

# Thermal analysis and microstructure of master alloys used for modification of silumins

J. Piątkowski<sup>a,\*</sup>, J. Szysmal<sup>a</sup>

<sup>a</sup>Chair of Metal Alloys and Composites Engineering, Silesian University of Technology  
Kraśińskiego 8, 40-019 Katowice, Poland

\*Corresponding author. E-mail address: jaroslaw.piatkowski@polsl.pl

Received 15.04.2009; accepted in revised form 24.04.2009

## Abstract

The study presents the technological backgrounds of the process of melting and casting Al-Co, Al-Ni, and Al-Ti master alloys, used as refiners of the microstructure of cast silumins. Basing on the analysis of phase equilibrium diagrams for an Al-Me (Co, Ni, Ti) system at a temperature of 900°C, the characteristic intermetallic phases of  $Al_xMe_y$  were investigated. Due to their similarity with Al and Si in respect of both structure and lattice arrangement, these phases may act as heterogeneous nuclei and promote solution hardening during, e.g., heat treatment. Using the method of thermal analysis ATD, the temperature was plotted in function of time, and then the characteristic values of the solidification parameters of master alloys were read out from the respective curves.

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

## 1. Introduction

Additions alloys Cr, Mo, W, Co, and recently also Ti and B [1-3], considered complex modifiers of the new cast aluminium alloys. This form silicides, aluminides and other intermetallic phases which, occurring as separate precipitates, can play the role of the nuclei of crystallisation [4]. The presence of silicides and aluminides indicates that they can improve the characteristics of  $\alpha$ (Al) and  $\beta$ (Si) solutions. The inclusions of intermetallic phases contribute to an increase of the alloy hardness. In this paper [2], the crystallisation of  $Al_{12}W$ ,  $Al_{12}Mo$  aluminides,  $Cr_3Si$ ,  $W_3Si$ ,  $Mo_3Si$  silicides, and complex intermetallic phases of  $Al_{13}Cr_4Si_2$  type improves the hardening behaviour of  $\alpha$ (Al) solution, which means considerable improvement of the mechanical properties ( $R_m = 400-520MPa$  and hardness from 145 to 210HB, with elongation  $A_5 = 0,5$  to 5,0%) [4].

## 2. Methods of investigation

A much more effective method of introducing the high-melting point elements (Co, Ni and Ti) to alloy melt is by preparing master alloys of predetermined chemical composition. The general assumption is that master alloys of this type should play a double role:

- introduce to silumin the intermetallic compounds of  $Al_xMe_y$ , which can play the role of heterogeneous nuclei,
- introduce to silumin ( $\alpha$  solution) the alloying additives that will harden this solution, e.g. during heat treatment.

So, the composition of master alloys should include a eutectic ( $Al+Al_xMe_y$ ) and a hypereutectic (primary) intermetallic compound of  $Al_xMe_y$ . The Al – Me master alloys should have possibly low solidification point, which will ensure the presence of the heterogeneous nuclei of  $Al_xMe_y$  in the liquid phase, and

hence the required content of the low-melting point eutectic in master alloy. The temperature should not go much in excess of a temperature optimum for the silumin casting process. Excessive overheating of liquid metal may increase the gas content in melt and result in porosities after casting solidification, deteriorating the utilisation properties. Optimum pouring temperature of hypereutectic silumins containing from 18 to 22% Si ranges from 820 to 850°C. Hence it follows that the temperature  $T_{liq}$  of the master alloy should not exceed 900°C. From the Al - Me phase equilibrium diagram it follows that the point of liquidus raises very rapidly with the increasing content of alloying constituent. On one hand, the content of the alloying constituent should be the highest possible, since it raises the effectiveness of modification when the master alloy is introduced to silumin, while – on the other – there are some restrictions imposed by temperature. Therefore the correct composition of master alloy demands that during melting a high dissolution rate of the alloying constituent in aluminium is ensured. This requires maintaining the temperature of liquid aluminium at a proper level, using proper melt coating slags, and observing optimum melting time, ensuring maximum dissolution rate of the alloying constituent.

The analysis of phase equilibrium diagrams [5] enables drawing the following conclusions:

1. In Al – Co system, the temperature of 900°C is corresponding to the content of 5 at.% Co (10 wt.% Co). At that temperature, the  $Al_4Co$  compound is precipitating from the liquid; it is present as a constituent of Al +  $Al_4Co$  eutectic, crystallising at a temperature of 651÷657°C.
2. In Al – Ni system, the temperature of 900°C is corresponding to the content of 17 at.% Ni (30 wt.% Ni). At that temperature, the  $Al_3Ni$  compound is precipitating from the liquid; it is present as a constituent of Al +  $Al_3Ni$  eutectic, crystallising at a temperature of 650÷640°C.
3. In Al – Ti system, the temperature of 900°C is corresponding to the content of 3 at.% Ti (5,2 wt.% Ti). At that temperature, the  $TiAl_3$  compound is precipitating from the liquid; it is present as a constituent of Al+ $TiAl_3$  eutectic, crystallising at a temperature of 665°C.

For selected master alloys, the content levels of the phases crystallising at a temperature of 900°C are compared in Table 1.

Table 1.

Chemical compositions to be obtained in master alloys

Master alloy	The phase	Temperature, °C	at. %	wt. %
Al-Co	$Al_4Co$	651÷657	5 at. % Co 95 at. % Al	10 wt.% Co 90 wt.% Al
Al-Ni	$Al_3Ni$	640÷650	17 at. % Ni 83 at. % Al	30 wt. % Ni 70 wt. % Al
Al-Ti	$TiAl_3$	665	3 at. % Ti 97 at. % Al	5,2 wt. % Ti 94,8 wt.% Al

### 3. The results of investigation

Before the casting process started, the total weight of the metallic charge was determined (1000g) and individual values of the melting loss were established for selected master alloys. Then

the master alloys were melted in a Balzers VSG-02 induction vacuum furnace under the atmosphere of nitrogen N5, having applied the vacuum first.

Molten master alloys were held at a temperature of 1100°C for 15 minutes, and poured next into a bentonite-bonded sand mould. The signal from a Pt-Rh10 thermocouple was fed to a Crystal-digraph PC NT38K multi-channel measuring device, and as a next step, using a Lab W2.25 program, the curves from the thermal analysis ATD were plotted. An example of the ATD curve plotted for an Al-Co and Al-Ni master alloy are shown in Figure 1.

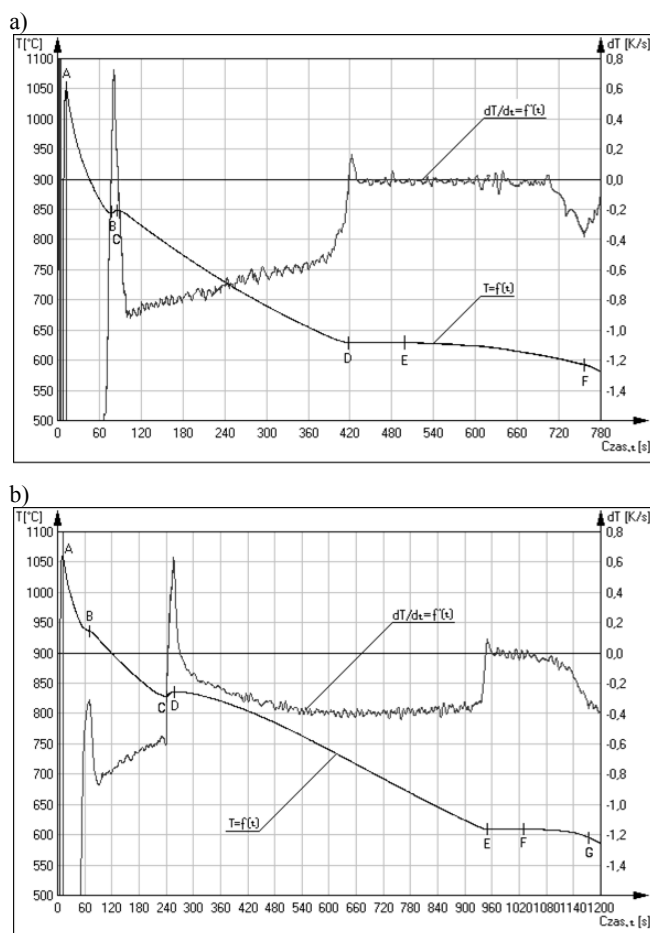


Fig. 1. The curve of ATD thermal analysis plotted for: a) Al-Co and b) Al-Ni master alloy

The, read out from the ATD curves, characteristic parameters describing the solidification process of master alloys are compiled in Table 2.

Table 2.

Parameters of master alloy crystallisation read out from the ATD

Master alloy	Temperature, °C			
	$T_{liq\ phase\ 1}$	$T_{liq\ phase\ 2}$	$T_E$	$T_{sol}$
Al-Co	720	723	631	612
Al-Ni	816	835	610	595
Al-Ti	-	868	647	599

From the region where the casting temperature had been measured, a sample was taken for the chemical analysis executed on a Solaar M6 spectrometer by AAS flame technique (Foundry Research Institute in Cracow), that are compiled in Table 3.

Table 3.

The results of chemical analysis of the composition actually obtained in master alloys

Master alloy	Chemical comp.	Wt. %			The yield addition alloy, %
		Addition alloys	Al	Rest (Fe, S <sub>2</sub> )	
Al-Co	theoretical	10,0	90,0	-	54,00
	real	5,4	94,0	0,60	
Al-Ni	theoretical	30,0	70,0	-	96,33
	real	28,9	70,3	0,80	
Al-Ti	theoretical	5,2	94,8	-	82,70
	real	4,3	95,0	0,70	

To identify the intermetallic phases present in individual master alloys, microstructural examinations were made (Fig. 2), followed by X-ray phase analysis and X-ray microanalysis, that are show in Figure 3.

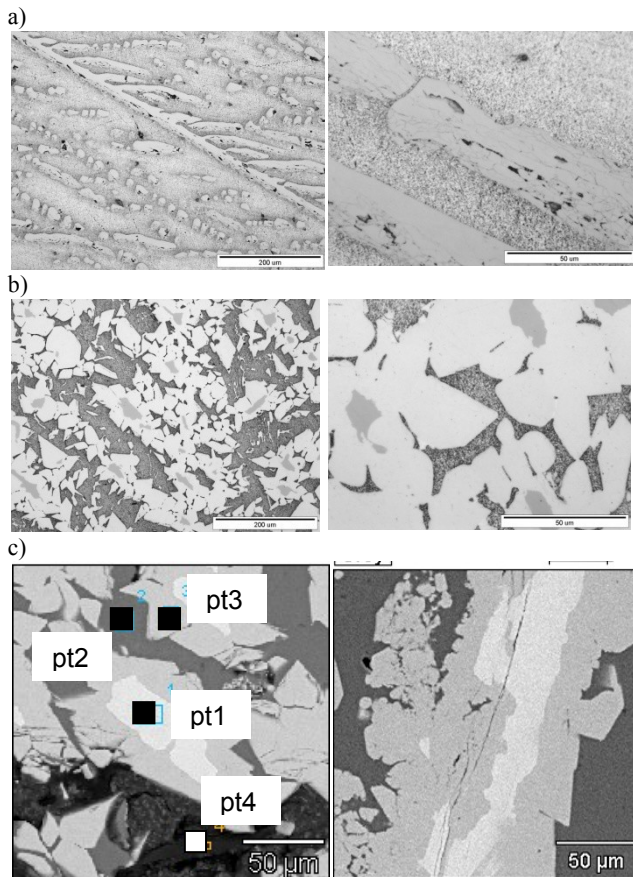
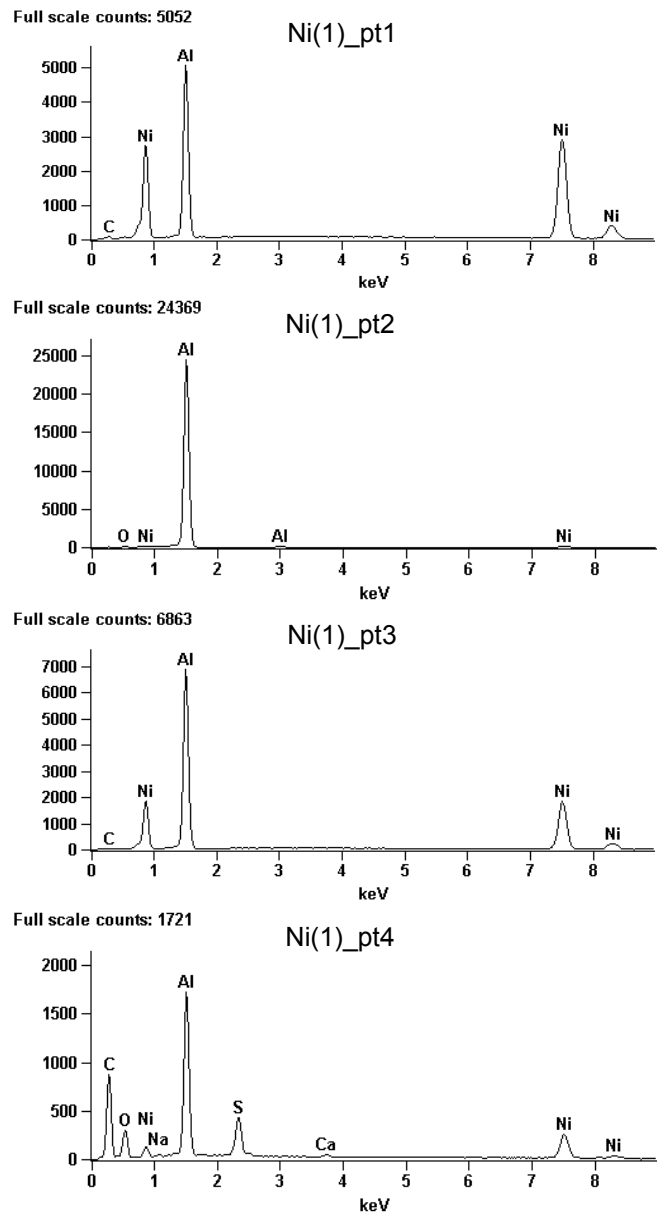


Fig. 2. Microstructures of master alloys: a) Al-Co; b) Al-Ni, c) SEM micrograph master alloy Al-Ni



We %	Na-K	Al-K	S-K	Ca-K	Ni-K
Ni pt1		43,20			56,80
Ni pt2		95,14			4,86
Ni pt3		57,66			42,34
Ni pt4	1,32	53,73	16,58	0,90	27,47

At %	Na-K	Al-K	S-K	Ca-K	Ni-K
Ni pt1		62,34			37,66
Ni pt2		97,70			2,30
Ni pt3		74,77			25,23
Ni pt4	1,88	65,16	16,92	0,73	15,31

Fig. 3. X-ray microanalysis and results of EDS in points of Al-Ni master alloy

## 4. Summary and discussion

As follows from the literature and own investigations, the selected Al – Me (Co, Ni and Ti) master alloys should have a predetermined crystallisation temperature, which will ensure the presence of the heterogeneous  $Al_xMe_y$  nuclei in the liquid phase, combined with rapid melting and dissolution of the alloying constituents in liquid silumin. An optimum temperature of casting the hypereutectic piston silumins containing from 18 to 22% Si ranges from 820 to 850°C [3]. Hence it follows that the temperature  $T_{liq}$  of the master alloy should not go much in excess of this range. From the phase equilibrium diagram of Al - Me systems it follows that the point of liquidus increases rapidly with the increasing content of an alloying constituent, and for this reason, in calculation of the atomic and weight percent fractions of master alloys, the temperature of 900°C has been adopted. This explains the varied content of individual high-melting point elements in master alloys (Tabl. 1).

The next important step in the research program was the development of master alloy melting and casting technology. The most important problem was to ensure during melting the high dissolution rate of the alloying constituent in aluminium, which is considered the condition indispensable for a correct composition of the master alloy. Proper vacuum level and protective atmosphere, and especially the repeatable conditions of crystallisation (in respect of the time-temperature) regime were obtained by experiments.

The thermal analysis ATD was made for all the examined master alloys. From the respective ATD curves, the characteristic crystallisation parameters were read out. Also from ATD diagrams, one can conclude that the pouring temperature ( $T_{max}$ ) is similar in each experiment and amounts to about 1100°C, which is consistent with the initial guidelines developed for the master alloy melting process. The temperatures ( $T_{liq\ fazy\ 1}$  and  $T_{liq\ fazy\ 2}$ ) refer to the temperature at which the primary intermetallic phases of  $Al_xMe_y$ , forming a constituent of the Al –  $Al_xMe_y$  eutectic, start precipitating from the liquid. The next parameters are undercooling ( $T_p$ ), the temperature of the Al –  $Al_xMe_y$  eutectic crystallisation ( $T_E$ ), and the point of solidus ( $T_{sol}$ ), which ends the process of solidification.

As follows from the data compiled in Table 3, the highest yield of the alloying elements offer the Al-Ni (96,3%) master alloys. Slightly lower yield was reported for the Al-Ti (82,7%) master alloys, and the lowest yield was that of tungsten in an Al-Co (54%) master alloy.

The role of master alloys is to introduce to alloy melt the intermetallic  $Al_xMe_y$  phases, which can act as heterogeneous nuclei and harden the  $\alpha$  solution. To confirm the presence of intermetallic phases in the fabricated master alloys, microstructural examinations, X-ray microanalysis and X-ray phase analysis were carried out. Microstructures of the obtained master alloys shown in Figure 2 indicate that the content of alloying additions varies and depends on the yield. In appearance has the microstructure of Al-Ni; against the background of aluminium matrix, one can see the “Christmas tree” precipitates of  $Al_3Ni$ .

## 5. Conclusions

From the studies and analysis of the obtained results, the following conclusions can be formulated:

1. The developed technology of melting and casting of Al-Co, Al-Ni and Al-Ti master alloys offers the highest yield for Al-Ni (96%), Al-Ti (83%) and Al-Co (54%). The yield of the remaining master alloys is at a lower level, though still sufficient for refining of hypereutectic silumins.
2. The guarantee of the yield so high is the correctly conducted process of melting and casting of master alloys, with the required time-temperature parameters kept constant.
3. The intermetallic  $Al_3Ni_2Co$  phase has been detected. They can play the role of substrates for heterogeneous nucleation of silicon crystals in silumins.

## References

- [1] S. Pietrowski, Silumines. Technical University of Łódź. 2001 (in Polish).
- [2] J. Piątkowski, The dissertation scientific paper. Silesian University of Technology, Katowice, 2000 (in Polish).
- [3] Z. Gómy, J. Sobczak, Non-ferrous metals based novel materials in foundry practice. ZA-PIS Cracow 2005 (in Polish).
- [4] S. Pietrowski, Complex silumin, Journal of Achievements in Materials and Manufacturing Engineering, (2007) Issue 1, vol. 24, p. 101-105.
- [5] M. Hansen, K. Anderko, Constitution of binary alloys, McGraw – Hill Book Company, INC, New York 1958.