Coefficient of crystal lattice matching as a parameter of substrate - crystal structure compatibility in silumins

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Abstract

Adding high-melting point elements (Mo, Nb, Ni, Ti, W) to complex silumins results in hardening of the latter ones, owing to the formation of new intermetallic phases of the Al_xMe_y type, with refinement of dendrites in α solution and crystals in β phase. The hardening is also due to the effect of various inoculants. An addition of the inoculant is expected to form substrates, the crystal lattice of which, or some (privileged) lattice planes and interatomic spaces should bear a strong resemblance to the crystal nucleus. To verify this statement, using binary phase equilibria systems, the coefficient of crystal lattice matching, being one of the measures of the crystallographic similarity, was calculated. A compatibility of this parameter (up to 20%) may decide about the structure compatibility between the substrate and crystal which, in turn, is responsible for the effectiveness of alloy modification. Investigations have proved that, given the temperature range of their formation, the density, the lattice type, and the lattice parameter, some intermetallic phases of the Al_xMe_y type can act as substrates for the crystallisation of aluminium and silicon, and some of the silumin hardening phases.

Keywords: Theoretical fundamentals of the crystallisation process, Lattice parameter, Nucleation, Silumins

1. Introduction

The wide range of silumins application is mainly due to their good utilisation properties, low density, low melting point, good thermal and electrical conductivity, and dimensional stability [1, 2]. All these features are formed during the process of alloy crystallisation and are reflected in the type of primary structure, which can be changed later through application of a modification treatment. Therefore, the main aim of modification is to increase the grains density, that is, the metal nucleating capacity, affecting the kinetics of solidification, which is considered a derivative of the nucleation coefficient and similarity between the crystallographic lattice of the substrate and crystal [3, 4].

2. The present state of the art

Since, considered in terms of temperature, the kinetics of the crystallisation is reflected on a temperature curve, thermal analysis ATD is the tool often used in investigations of the modification process. The use of this analysis enables us to determine a maximum degree of undercooling ΔT_{max} during the initial period of crystallisation (since pouring till equilibrium temperature) and correlate it with the grains density in casting. Increased density of nuclei depends on the following factors: reduced surface tension at the liquid metal - nucleus phase boundary, reduced contact angle between the cluster and substrate, the number of new phases formed in melt due to the

modification treatment, and reduced coefficient of the crystal growth [5].

From the above statements it follows that inoculants can be divided into the following groups:

- reducing the nucleus-substrate contact angle, thus reducing ΔT_{max} and increasing grains density,
- substrate-forming, i.e. increasing the density of the nucleation-capable substrates,
- impeding the crystal growth rate.

If the inoculant introduced to metal reduces the contact angle or surface tension at the liquid metal - nucleus phase boundary, the value of the critical dimension of the substrate decreases with the corresponding increase in the density of nuclei. From this fact follows a conclusion that the inoculant should form substrates in which the crystal lattice, or some (privileged) lattice planes and interatomic spaces will be similar to the crystal nucleus. One of the measures of the similarity is the coefficient of crystal lattice matching expressed by the following formula: [5]:

$$\gamma = \frac{X_P - X_K}{X_K} \cdot 100\% \tag{1}$$

where:
X_p – the crystal lattice parameter for substrate orientation,
X_k - the crystal lattice parameter for crystal orientation.

3. The results of investigations

The coefficient of structure matching (up to 15%) between the substrate and crystal was determined for the intermetallic phases present in a binary Al_xMe_y system [6]. Table 1 shows possible phases that in first approximation can play the role of substrates for the nucleation of Si crystals.

Table 1.
Coefficient of lattice matching for Si crystals

Phase	Lattice type	Lattice parameters, Å			*Wds %
		a; b; c			
Cu_5Si	A13, cubic	a = 6,21			85
Al_9Co_2	monoclinic	6,213	6,29	8,556	85
AlSb	B3, cubic	a = 6,095			88
Al_2Cu	C16, tetragonal	a = 6,054	c = 4,864		88
Fe_3Si	DO3, cubic	a = 5,644			96
AlP	B3, spatial	a = 5,42			100
$NiSi_2$	cubic	a = 5,395			100
W_3Si	cubic	a = 4,91			109
Mo_3Si	cubic	a = 4,878			110
Cr_3Si	cubic	a = 4,62			115
CrSi	cubic	a = 4,62			115
Cr_7Si	cubic	a = 4,62			115
MnSi	B20, cubic	a = 4,548			116
FeSi	B20, spatial	a = 4,479			116

*Wds – coefficient of crystal lattice matching calculated from relationship (1) for silicon crystals

Table 2 shows phases that, in first approximation, can possibly play the role of nucleation substrates for aluminium dendrites.

Table 2.
Coefficient of lattice matching for Al dendrites

Phase	Lattice type	Lattice parameters, Å		*Wds %
		a; b; c		
Cr_3Si	cubic	a = 4,62		86
CrSi	cubic	a = 4,62		86
Cr_7Si	cubic	a = 4,62		86
MnSi	B20, cubic	a = 4,548		87
FeSi	B20, spatial	a = 4,479		89
$Cr(Si,Al)_2$	C40, hexagonal	a = 4,496	c= 6,377	89
Al_4Sr	D3, tetragonal	a = 4,45	c= 11,05	90
TiB	B3, cubic	a = 4,2		96
$AlNaSi_4,$	C38, tetragonal	a = 4,13	c = 7,4	98
AlTi	L1O, tetragonal	a = 3,997	c= 4,062	101
Al_3Ti	DO22, tetragonal	a = 3,84	c= 8,579	105
TiB_2	C32, tetragonal	a = 3,02	c = 3,22	121
AlB_2	C32, hexagonal	a = 3,01	c = 3,23	122

*Wds - coefficient of crystal lattice matching calculated from relationship (1) for aluminium dendrites

As follows from the data compared in Tables 1 and 2, the coefficient of lattice matching, calculated from relationship (1) as a first approximation of structure matching between the substrate and nucleus, has the values similar to silicon crystals and aluminium dendrites. Hence a conclusion follows that some intermetallic compounds can act as substrates for the heterogeneous nucleation of both Al dendrites and Si crystals. These phases are listed in Table 3.

Table 3.
Coefficients of lattice matching for Si and Al

Phase	Lattice type	Lattice parameters, Å		*Wds Si %	*Wds Al %
		a; b; c			
TiB_2	C32, tetragonal	3,02	3,22	144	121
TiB	B3, spatial	4,2		123	96
FeSi	B20, spatial	4,479		117	89
$Cr(Si,Al)_2$	C40, hexagonal	4,496	6,377	117	89
Al_4Sr	D3, tetragonal	4,45	11,05	118	90

*Wds_{Si} coefficient of crystal lattice matching calculated from relationship (1) for silicon crystals
*Wds_{Al} coefficient of crystal lattice matching calculated from relationship (1) for aluminium dendrites

3.1. The measurement of undercooling degree

As mentioned previously, the consequence of high nucleating capacity of metals and alloys is change in the crystallisation process kinetics, visible on the temperature curve plotted in function of time. On account of this, thermal analysis ATD is the

tool used often in an evaluation of the crystallisation process and inoculation effectiveness, and also in forecasting of the mechanical properties. The said analysis enables, among others, the determination of a maximum degree of undercooling ΔT_{max} at the initial stage of crystallisation, where the said degree of undercooling is acting as a catalyst for the heterogeneous nucleation of phases in alloy undergoing the solidification process. This value affects in a very significant way the effectiveness of modification, since the increasing degree of undercooling ΔT_{max} results in higher density of the crystallisation nuclei, and hence in better effectiveness of the modification. A schematic division of the alloy cooling curve is shown in Figure1.
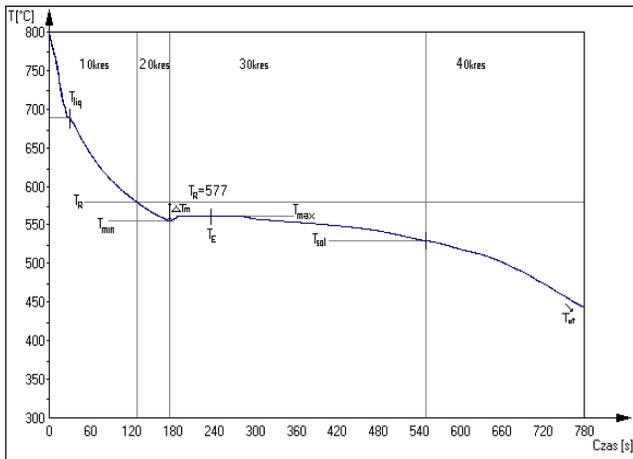

Fig. 1. Cooling curve plotted for an Al-Si alloy, where:

T_{liq} – the liquidus temperature

T_R – the equilibrium crystallisation temperature of Al-Si = 577°C

T_{min}- the minimum temperature of liquid undercooling

T_E – the crystallisation temperature of α(Al) - β(Si) eutectic

T_{max} – the maximum temperature of liquid undercooling

T_{sol} – the solidus temperature

Stage 1 – the crystallisation from pouring temperature to the equilibrium temperature T_R

Stage 2 – the crystallisation from equilibrium temperature to the minimum temperature T_{min}

Stage 3 – the crystallisation from minimum temperature T_{min} to the solidus temperature T_{sol}

Stage 4 – the solidification to ambient temperature T_{ot}

ΔT_{max} –the maximum degree of undercooling.

At the second stage of investigations, the values of the undercooling degree ΔT_{max} were calculated for hypereutectic AlSi18 alloy after modification with phosphorus (CuP) and an addition of the alloying element (Cr, Mo, Co, Ti, W) introduced in the form of master alloy. Modification added in an amount of 0,05 wt.% P was carried out using Cu-P master alloy. Refining was made with 0,03 wt.% „Rafglin-3". The interpretation of the inoculant effect on the degree of undercooling was based on the results of thermal analysis ATD. Figure 2 shows these results as obtained on an AlSi18 silumin after modification with phosphorus and with Al-Co as well as Al-W master alloys.
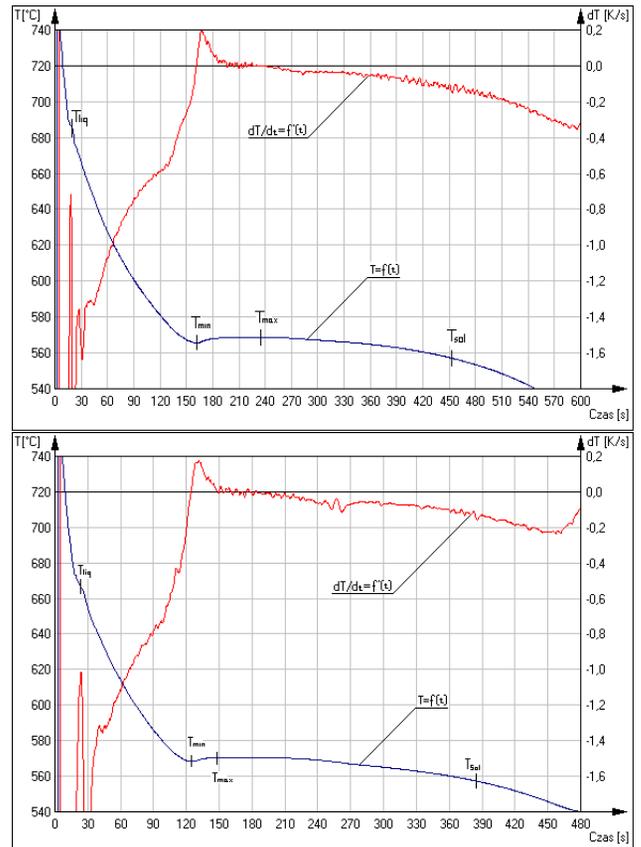

Fig. 2. The results of thermal analysis plotted for AlSi18 silumin after modification with a) Al-CuP-Co and b) Al-CuP-W

Basing on the plotted cooling curves obtained by ATD method for the AK18 silumin after adding Al_xMe_y master alloy, the maximum degree of undercooling ($\Delta T_{max} = T_R-T_{min}$) T_R=577°C and the point of recalescence ($R = T_{max}-T_{min}$) were calculated. The results are shown in Table 4.

Table 4.
Parameters of crystallisation obtained for the AK18 silumin after modification with various master alloys

Type of master alloy	Crystallisation parameters, ^{o}C			
	T_{min}	ΔT_{max}	T_{max}	R
CuP	566	11	569	3
CuP+AlCo	565	12	569	4
CuP+AlCr	566	11	568	3
CuP+AlMo	568	9	570	2
CuP+AlNb	569	8	571	2
CuP+AlNi	564	13	565	1
CuP+AlTi	570	7	571	1
CuP+AlTiB	571	6	572	1
CuP+AlW	568	9	571	3
CuP+AlZr	569	8	570	1

As follows from the data in Table 4, the highest degree of undercooling ΔT_{max} = 13°C was obtained for the AlSi18 alloy

after modification with CuP+AlNi master alloy; the undercooling $\Delta T_{max} = 12^{\circ}C$ was obtained for the CuP+AlCo master alloys. Figure 3 shows examples of the AlSi18 silumin microstructure after modification with these master alloys.
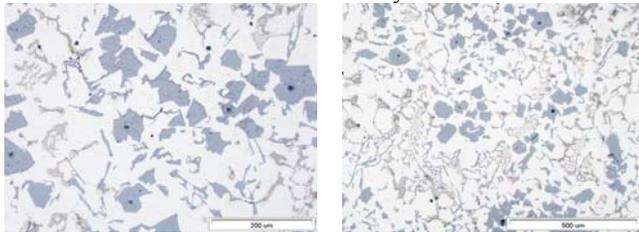

Fig. 3. Microstructure of AlSi18 alloy after modification with:
a) CuP+AlNi; b) with CuP+AlCo master alloy;

4. Summary

As follows from the available data (Table 1), the coefficient of matching determined by relationship (1) for substrate used in the nucleation of silicon crystals assumes the value of 100% for the AlP and $NiSi_2$ phases and close to 100% for the Fe_3Si and W_3Si phases. The remaining values of the coefficient are still comprised in a range of 100 +/– 15%, which means that, from the structural point of view, these phases can act as potential substrates for the heterogeneous nucleation of Si crystals.

Similar values of the coefficient of lattice matching were obtained for the Al_xMe_y phases responsible for the nucleation of Al dendrites. As follows from Table 2, except borides, all other phases had the values of the coefficient of matching comprised in a range of 85 to 115%. This means that the required compatibility between the lattice parameters of the substrate and nucleus has been achieved. Yet, it should be remembered that, as stated previously, good structural matching between the substrate and nucleus is only the first approximation to a modification effect. The nucleus-substrate contact angle and surface tension at the liquid metal – nucleus phase boundary also play a very important role, as well as a topography of the substrate surface, local "saggings" and changes of the curvature, the similarity of chemical bonds and differences in electrostatic potential of the substrate and nucleus [5].

Economic issues, i.e. the cost of the inoculant, as well as the problems of occupational safety should also be taken into account. As follows from the obtained data [7], an ideal match with the structural lattice of silicon offer, besides AlP, also gallium phosphides GaP and indium phosphides InP. Table 5 gives a comparison of the lattice types, lattice parameters, and coefficient of matching values for the above mentioned phosphides.

Table 5.
Crystallographic parameters GaP, InP and AlP

Phase	Lattice type	Lattice parameter, Å	Coefficient of lattice matching, %	
			for Si	for Al
GaP	cubic	5,4512	99	65
InP	cubic	5,8686	96	55
AlP	cubic	5,4635	99	65

The synthesis of indium phosphide, which consists in combining indium and phosphorus into one chemical compound, is both difficult and dangerous. This is due to the fact that the process is carried out at high temperature (1100°C) with pressure of the phosphorus vapours reaching 30 atm. Since the process is proceeding in a closed quartz ampule, the pressure reaching 3 MPa must be very precisely compensated.

In spite of an almost ideal structure matching between the above mentioned phases and Si crystals, phosphides of GaP and InP are not used because of the occupational safety regulations. These are the inorganic chemical compounds of very toxic character, used mainly for elements of semi-conductors in laser and optical applications. Their application in metallurgy has been considerably restricted.

Examples of the results obtained by thermal analysis ATD on the AlSi18 silumin modified with additions of Al-CuP-Co and Al-CuP-W master alloys are shown in Figure 2. From these investigations it follows that the temperature of the hypereutectic silicon precipitation (T_{liq}) is 689°C for alloy modified with phosphorus and Al-CuP-Co master alloy, raising to 695°C when the Al-CuP-W master alloy is added. The increase of temperature T_{liq} in alloy after the process of modification indicates that the modification has been carried out in a correct way. This fact is additionally confirmed by the presence of undercooling ΔT_{max}. From the data compared in Table 4 it follows that, at the second stage of the AlSi18 silumin solidification (Fig. 1), this undercooling changes from 0 to ΔT_{max}, thus activating the substrates of over-critical dimensions. Introducing the inoculating master alloys to liquid silumin results in the formation of particles that can serve as additional substrates for the heterogeneous nucleation of Si crystals and Al dendrites.

In the examined alloys, the temperature of the crystallisation of the $\alpha(Al)$-$\beta(Si)$ eutectic (T_{max}) was practically the same and comprised in a range from 565 to 572°C, thus serving as a starting point for further calculations of the point of recalescence, considered a measure of difference between the temperatures T_{max} and T_{min}. From the ready castings, specimens were taken for metallographic examinations. The images of the metallographic structures indicate that the structure of casting with an addition of phosphorus has undergone the modification process. The silicon precipitates are fine and distributed evenly in the matrix.

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