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Proeutectic crystallisation in hypereutectic silumins modified with Al-CuP-Me master alloys

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Abstract

Using thermal analyses TA and ATD, within a narrow range of the crystallisation period, i.e. until reaching an equilibrium temperature, the occurrence of exothermic effect was stated. Most probably, the said effect is due to a proeutectic crystallisation of α phase or of β phase crystals. The said effect was observed to occur only in alloys after the process of modification with an addition of high-melting point elements. Complex inoculants of Al-CuP-Me (Me = Mo, Co, Cr, Nb, TiB, W) type cause hardening of silumins, due to the formation of new phases of the Al_xMe_y type, which can act as substrates for the nucleation of α dendrites and crystals of β phase. The experiments carried out on castings solidifying with different rates of heat transfer have proved that proeutectic crystallisation does not occur when free solidification conditions (microspheres) are provided. This fact can be related to the heat transfer rate.

Keywords: Theoretical fundamentals of the crystallisation process, Modification, Proeutectic crystallisation, Silumins

1. Introduction

Crystallisation, examined as a complex of transformations that take place during the transition of a body from liquid into crystalline state, is the result of simultaneous occurrence of a number of different physico-chemical phenomena [1]. In cast alloys, crystallisation takes place within the range of temperatures marking the beginning (T_{liq}) and end (T_{sol}) of the solidification process. The kinetics of crystallisation is reflected in the shape of the cooling curve, which enables evaluating the quality of molten metal and the consequences of its refining and modification treatment. From the run of this curve one can judge about the characteristic arrests and inflexion points that occur on the temperature derivative in function of time. The arrests are caused by the effect of external heat sources. Their value depends on the thermal effects originating from the crystallisation of compounds, eutectics and intermetallic phases [2]. A tool for the investigation of temperature changes in time is thermal analysis ATD [3].

2. Research methods and materials

Investigations of exothermic heat effects during crystallisation were carried out by the thermal analysis ATD. As mentioned previously, it enables determination of individual phases in casting. For studies of the thermal effects taking place in a range from T_{liq} to T_E, AlSi20 silumin modified with complex master alloys of the Al-CuP-Me (Me = Cr, Co, Mo, Nb, TiB, W, Zr) type was selected. Chemical composition of this silumin, with 0,05%P (CuP) and with Al-Me master alloys is given in Table 1.

Table 1
Chemical analysis of the examined silumin

Sample	Content, wt.%						
	Al	Si	Cu	Ni	Mg	Fe	Mn
AlSi20	76,824	20,265	1,061	0,307	0,488	0,835	0,16

3. The results of investigations

The exothermic heat effects present during proeutectic crystallisation of AlSi20 silumin modified with complex master alloys of the Al-CuP-Me type were interpreted using the results of thermal analysis ATD. Figure 1 shows these results as obtained on the examined silumin after modification with phosphorus and Al-Zr and Al-Ti master alloys within a narrow range of the solidification temperatures (from T_{liq} to T_E).

As follows from respective diagrams, at the initial stage of solidification of the AlSi20 silumin after modification with phosphorus and Al-Zr and Al-Ti master alloys in a range between the temperature of the precipitation of the primary silicon crystals (T_{liq}) and the temperature of the crystallisation of the α(Al) -β(Si) eutectic, the second exothermic effect takes place. This effect is probably due to the proeutectic crystallisation of either aluminium dendrites, or silicon crystals, or another intermetallic phase. It is quite interesting to note that it occurs only in alloys after the process of modification with phosphorus introduced in the form of CuP10 master alloy, with the effect of modification additionally enhanced by an addition of high-melting point element.

Table 2 compares the characteristic temperature values obtained for all the examined melts.

Table 2.
Characteristic temperature values at the initial stage of AlSi20 silumin solidification after the modification with phosphorus and Al-CuP-Me master alloys

Sample type	Solidification temperature, °C				
	$T_{zal.}$	$T_{liq.}$	$\mathbf{T_{efekt}}$	$T_{min.}$	T_E
AlSi	777	642	-	569	570
AlSi+P	780	691	**671**	567	569
CuP+AlCo	776	687	**670**	565	569
CuP+AlCr	789	689	**680**	565	568
CuP+AlMo	769	692	**671**	568	570
CuP+AlNb	776	667	**653**	569	571
CuP+AlNi	774	668	**661**	564	565
CuP+AlSr	775	713	**664**	567	569
CuP+AlTi	780	695	**671**	570	571
CuP+AlTiB	780	728	**682**	571	572
CuP+AlW	766	692	**666**	568	571
CuP+AlZr	778	691	**663**	569	571

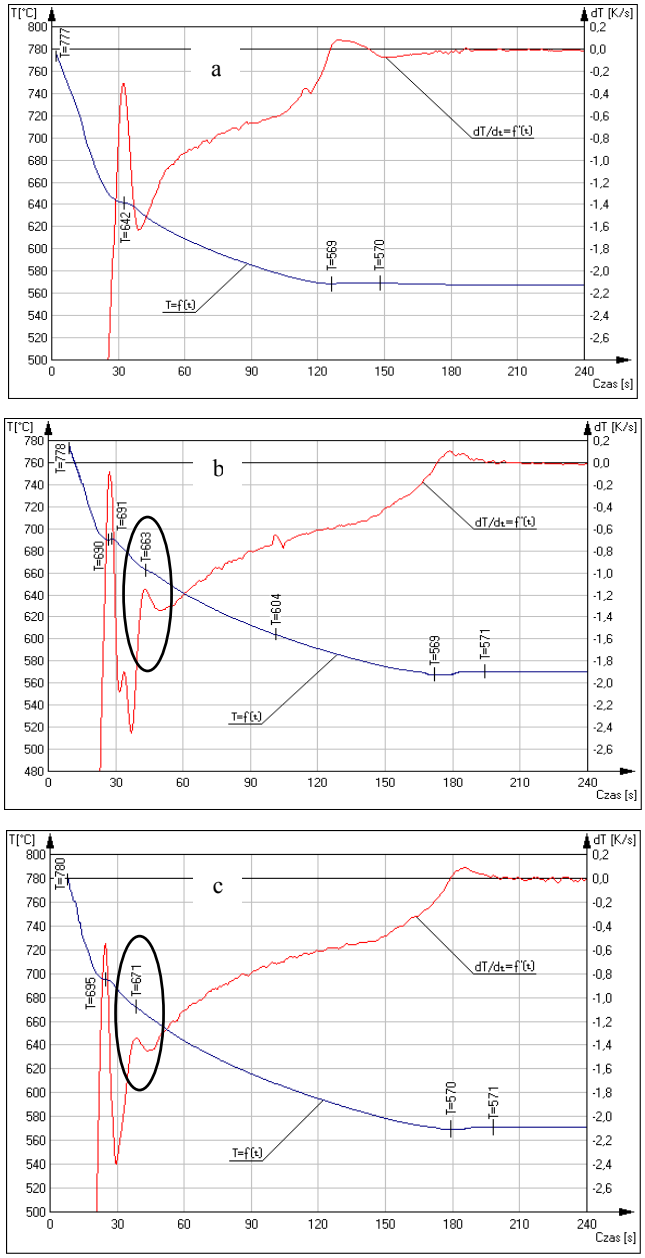


Fig. 1. The beginning of the AlSi20 silumin cooling curve: a) before modification; b) after modification with P+Al-Zr; c) after modification with P+Al-Ti

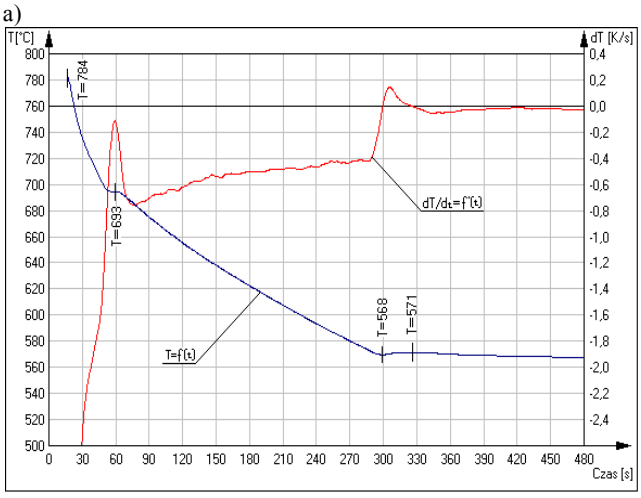
As follows from the data compared in Table 2, the exothermic effect of proeutectic crystallisation (T_{efekt}) occurs only in alloys modified with phosphorus, and with the modification effect additionally enhanced by an addition of master alloy. The temperature range when this effect takes place is from 653 to 682°C, and since this is the range of pure aluminium melting, it might be judged that the effect is due to a proeutectic crystallisation of Al dendrites [4]. On the other hand, it is interesting to note that the said effect has not been observed in silumins without modification, and the latter fact makes the above

conclusion sound very unlikely. If this effect occurs only in the case of modification, a consequence of which are obvious structural changes, like the grain refinement and a uniform distribution of the primary silicon precipitates, a much more probable conclusion is that its occurrence is due to nothing else but the modification process itself.

The temporary occurrence of an exothermic reaction between T_{liq} and T_E indicates that the phase in formation can act as a substrate for the heterogeneous nucleation of eutectic mixture.

Since all experiments of the AlSi20 silumin solidification after its modification with complex master alloys of the Al-CuP-Me type were conducted at a constant cooling rate, and it is the fact well known that the conditions of heat transfer exert an important effect on the type of the produced primary structure, it has been decided to examine the effect of cooling rate (the type of foundry mould) on the proeutectic crystallisation process taking place in silumins.

a)



b)

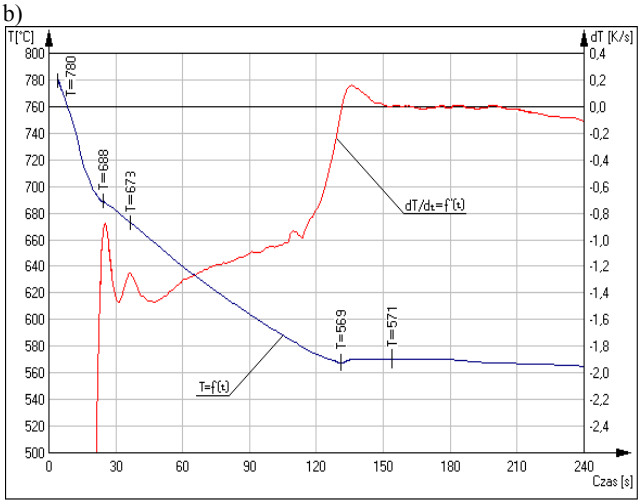


Fig. 2. Diagram of thermal analysis ATD plotted for AlSi20 silumin after modification with 0,05% P cast into: a) mould based on microspheres; b) conventional sand mould with bentonite binder

The results of ATD performed on AlSi20 alloy modified with phosphorus and poured into a mould based on microspheres and, for the sake of comparison, into a mould prepared from the bentonite-bonded sand mixture are shown in Figure 2.

An explanation of the phenomenon of the exothermic heat effect taking place between the crystallisation of primary silicon precipitates and eutectic can possibly be sought in the structure of these alloys. Figure 3 and 4 shows examples of the AlSi20 silumin microstructure after modification with Al-CuP-Me master alloys.

a) b)

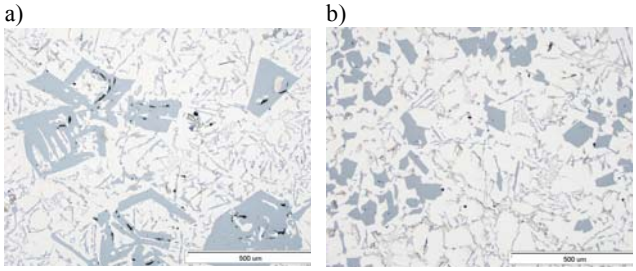
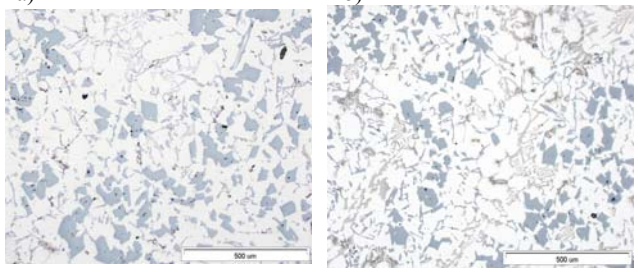


Fig. 3. Microstructure of AlSi20 alloy; a) before modification; b) after modification with 0,05%P master alloy

a) b)



c) d)

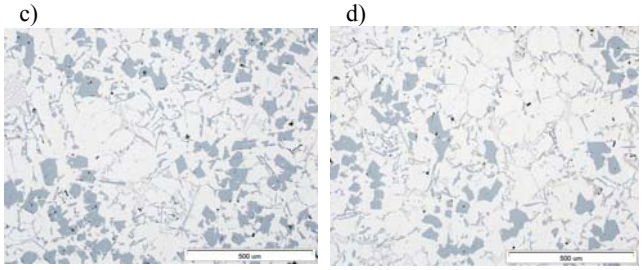


Fig. 4. Microstructure of AlSi20 alloy; a) after modification with CuP+AlCo master alloy; b) after modification with CuP+AlTi master alloy; c) after modification with CuP+AlZr master alloy; d) after modification with CuP+AlMo master alloy

4. Summary

From the data comprised iu Table 1 it follows that the exothermic effect of proeutectic crystallisation (T_{efekt}) occurs only in alloys after modification with phosphorus, or with an addition of complex master alloys of the Al-CuP-Me (Me= Cr, Co, Mo, Nb, TiB, W, Zr) type. The temperature range of the crystallisation

is from 653 to 682°C, a thermodynamic consequence of which is the exothermic heat effect distinctly visible on a cooling curve.

Very important in the formation of primary structure during the solidification of silumins are also the conditions of heat transfer. Slow crystallisation results in coarse-grain structure. Increasing the rate of heat transfer results in structure modifications. The thermodynamic aspects of the crystallisation process affect also the formation of silicon crystals, aluminium dendrites and intermetallic phases [5, 6].

A consequence of the heat transfer rate from the examined system to the environment is also the second, additional effect of proeutectic crystallisation taking place in the examined silumins. To check this statement in practice, the solidification of AlSi20 silumin after modification with phosphorus was examined, pouring the said alloy into a mould based on microspheres and, for the sake of comparison, into another mould prepared from sand bonded with bentonite. The results are compared in Figure 2. From the obtained results it follows that the exothermic heat effect of proeutectic crystallisation takes place only in the alloy cast into a sand mould (higher rate of heat transfer). Hence a conclusion follows that free conditions of the heat transfer contribute to the elimination of the above mentioned thermal effect.

More comprehensive explanation of the occurrence of the exothermic heat effect, responsible for the proeutectic crystallisation of an unknown phase, is to be sought in the microstructure of the examined silumins.

The images of metallographic structures indicate that the structure of casting containing an addition of phosphorus has undergone some modifications. The precipitates are fine and distributed evenly in the matrix. The modification with Al-CuP-Me type master alloys also refines the silicon crystals and distributes them evenly in the matrix of aluminium solution, but in this case, besides the commonly encountered fine silicon crystals, other crystals of slightly different morphology appear as well. It is quite possible that these uncommon crystals are responsible for the appearance of the additional heat effect. In other words, they crystallise as secondary precipitates, and the appearance of thermal effect is a consequence of this situation. It is also worth noting that the second additional thermal effect is less intense than the effect caused by the precipitation of the crystals of primary silicon. Perhaps the secondary crystallisation of silicon characterised by different morphology results in a lower rate and volume of the heat evolution. The traditional metallographic examinations can contribute little to the identification of other intermetallic phases.

For more complete explanation of the proeutectic crystallisation it is necessary to carry out additional examinations by RTG, SEM, and – especially - by calorimetry. These additional investigations are expected to enable more complete identification of the phase that crystallises in hypereutectic silumins between the temperature T_{liq} and the solidification point of α(Al)-β(Si) eutectic mixture.

The studies done by other authors [1-6] as well as own metallographic examinations have confirmed the segregation effect of silicon and other alloying elements in hypereutectic silumins. The segregation is due to the presence in liquid state of the areas of higher and lower silicon concentration (areas I and II). The analysis of phase equilibrium diagrams (Si, Cu, Ni, Mg) – P [7] indicates that various alloying additions have different effect on the phosphorus solubility in liquid silumin. Silicon reduces this solubility by promoting phosphorus precipitation from the liquid solution at an early stage of the process. The alloying additives like Cu, Ni, Mg improve phosphorus solubility in the solution, which retards its precipitation from the melt (lower temperature).

Phosphorus starts precipitating when the temperature of molten silumin after having been cast into a mould decreases to certain value (as a result of the combined effect of all the elements). At a temperature above 500°C phosphorus evaporates. The process of evaporation may cause in some microregions a severe undercooling ΔT. The forming bubbles (the phosphorus vapours have very high pressure) undergo sudden expansion. This effect may additionally increase the value of the undercooling ΔT. While moving towards the surface of the liquid silumin, the chemically active vapours of phosphorus are entering into reaction with aluminium, forming aluminium phosphides. And this is the reason why nearly all phosphorus gathers at the casting surface.

In the areas characterised by high silicon concentration, the temperature T_{liq} (from Al-Si phase equilibrium diagram) is so high that local temperature drop due to phosphorus evaporation (the expansion of bubbles) causes undercooling ΔTp. This undercooling is the driving force for the process of crystal nucleation and growth. In the areas of lower silicon concentration, the evaporation of phosphorus (the expansion of bubbles) is not strong enough to create for the undercooling ΔTp the conditions which would promote its drop below the equilibrium temperature T_{liq}. So, in these areas, the effect of modification does not occur.

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