

Effect of Cr and W on the Crystallization Process, the Microstructure and Properties of Hypoeutectic Silumin to Pressure Die Casting

T. Szymczak *, G. Gumienny, T. Pacyniak

Department of Materials Engineering and Production Systems, Lodz University of Technology,
Stefanowskiego 1/15 Street, 90-924 Łódź, Poland

* Corresponding author. E-mail address: tomasz.szymczak@p.lodz.pl

Received 31.03.2016; accepted in revised form 15.04.2016

Abstract

This article presents the results of studies in the hypoeutectic silumin destined for pressure die casting with the simultaneous addition of chromium and tungsten. The study involved the derivative and thermal analysis of the crystallization process, metallographic analysis and mechanical properties testing. Silumin 226 grade was destined for studies. It is a typical silumin to pressure die casting. AlCr15 and AlW8 preliminary alloys were added to silumin. Its quantity allowed to obtain 0.1, 0.2, 0.3 and 0.4% of Cr and W in the tested alloy. Studies of the crystallization process as well as the microstructure of the silumin poured into DTA sampler allowed to state the presence of additional phase containing 0.2% or more Cr and W. It has not occurred in silumin without the addition of above mentioned elements. It is probably the intermetallic phase containing Cr and W. DTA studies have shown this phase crystallizes at a higher temperature range than α (Al) solid solution. In the microstructure of each pressure die casting containing Cr and W the new phases formed. Mechanical properties tests have shown Cr and W additives in silumin in an appropriate amount may increase its tensile strength R_m (about 11%), the yield strength $R_{p0.2}$ (about 21%) and to a small extent elongation A.

Keywords: Theory of crystallization, Innovative foundry technologies and materials, Pressure die casting, Multicomponent silumins, DTA method.

1. Introduction

Silumins can be cast to an expendable moulds as well as permanent. Casting into sand or ceramic moulds results in the formation of the unfavorable coarse grain microstructure. It is caused by the relatively low heat transfer from the casting to the mould. Higher heat transfer can be achieved by the use of permanent or pressure molds. Size reduction in the microstructure and thereby an improvement of silumin properties can be obtained

in this way [1]. The intensification of the cooling process can also be achieved using an appropriate cooling medium of metal mould [2]. The microstructure as well as mechanical properties of Al-Si alloys can also be improved through their refining, modification, heat treatment, using an alloying elements or the crystallization in a magnetic field [3-5].

Among the alloying elements the group of high-melting elements such as Cr, V, Mo and W can be distinguished. The results comprising silumins containing these additives are

presented in papers [6-13]. The aforementioned elements are characterized by a lack of solubility in aluminum in the solid state with a consequent causes the formation of intermetallic phases in the silumin microstructure. These phases significantly increase the fragility of the alloy. A particular importance may have the use of Cr, Mo, V and W in silumins for pressure casting. A relatively small wall thickness of the pressure die casting, which generally does not exceed 6 mm, and a high heat transfer from the casting to the permanent mould may cause a supersaturation of solid solution with aforementioned elements and consequently improving alloy properties. In the literature you can find information about silumin to pressure die casting containing a variety of combinations W, V and Mo [1, 14, 15].

This paper is devoted to the study of hypoeutectic silumin destined for pressure die casting containing Cr and W.

In Figure 1 the Al-Cr phase diagram is presented [16]. The types of phases in the Al-Cr phase diagram and its crystallographic parameters are presented in Table 1 [16].

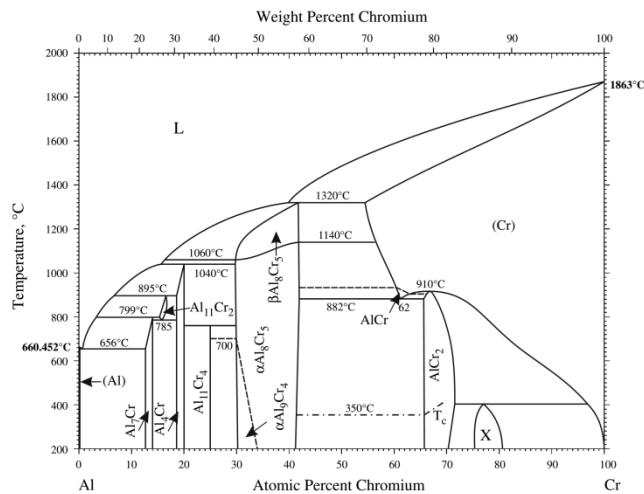


Fig. 1. Aluminum-chromium phase diagram [16]

Table 1. The types of phases in the Al-Cr phase diagram and its crystallographic parameters [16]

Phase	Composition, at % Cr	Pearson Symbol	Space group
(Al)	0	<i>cF4</i>	<i>Fm$\bar{3}m$</i>
Al ₇ Cr	12.5 – 14	<i>mC104</i>	<i>C2/m</i>
Al ₁₁ Cr ₂	15.2 – 17	<i>mP48</i>	<i>P2</i>
Al ₄ Cr	18.5 – 20	<i>mP180</i>	<i>P2/m</i>
Al ₁₁ Cr ₄	25	<i>aP30</i>	<i>P$\bar{1}$</i>
α Al ₉ Cr ₄	30 – 34	<i>cI52</i>	<i>I$\bar{4}3m$</i>
β Al ₈ Cr ₅	30 – 42
α Al ₈ Cr ₅	30 – 42	<i>hR26</i>	<i>R$\bar{3}m$</i>

The solubility of chromium in aluminum according to [16] amounts to 0%, while according to [17] is negligible and amounts to 0.71% at a temperature of 661.5°C and decreases to 0.0% with decrease in the temperature. The maximum solubility of Al in Cr takes place at the temperature of 1320°C and amounts to 45.5%. β Al₈Cr₅, Al₄Cr, Al₁₁Cr₂ and Al₇Cr phases are formed during the peritectic transformations taking place at a temperature of 1320,

1040, 895 and 799°C, respectively. AlCr₂, Al₁₁Cr₄ and X phases are formed during peritectoid transformations at a temperature of 910, 760 and ~400°C, respectively.

In papers [14, 17] an aluminum-tungsten phase diagram is presented. According to the data contained in aforementioned papers there is the possibility of crystallize intermetallic phases as the product of peritectic transformations as well as there is the lack of solubility of tungsten in aluminum in the solid state. Al solubility in W amounts to maximum 2.2% at 1302°C. The addition of tungsten resulting in the increase in the temperature of Al-W alloy crystallization.

In paper [18] Cr-W phase diagram is presented. It follows from it Cr and W create a solid solution (α Cr, W) with unlimited solubility of these two elements characterized by body centered cubic crystal structure (A2). (α Cr, W) solution at a temperature of 1677°C is decomposed into two solid solutions (α 1) - rich in Cr and (α 2) - rich in W.

2. Methodology of research

The tested silumin was melted under production conditions in Wifama-Prexer Company, Ltd. For testing the hypoeutectic silumin 226 grade to pressure die casting was used. Its chemical composition is given in Table 2.

Table 2. The chemical composition of the tested 226 silumin

Chemical composition, % mass.							
Si	Cu	Zn	Fe	Mg	Mn	Ni	
8.52	2.04	0.87	0.95	0.27	0.23	0.10	
						Al	rest

Silumin was melted in a shaft furnace heated with gas with a capacity of 1.5 tons. After melting silumin was refined with use of solid refiner Ecosal Al 113.S. Refining process was carried out inside the shaft furnace. After smelting and refining silumin was poured into a ladle, where deslagging took place and afterwards transported to the holding furnace near to the pressure casting machine Idra 700S with a horizontal cold pressure chamber. Inside the holding furnace the AlCr15 and AlW8 preliminary alloys were added to silumin. The concentration of Cr and W amounted to approximately 0.1; 0.2; 0.3 and 0.4%. The research of 226 silumin without Cr and W additives were also performed (chemical composition as in Tab. 2).

For each chemical composition of silumin pressure die castings of the roller shutter cover were made. The vast majority of the casting wall thickness was 2 mm. For testing the crystallization process the derivative thermal analysis (DTA) was used. It is a universal method for the study of the crystallization process of various alloys. It was previously used to study: iron, aluminum, copper, magnesium and cobalt alloys [19-22].

For recording the DTA curves PtRh10-Pt thermoelement was used. It was located in the thermal center of the DTA10-TUL sampler made of moulding sand. Before filling the sampler each alloy was overheated to ~1100°C.

The tests of the mechanical properties of pressure-cast silumins were carried out. In the tensile test the tensile strength R_m , yield strength $R_{p0.2}$ and elongation A were determined. Tensile tests were performed on an Instron 3382 testing machine. To perform the test, a flat specimens with a rectangular cross

section 2×10 mm were used. This cross-section is recommended by the standard [23]. For each tested silumin three specimens from die casting were cut out. Tensile test was performed using the speed 1 mm/min. Brinell hardness test of the silumin was carried out with use of HPO-2400 hardness tester machine. To the test the ball with a diameter $d = 2.5$ mm, force 613 N and time 30 seconds were used.

Silumin microstructure was studied on specimens cut out from pressure die castings. Metallographic specimens were etched with 2% aqueous solution of HF and viewed on a metallurgical microscope Eclipse MA200 by Nikon.

3. Results

In Figure 2 DTA curves of "pure" silumin 226 without Cr and W are presented. The crystallization process and microstructure of silumin are also shown in papers [1, 14-15].

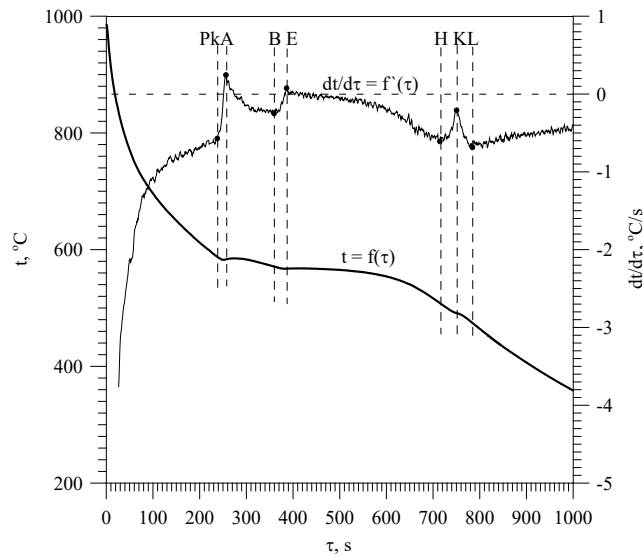


Fig. 2. Representative DTA curves of 226 silumin

There are three thermal effects on the curves in Fig. 2. PkAB effect was caused by the crystallization of α (Al) solid solution. Subsequent thermal effects, BEH and HKL are stemmed from the triple eutectic crystallization: $\alpha + Al_9Fe_3Si_2 + \beta$ and quadruple: $\alpha + Al_2Cu + AlSiFeCuMgMnNi + \beta$. Values of the temperature "t", and the cooling rate "dt/dτ" of the tested silumins are shown in Table 3 (a, b). The crystallization process took place at the temperature between $t_{Pk} = 588^\circ C$ and $t_L = 474^\circ C$. DTA curves of 226 silumin containing approximately 0.1% Cr and W have a similar run as the curves of silumin without these additives. There are three similar thermal effects as it did in the case of "pure" silumin. It results from the data presented in Tab. 3 (a) the additives 0.1% Cr and W has increased the temperature in each characteristic point of the DTA curves. The lack of solubility of Cr and W in solid solutions at ambient temperature and relatively low cooling rate in the DTA sampler as well as the lack of additional thermal effects on the DTA curves of the silumin containing approximately 0.1% Cr, and W may cause locating these elements in the intermetallic phases. The most likely is the

occurrence of Cr and W in the quadruple eutectic. This eutectic should be in the form: $\alpha + Al_2Cu + AlSiFeCuMgMnNiCrW + \beta$ in silumin containing 0.1% Cr and W.

DTA curves of silumin containing approximately 0.2% Cr, and W are shown in Figure 3.

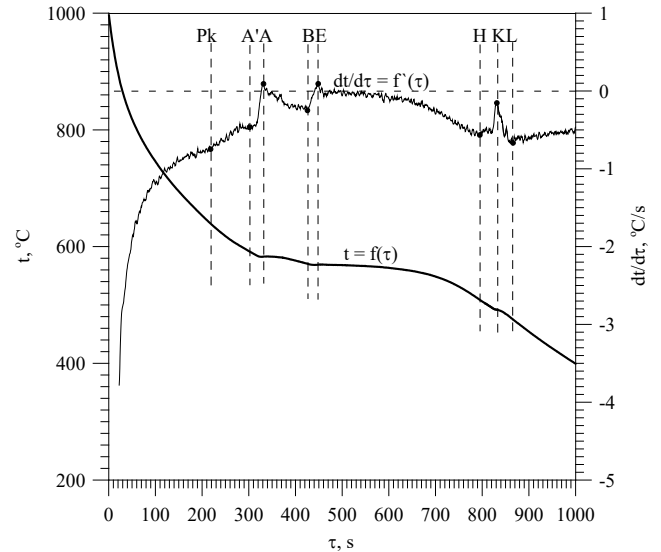


Fig. 3. Representative DTA curves of silumin containing approximately 0.2% Cr and W

The presented data show the additions of Cr and W in amount of approximately 0.2% results in an additional thermal effect marked as PkA' in the DTA curves (Fig. 3). This effect occurs before the A'AB effect stemming from α (Al) crystallization. Its occurrence in the curves is probably caused by crystallization of intermetallic phases containing Cr and W.

Table 3 (a, b).

Values of temperature (a) and cooling rate (b) in the characteristic points of the 226 silumin containing 0.1 - 0.4% Cr and W

Concentration Cr and W, %	Temperature t, °C							
	Pk	A'	A	B	E	H	K	L
0.0	588	-	583	571	568	508	491	474
0.1	599	-	585	581	572	515	498	483
0.2	639	592	583	571	569	509	492	475
0.3	648	598	589	574	572	514	497	481
0.4	633	593	589	578	575	507	497	473

Concentration Cr and W %	dt/dτ, °C/s							
	Pk	A'	A	B	E	H	K	L
0.0	-0.57	-	0.24	-0.25	0.08	-0.61	-0.21	-0.69
0.1	-0.59	-	0.10	-0.27	0.07	-0.59	-0.01	-0.69
0.2	-0.75	-0.47	0.09	-0.25	0.09	-0.57	-0.15	-0.67
0.3	-0.70	-0.59	0.25	-0.28	0.09	-0.68	-0.16	-0.68
0.4	-0.72	-0.55	0.05	-0.26	0.07	-0.60	-0.09	-0.63

The occurrence of the aforementioned phase extends the crystallization temperature range of silumin. It results from Tab. 3 (a) for silumin containing about 0.2% Cr, this range is from $t_{Pk} = 639^{\circ}\text{C}$ to $t_L = 475^{\circ}\text{C}$. The other two thermal effects (BEH and HKL) in the curves are similar to effects in the curves of silumin containing 0.1% Cr and W. These effects are caused by the eutectic mixtures crystallization: triple ($\alpha + \text{Al}_9\text{Fe}_3\text{Si}_2 + \beta$) and quadruple ($\alpha + \text{Al}_2\text{Cu} + \text{AlSiFeCuMgMnNiCrW} + \beta$), respectively. Further increasing concentration of chromium and tungsten to 0.3% and 0.4 did not change DTA curves in relation to the silumin containing approximately 0.2% Cr and W.

Figure 4 shows an exemplary microstructure of the silumin containing approximately 0.4% Cr and W poured into DTA sampler. Intermetallic phases containing Cr and W are visible in the microstructure as a light gray precipitates with complex structure. They have occurred also in the microstructure of silumin containing 0.2 and 0.3% Cr and W poured into DTA sampler.

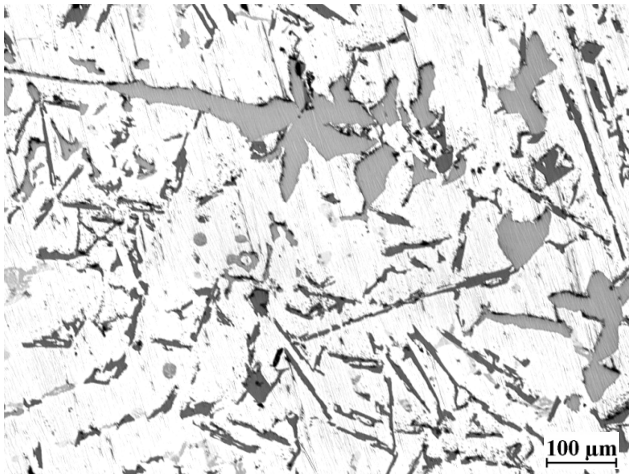
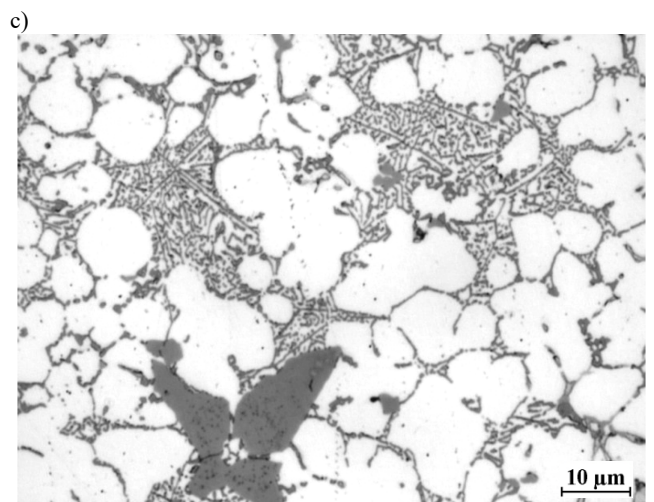
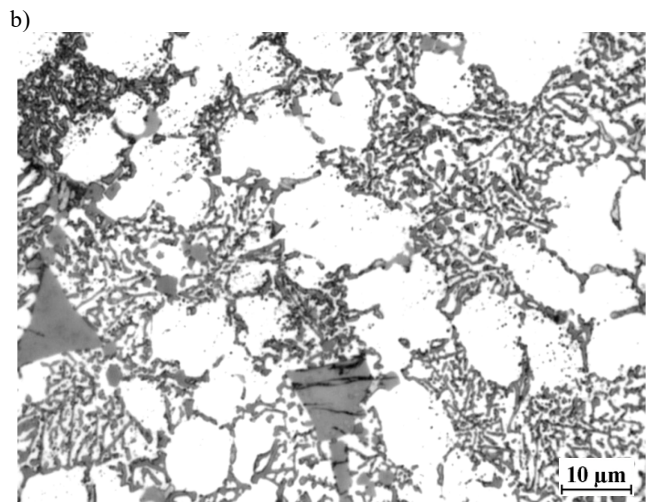
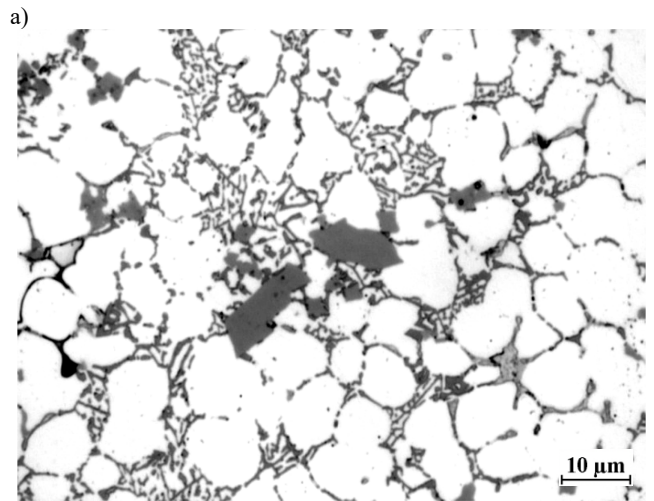


Fig. 4. The microstructure of silumin containing approximately 0.4% Cr and W obtained in the DTA sampler: α , $\alpha + \text{Al}_9\text{Fe}_3\text{Si}_2 + \beta$, $\alpha + \text{Al}_2\text{Cu} + \text{AlSiCuFeMgMnNi} + \beta$

The microstructure of 226 silumin in pressure die casting is presented in papers [1, 14-15]. It consists of a α solid solution dendrites and eutectic mixtures: triple ($\alpha + \text{Al}_9\text{Fe}_3\text{Si}_2 + \beta$) and quadruple ($\alpha + \text{Al}_2\text{Cu} + \text{AlSiCuFeMgMnNi} + \beta$). It is similar as in the DTA sampler in terms of phase composition. There are differences only in case of precipitates size. For alloy from the DTA sampler the size of α dendrites as well as eutectic compositions is relatively large. It is caused by the relatively slow crystallization process inside the sand mold. The crystallization process of casting wall thickness $g \approx 2$ mm in the pressure die casting runs much more intense. It results in a substantial fragmentation of the microstructure.

The microstructure of pressure die cast silumin with Cr and W is shown in Figure 5 (a-d).



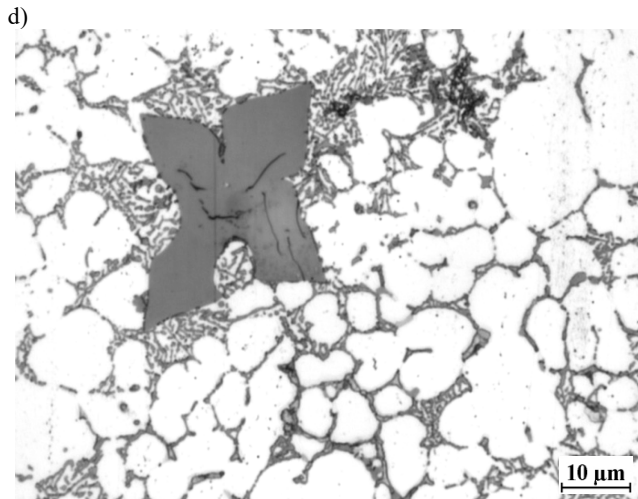


Fig. 5 (a-d). The microstructure of die casting made of the tested silumin containing Cr and W approximately: a – 0.1%, b – 0.2%, c – 0.3% i d – 0.4%: α , $\alpha + \text{Al}_6\text{Fe}_3\text{Si}_2 + \beta$, $\alpha + \text{Al}_2\text{Cu} + \text{AlSiCuFeMgMnNiCrW} + \beta$

Cr and W additives in amount of 0.1 - 0.4% have caused the crystallization of an additional phase which are not occurred in alloy without these additives. This is probably the intermetallic phase containing Cr and W. These phases are characterized by structure similar to silicon and its size increases with increasing concentration of Cr and W. In silumin containing ~0.1% Cr and W the biggest separations can reach ~10 μm at a concentration of ~0.2% Cr and W, and they can reach up to ~15 μm . Additives 0.3 and 0.4% Cr and W cause creating 20-30 μm size phases.

The mechanical properties of the pressure die casting silumin are shown in Table 4 and in Figure 6 (a-c).

Table 4.

The mechanical properties of the tested silumin, without and with the addition of Cr and W

Concentratio n Cr and W, %	Mechanical properties			
	R_m , MPa	$R_{p0,2}$, MPa	A, %	HB
0.0	251	120	3,7	113
0.1	279	145	3,9	113
0.2	266	139	3,9	113
0.3	264	126	3,6	108
0.4	228	130	2,6	110

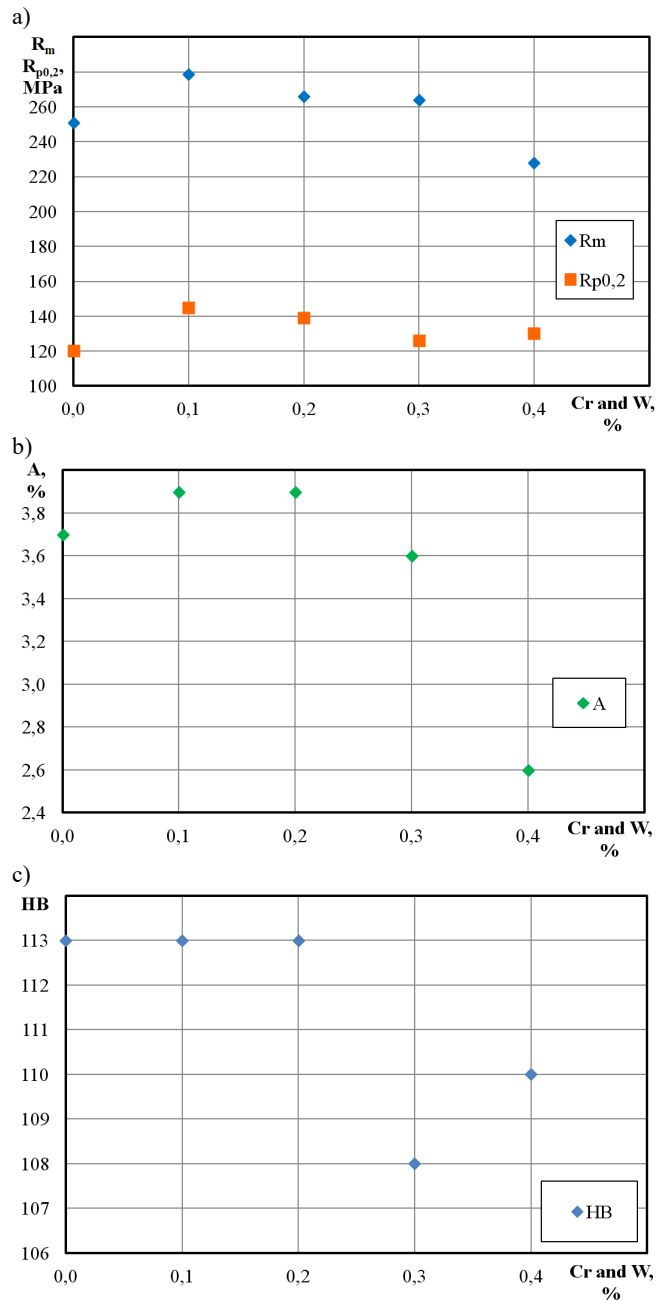


Fig. 6 (a-c). The mechanical properties of the tested silumin, without and with the addition of Cr and W: a – R_m and $R_{p0,2}$; b – A; c – HB

The largest value of tensile strength $R_m = 279$ MPa and the yield strength $R_{p0,2} = 145$ MPa was obtained for the silumin containing about 0.1% Cr and W. It resulted in an increase in 11 and 21% in relation to the silumin without Cr and W. The largest value of elongation $A = 3.9\%$ was obtained for silumin with 0.1 and 0.2% Cr and W. Accordingly, the increase in "A" was 5% in relative to the "pure" 226 silumin. However there was not an increasing in HB hardness in silumins containing Cr and W.

4. Conclusions

The test results indicated the following conclusions:

- there are three thermal effects derived from the phase α (Al) crystallization, triple and quadruple eutectics in the DTA curves of the silumin without additives and containing 0.1% Cr and W,
- chromium and tungsten additives to silumin in an amount of 0.2, 0.3 and 0.4% resulting in an additional thermal effect in the DTA curves; it probably comes from the crystallization of phase containing the aforementioned elements,
- in the pressure die casting microstructure of silumin containing Cr and W the new phases are formed which did not occur in the "pure" 226 silumin,
- Cr and W additives in a suitable amount resulted in an increase the tensile strength R_m , the yield strength $R_{p0.2}$ and elongation A of the tested alloy.

Acknowledgements

Project financed from means of the National Centre for Research and Development in years 2013 ÷ 2015 as project UDA-POIG.01.04.00-10-079/12.

References

- [1] Szymczak, T., Gumienny, G., Walas, K. & Pacyniak, T. (2015). Effect of Tungsten and Molybdenum on the Crystallization, Microstructure and Properties of Silumin 226. *Archives of Foundry Engineering*. 15(3), 61-66.
- [2] Władysiak, R. & Kozuń, A. (2015). Structure of AlSi20 Alloy in Heat Treated Die Casting. *Archives of Foundry Engineering*. 15(1), 113-118.
- [3] Pietrowski, S. (2001). *Silumins*. Łódź: Publishing house of Lodz University of Technology.
- [4] Piątkowski, J. (2013). Influence of overheating temperature on the shape of primary silicon crystals in hypereutectic Al-Si cast alloy. *Solid State Phenomena*. 203-204, 417-422.
- [5] Wróbel, T. & Szajnar, J. (2013). Modification of pure Al and AlSi2 alloy primary structure with use of electromagnetic stirring method. *Archives of Metallurgy and Materials*. 58(3), 941-944.
- [6] Binczyk, F. & Piątkowski, J. (2003). Crystallization of AlSi17 silumin with additive of Cr, Co and Ti. *Archives of Foundry*, 3(9), 39-44. (in Polish).
- [7] Sahoo, K.L. & Pathak, B.N. (2009). Solidification behaviour, microstructure and mechanical properties of high Fe-containing Al-Si-V alloys. *Journal of Materials Processing Technology*. 209, 798-804.
- [8] Sahoo, K.L., Das, S.K. & Murty B.S. (2003). Formation of novel microstructures in conventionally cast Al-Fe-V-Si alloys. *Materials Science and Engineering*. 355(1-2), 193-200.
- [9] Pietrowski, S., Władysiak, R., Pisarek, B. (1999). Crystallization, structure and properties of silumins with cobalt, chromium, molybdenum and tungsten admixtures. In International Conference Light Alloys and Composites, 13-16 May 1999 (77-83).
- [10] Pietrowski, S., Władysiak, R. & Pisarek, B. (1998). Eutectic silumin with an additions of Cr, Mo, W, and Co. *Solidification of metals and alloys*. 13, 103-108.
- [11] Pietrowski, S. & Szymczak, T. (2009). Silumins alloy crystallization. *Archives of Foundry Engineering*. 9(3), 143-158.
- [12] Pietrowski, S., Szymczak, T., Siemińska-Jankowska, B. & Jankowski, A. (2010). Selected characteristic of silumins with additives of Ni, Cu, Cr, Mo, W and V. *Archives of Foundry Engineering*. 10(2), 107-126.
- [13] Pietrowski, S. & Szymczak, T. (2010). Modification of silumins with an alloying elements. In S. Pietrowski (Eds.), *Tendencies of Optimization of the Production System in Foundries*. 277-290. Katowice-Gliwice: Polish Academy of Sciences, Foundry Commission. (in Polish).
- [14] Szymczak, T., Gumienny, G. & Pacyniak, T. (2015). Effect of tungsten on the solidification process, microstructure and properties of silumin 226. *Transactions of the Foundry Research Institute*. 55(3), 3-14.
- [15] Szymczak, T., Gumienny, G. & Pacyniak, T. (2015). Effect of Vanadium and Molybdenum on the Crystallization, Microstructure and Properties of Hypoeutectic Silumin. *Archives of Foundry Engineering*. 15(4), 81-86.
- [16] Okamoto, H. (2008). Al-Cr (Aluminum-Chromium). *Journal of Phase Equilibria and Diffusion*. 29(1), 111-112. DOI: 10.1007/s11669-007-9225-4
- [17] Alloy Phase Diagrams. ASM Handbook Vol. 3. 1992.
- [18] Nagender Naidu, S.V., Sriramamurthy, A.M. & Rama Rao, P. (1984). The Cr-W (Chromium-Tungsten) System. *Bulletin of Alloy Phase Diagrams*. 5(3), 289-292.
- [19] Pietrowski, S., Pisarek, B., Władysiak, R., Gumienny, G. & Szymczak, T. (2009). TDA curves of metals alloys and the control of their quality. In Szajnar J. *Advances In Theory and Practice Foundry*, 345-377, Katowice – Gliwice, PAN. (in Polish).
- [20] Pisarek, B.P. (2013). Model of Cu-Al-Fe-Ni Bronze Crystallization. *Archives of Foundry Engineering*. 13(3), 72-79.
- [21] Rapiejko, C., Pisarek, B., Czekaj, E. & Pacyniak, T. (2014). Analysis of the Crystallization of AZ91 Alloy by Thermal and Derivative Analysis Method Intensively Cooled in Ceramic Shell. *Archives of Foundry Engineering*. 14(1), 97-102.
- [22] Kacprzyk, B., Szymczak, T., Gumienny, G. & Klimek, L. (2013). Effect of the Remelting on Transformations in Co-Cr-Mo Prosthetics Alloy. *Archives of Foundry Engineering*. 13(3). 47-50.
- [23] PN-EN 1706:2011. Aluminum and aluminum alloys. Castings. The chemical composition and mechanical properties. (in Polish).