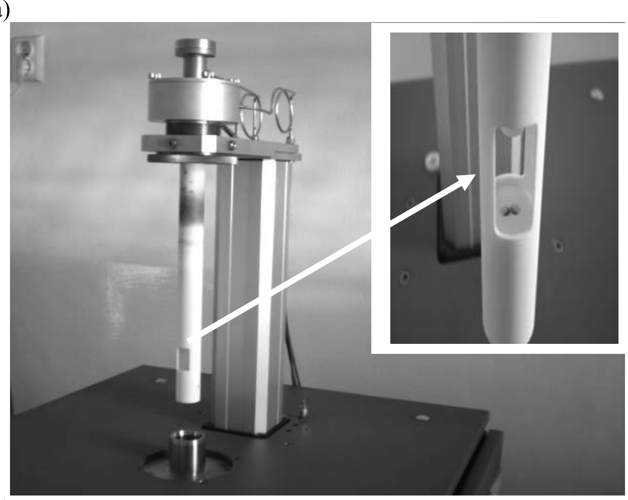
to which it was possible to determine in an easy way the enthalpy of the investigated phase transformations.
The results of the analysis are given in Table 1.

Table 1.
Analysis of chemical composition of the examined silumins

Sample	Al	Si	Cu	Ni	Mg	Fe	Ti
AlSi3	93,850	3,205	0,142	0,004	0,013	0,236	0,004
AlSi6	90,236	6,871	0,114	0,005	0,010	0,373	0,006
AlSi9	89,104	10,02	0,026	0,103	0,011	0,711	0,007

Phase transformations were examined by a scanning Multi HTCS60 calorimeter under the protective atmosphere of argon, applying the heating and cooling rate of 10ºC/min. The ∅3×5mm specimens had a cylindrical shape and the same weight of 94 mg each. The crucible of the calorimeter and a view of the Setsoft program are depicted in Figure. 1.

a)



b)

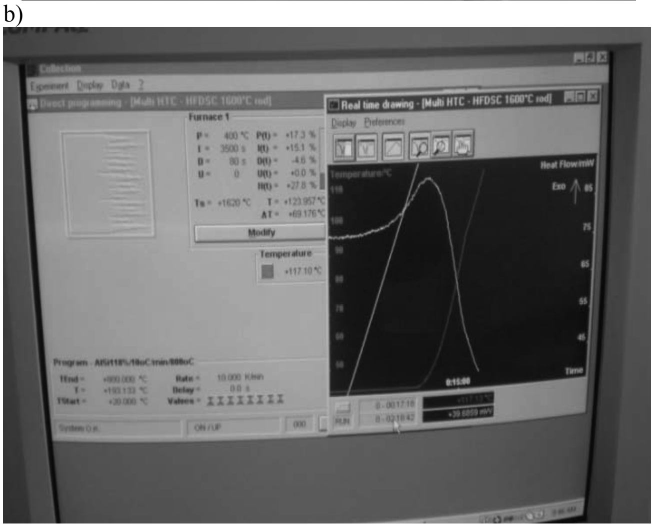
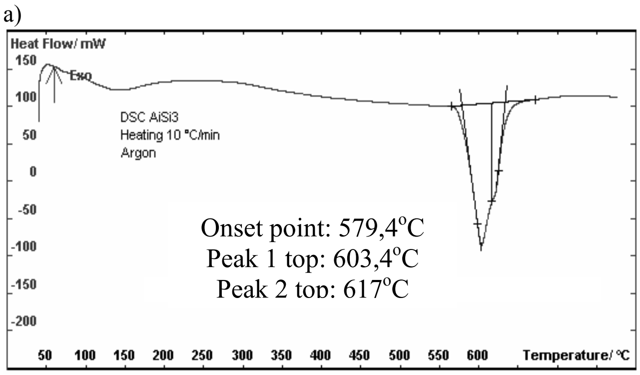


Fig. 1. A multi HTCS calorimeter: a) a view of crucible, b) Setsoft program

3. The results of investigation and their analysis

Figure 2 shows diagram plotted from the results of DSC calorimetry for AlSi3 silumin during heating and cooling.

a)



b)

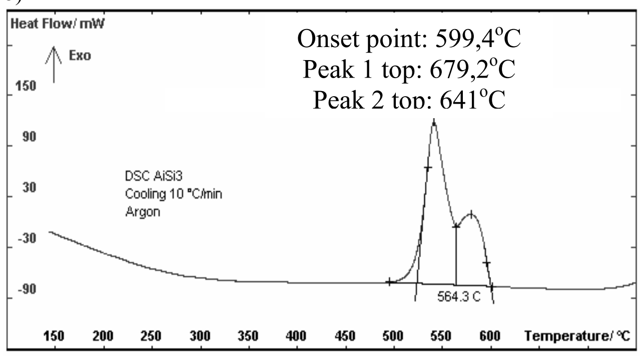


Fig. 2. DSC diagram for AlSi3 silumin during a) heating; b) cooling

From the plotted diagrams and using the SetSoft program, which configures the DSC diagrams in a heat flux - temperature system in function of time, the characteristic values of temperature and enthalpy of phase transformations during heating and cooling of the examined hypereutectic silumins were determined. The results of these computations are shown in Table 2 and Table 3.

Table 2.
Temperature and enthalpy of transformations during heating

Alloy	Value	Melting	
		Eutectic	Dendrites Al
AlSi3	T_p, ºC	579,36	612,01
	T_k, ºC	603,39	616,99
	E, J/g	+119,60	+108,51
AlSi6	T_p, ºC	575,83	611,34
	T_k, ºC	586,68	635,82
	E, J/g	+176,19	+199,10
AlSi9	T_p, ºC	579,26	*
	T_k, ºC	601,58	
	E, J/g	+408,21	

• - two thermal effects that overlap

Table 3.
Temperature and enthalpy of transformations during cooling

Alloy	Value	Solidification	
		Dendrites Al	Eutectic
AlSi3	T_p, ºC	599,38	564,31
	T_k, ºC	579,23	540,93
	E, J/g	-132,82	-106,69
AlSi6	T_p, ºC	579,71	564,64
	T_k, ºC	565,13	636,17
	E, J/g	-234,31	-139,30
AlSi9	T_p, ºC	636,59	564,60
	T_k, ºC	618,01	535,20
	E, J/g	-78,43	-491,12

where: T_p – temperature of the beginning of solidification, T_k - temperature of the end of solidification, E – the value of enthalpy.

From the phase equilibrium diagram of Al-Si system [4], the phase constitution of the examined alloys was determined, i.e. the fraction of eutectic and dendrites aluminum. At the first stage of investigations, the phase constitution of the examined silumins was calculated from the content of aluminum and using a „lever-arm principle" [5], that given in Table 4.

Table 4.
Calculated phase constitution of the examined silumins

Alloy / Fraction of structural constituen	AlSi3	AlSi6	AlSi9
Eutectic	14,3	47,7	76,4
Dendrites aluminum	85,7	52,3	23,6
Total:	100	100	100

Silumins AlSi3; AlSi6 and AlSi9 modified by AlSr10 showed at Fig. 3.

4. Summary

As follows from the plotted diagrams and analysis of the scanning calorimetry, the values of the enthalpies of transformations change with increasing percent content of aluminum. This is caused by the fraction of eutectic phase reduced in favor of the aluminum dendrites phase.

The DSC curve for AlSi3 alloy (Fig. 1) shows two endothermic effects that occur during melting and two exothermic effects that occur during the solidification of silumin. The first endothermic effect takes place at 579°C, which is the temperature when the eutectic starts melting. During this period, the process of silicon dissolution in molten alloy begins to end at a temperature of about 603°C. Immediately after this point, the second endothermic effect appears on the DSC curve. It is caused by melting of α dendrites within the temperature range of 612°C to 617°C. The total heat of the AlSi3 silumin melting is ΔH = + 228,1 J/g. The melting heat of a eutectic (α+β) mixture is 119,6 J/g, while the melting heat of aluminium dendrites is equal to 108,5 J/g. On cooling, the first exothermic effect, related with the solidification of aluminium dendrites, occurs within the temperature range of 599°C to 579°C. The second exothermic effect, related with the solidification of (α+β) eutectic, occurs within the temperature range of 564°C to 541°C. The total value of the solidification enthalpy for this alloy is ΔH = - 239,5 J/g. The heat of the solidification of aluminium dendrites is - 132,8 J/g, and the heat of eutectic solidification equals - 106,6 J/g.

a)
b)
c)

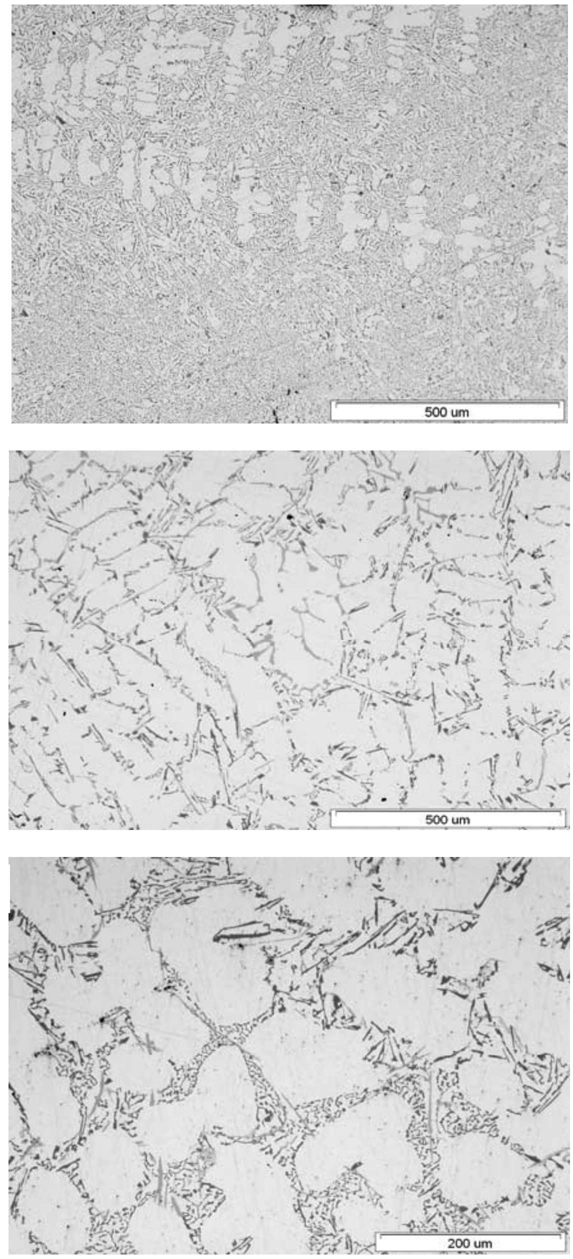


Fig. 3. Microstructure after modified AlSr10 alloy: a) AlSi3 silumin; b) AlSi6 and c) AlSi9 silumin

On the DSC curve plotted for AlSi6 alloy during heating, shows two endothermic effects related with heat absorption is observed. The first endothermic effect takes place at 575°C, which is the

temperature when the eutectic starts melting. During this period, the process of silicon dissolution in molten alloy begins to end at a temperature of about 586°C. Immediately after this point, the second endothermic effect appears on the DSC curve. It is caused by melting of α dendrites within the temperature range of 611°C to 635°C. The total heat of the AlSi6 silumin melting is ΔH = + 375,3 J/g. The melting heat of a eutectic (α+β) mixture is 176,2 J/g, while the melting heat of aluminium dendrites is equal to 199,1 J/g. On cooling, the first exothermic effect, related with the solidification of aluminium dendrites, occurs within the temperature range of 579°C to 565°C. The second exothermic effect, related with the solidification of (α+β) eutectic, occurs within the temperature range of 564°C to 636°C. The total value of the solidification enthalpy for this alloy is ΔH = - 373,6 J/g. The heat of the solidification of aluminium dendrites is - 234,3 J/g, and the heat of eutectic solidification equals - 139,3 J/g.
The DSC curve of AlSi9 alloy reveals on heating the presence of one endothermic effect. In this case, melting of eutectic takes place within the temperature range of 579°C to 601°C, and the value of the melting enthalpy is ΔH = +408,2 J/g. On cooling, the solidification of α dendrites occurs within the temperature range of 637°C to 618°C, while the solidification of eutectic takes place within the temperature range of 564°C to 535°C, with the total value of enthalpy ΔH = -569,5 J/g. The heat of solidfication of α dendrites is equal to - 78,4 J/g, while the heat of eutectic solidification is - 491,1 J/g. Analysing the values of enthalpy for the three examined silumins during heating and cooling view, that values are similar. This results are given in Table 5.

Table 5.
Analysis the values of enthalpy of the examined silumins

Alloy	AlSi3	AlSi6	AlSi9
Enthalpy during heating, J/g	+228,1	+375,3	+468,2
Enthalpy during cooling, J/g	-239,5	-373,6	-569,5
Difference, J/g	-11,4	+1,7	-101,3

As follows from Table 5, the values of enthalpy for examined silumines are similar. For AlSi9 alloy difference is large, because that there are two thermal effects that overlap. The endothermic effect related with melting of aluminium dendrites is so „small" that, the heat of eutectic melting „covers" the effect related with dendrites aluminium melting.
Using the results published in a master's thesis [4], where the solidification heat of the crystallizing eutectic, amounting to +468,2 J/g, was determined, the fraction of eutectic in the examined silumins was calculated from the following formula:

$$\begin{array}{c} 468{,}2\ \text{J/g} - 100\%\ \text{eutectic} \\ 119{,}6\ \text{J/g} - X\%\ \text{eutectic} \end{array} \qquad (1)$$

As follows from relationship (1) 25,5% of eutectic and 74,5% dendrites of the phase α. The results on examined silumines are compiled in Table 6 and compared with calculations based on the eutectic content, using a „lever-arm principle".
Analysing the values of enthalpy for the three examined silumins during heating one can observe that they have an increasing tendency and are directly proportional to the increasing percent content of silicon, which means that the more of silicon is present, the more of heat is absorbed. As regards the value of enthalpy on cooling, a similar tendency is observed, that is, the percent increase of silicon content is accompanied by the increase of enthalpy and of the related amount of absorbed heat.

Table 6.
A compilation of the results of calculations of the eutectic and dendrite aluminum constitution as obtained by calorimetric examinations and the lever-arm principle for example alloys

Alloys	AlSi3		AlSi6		AlSi9	
Fraction	Obl.	DSC	Obl.	DSC	Obl.	DSC
Dendrites,%	85,7	74,5	52,3	62,4	23,6	12,9
Eutectic,%	14,3	25,5	47,7	37,6	76,4	87,1

where: Calc. – values calculated by the lever-arm principle, DSC – values read out from calorimeter.

Basing on the phase equilibrium diagram, the phase composition of the examined alloys was calculated, i.e. the content of α dendrites and eutectic. In the eutectic point (577°C), in the alloy containing 1,65% Si, 100% of α phase dendrites are precipitating (the solubility of aluminium in solid state), while in the alloy containing 12,6% Si, 100% of (α+β) eutectic is precipitating.

5. Conclusions

Basing on the results of own investigations and calorimetric analysis, the following final conclusions were drawn:

1. A difference was stated in the values of the enthalpy of melting and solidification of silumins, which might be caused by sample used in calorimetric examinations.
2. It has been stated that the value of the enthalpy of melting and solidification is directly proportional to a percent increase of the silicon content. This is confirmed by the results of calculations of the phase constitution.
3. The place and technique of taking a sample for calorimetric examinations is of very great importance for the results of analysis of the scanning calorimetry.
4. A satisfactory correlation was obtained between the results of calculations of the phase constitution of the examined silumins done by the calorimetry and level-arm principle.

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