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Determination of melting and solidification enthalpy of hypereutectic silumins

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Abstract

The study was related with determination of the values of enthalpy of melting and solidification of hypereutectic AlSi18, AlSi21 and AlSi24 silumins modified with phosphorus in the form of Cu-P. The calorimetry, preceded by thermal analysis and derivative thermal analysis (TA and DTA, respectively) was carried out on a high-temperature scanning calorimeter, model MHTC-96, made by SETARAM, applying the method of direct determination of parameters of the high-temperature process, and in particular of the enthalpy of phase transformations. Modern control and measuring instruments coupled with PC computer provide a very precise tool for determination of these transformations. 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. Moreover, an additional thermal effect, related most probably with pre-eutectic crystallization of primary silicon, was observed and confirmed by calorimetric examinations.

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

1. Introduction

Phase transformations in cast alloys affect the formation of structure, physico-mechanical properties as well as alloys behaviour at high temperatures. 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. Methods of investigation

For investigations, the silumins from AlSi18, AlSi21 and AlSi24 family modified with Cu-P 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°C, the melt was subjected to a refining treatment with Rafglin-3, added in an amount of 0,3 wt.% and to modification with Cu-P (~9,95 %P). The temperature of pouring was controlled

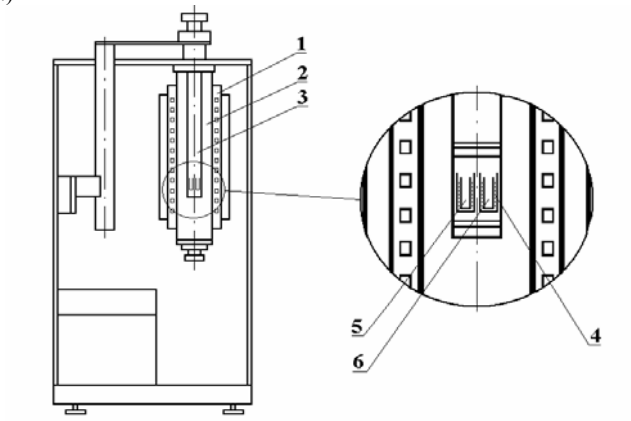
by a NiCr-NiAl TP-202K-800-1 thermocouple immersed in liquid melt. From the ready castings, samples were taken for analysis of the chemical composition. An additional advantage was development of appropriate software called „SETSOFT", owing to which it was possible to determine in an easy way the enthalpy 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
AlSi18	78,647	20,644	0,000	0,005	0,008	0,679	0,009
AlSi21	76,143	22,821	0,000	0,011	0,005	1,004	0,011
AlSi24	72,665	25,589	0,061	0,007	0,008	1,635	0,016

Phase transformations were examined by a scanning Multi HTCS60 calorimeter under the protective atmosphere of argon, applying the heating and cooling rate of 5ºC/min. The ∅3×5mm specimens had a cylindrical shape and the same weight of 94 mg each [2]. A schematic drawing of the calorimeter and a view of the measuring head are depicted in Figure 1.

a)



b)

Fig.1. A Multi HTCS calorimeter: a) the principles of operation, b) measuring head

3. The results of investigation and their analysis

Figure 2 gives an example of DTA curve plotted for the hypereutectic AlSi24 silumin, while Figure 3 shows diagram plotted from the results of DSC calorimetry for this silumin during heating and cooling.

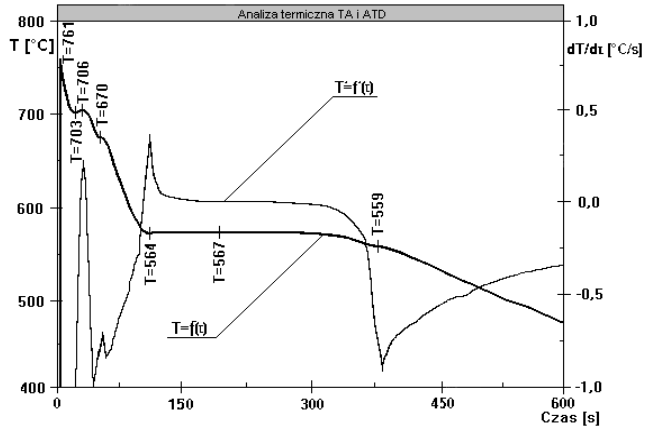
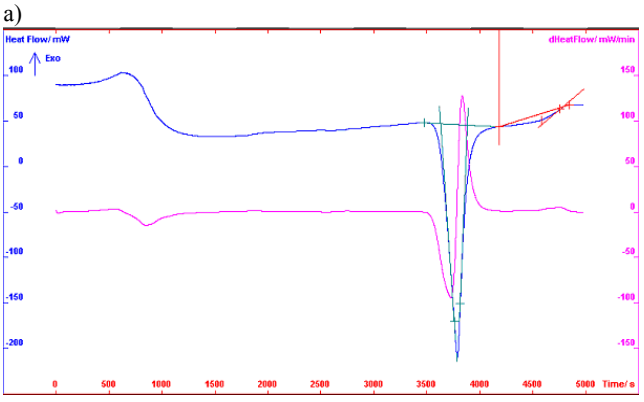


Fig. 2. DTA curve plotted for the hypereutectic AlSi24 silumin

a)



b)

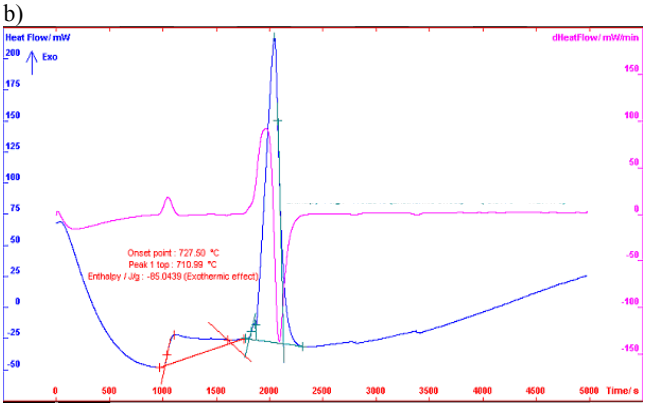


Fig.3. DSC diagram for AlSi24 silumin during a) heating; b) cooling

From the plotted diagrams and using the SetSoft program [3], 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	Silicon
AlSi18	T_p, ºC	578,31	645,92
	T_k, ºC	605,57	674,72
	E, J/g	+443,44	+9,66
AlSi21	T_p, ºC	578,74	664,84
	T_k, ºC	604,78	751,83
	E, J/g	+424,47	+49,19
AlSi24	T_p, ºC	578,39	667,88
	T_k, ºC	603,89	731,87
	E, J/g	+452,34	+29,03

Table 3
Temperature and enthalpy of transformations during cooling

Alloy	Value	Solidification	
		Silicon	Eutectic
AlSi18	T_p, ºC	657,43	565,01
	T_k, ºC	638,65	536,52
	E, J/g	-18,68	-423,01
AlSi21	T_p, ºC	752,31	564,85
	T_k, ºC	737,08	537,11
	E, J/g	-81,58	-386,27
AlSi24	T_p, ºC	727,50	579,64
	T_{k1}, ºC	710,99	570,66
	T_{k2}, ºC	-	538,58
	E_1, J/g	-85,04	-6,82
	E_2, J/g	-	-412,45

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 phase β. At the first stage of investigations, the phase constitution of the examined silumins was calculated from the content of silicon and using a „lever-arm principle".

$$X_E = \frac{100 - Si_x}{100 - Si_B} \cdot 100\% \quad (1)$$

$$X_{Si} = 100 - X_E \quad (2)$$

Table 4 gives calculated fractions of individual phases in the examined silumins.

Table 4
Calculated phase constitution of the examined silumins

Alloy / Fraction of structural constituent	AlSi18	AlSi21	AlSi24
Eutectic	93,7	90,3	86,8
Phase β	6,3	9,7	13,2
Total :	100	100	100

4. Summary and conclusions

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 silicon. This is caused by the fraction of eutectic phase reduced in favor of the silicon phase.
For AlSi18 alloy during melting of eutectic, the enthalpy is 443,44 J/g, and the heat of silicon melting is 9,67 J/g. During solidification, these values are different and amount to – 18,68 J/g for silicon crystallization, and – 423,01 J/g for the crystallization of eutectic. This is explained by different solidification rates. During calorimetric examinations, the solidification of the sample is proceeding with constant and relatively small drop of temperature (5°C/min). Moreover, the sample used in investigations is of small dimensions, which makes the conditions approach more the state of equilibrium, and hence during the solidification more of hypereutectic silicon is crystallizing on the cost of eutectic silicon.
The situation is much the same for AlSi21 alloy, where the value of enthalpy is also growing during silicon crystallization and drops during eutectic crystallization. Slow cooling promotes the diffusion of hypereutectic silicon, which is not entirely possible in DTA analysis, during which the silumin is let cool in the air and not together with the furnace, as it happens in the calorimetric analysis.

The situation is similar also in the case of AlSi24 silumin sample, the only difference lying in the fact that the values of enthalpy are lower than they are for the AlSi21 silumin sample. Although in each case the technique and place of taking the sample were the same, a macrosegregation has occurred, on account of which in the sample where the content of silicon should be higher it is in reality lower than in AlSi21. On the DSC diagram of AlSi24 sample during cooling, a distinct thermal effect has been observed. Probably, it is caused by pre-eutectic crystallization of dendrites α (Fig.2). During calorimetric analysis this effect was 6,82 J/g, basing on the results obtained in [5], where the heat of crystallization of phase α, amounting to 319,6J/g, was determined. The content of the crystallizing phase α in the examined silumin was calculated from the formula given below:

100 % dendrites α - 319,6 J/g
X % dendrites α - 6,82 J/g

$$X = \frac{100 \cdot 6{,}82}{319{,}6} = 2{,}13\% \qquad (3)$$

As follows from relationship (3), 2,13% of dendrites of the phase α have precipitated, and compared with the calculated phase constitution of AlSi24 alloy, where 13,2% is phase β, the precipitated dendrites make over 16% of the precipitated silicon. The observed effect occurred only in the case of cooling and appeared in one single sample only. Further investigations are needed to confirm that with no doubt the observed effect is a pre-eutectic crystallization of the dendrites of phase α.

Using the results published in a master's thesis [5], 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:

AlSi18

100 % eutectic – 468,2 J/g
X % eutectic – 443,44 J/g

$$X = \frac{100 \cdot 443{,}44}{468{,}2} = 94{,}71\%$$

AlSi21

100 % eutectic - 468,2 J/g
X % eutectic – 424,47 J/g

$$X = \frac{100 \cdot 424{,}47}{468{,}2} = 90{,}65\%$$

AlSi24

100 % eutectic - 468,2 J/g
X % eutectic – 452,34 J/g

$$X = \frac{100 \cdot 452{,}34}{468{,}2} = 96{,}60\%$$

The results are compiled in Table 5 and compared with calculations based on the silicon content, using a „lever-arm principle".

Table 5
A compilation of the results of calculations of the eutectic and phase β constitution as obtained by calorimetric examinations and the lever-arm principle.

Alloy / content of constituent	AlSi18		AlSi21		AlSi24	
	Calc.	DSC	Calc.	DSC	Calc.	DSC
Phase α+β	93,7	94,71	90,3	90,65	86,8	96,6
Phase β	6,3	5,29	9,7	9,35	13,2	3,4

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

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 different solidification rates of DTA sample (rapid cooling) and sample used in calorimetric examinations (slow cooling).
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. The additional thermal effect observed during calorimetric analysis of AlSi24 silumin sample on cooling is probably due to pre-eutectic crystallization of phase α. The dendrites α crystallise on the grains of primary silicon, which acts as a substrate for heterogeneous nucleation of this phase.
5. 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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