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THE NEW TYPE OF Al-Si-Mg Ca ALLOYS WITH DIFFERENT Ca AND THEIR IDENTIFICATION USING OF THE COLOR METALLOGRAPHY

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НОВЫЙ ТИП СПЛАВОВ Al-Si-Mg Ca С РАЗЛИЧНЫМИ Ca И ИХ ИНДЕТИФИКАЦИОННОЕ ИСПОЛЬЗОВАНИЕ ДЛЯ ЦВЕТНОЙ МЕТАЛОГРАФИИ

Aluminum and aluminum alloys application area is very wide and future uses of aluminum alloys are connected with further development of new alloys, but primarily with production technology and processing. The article presents some analysis of Ca influence considering amount variations such as 0,1% to a 1% Ca in order to offer the optimal amount to achieve desired technological, chemical and mechanical properties. The analysis of new alloys overall structural analysis an separate components identification of new Ca alloy structures using of the color metallography will be also undertaken. The application of color metallography is possible to differentiate and identify the presence of the intermetallic particles with different chemical composition.

Keywords: alloy Al-Si-Mg, color contrast, master alloys, alloying.

Introduction

An alloy AlSi7Mg0,3 is considered to be a classic representative of Al-Si alloys. The alloys is used for thin, extremely complex or medium-duty castings, it belongs to the class of hardening silumins which hardenability is guaranteed by Mg_2SI eliminating phase [1]. Mechanical properties are not the same as those of Al-Si-Ca alloy type, but on the other hand, comparing with the alloys af this type, corrosion resistance is significantly impoved. One of the possibilities how to improve mechanical properties can be rare alkaline earth metals application, which considerably reduces dendrite porosity [2]. The structure and properties of the casting alloys can be affected by adjustments of liquid metals inherent in adding a small quantity of resting properly chosen substance that affects the process of crystallization. The modify is process by witch the melt is treated in order to influence the mechanism of eutectic solidification. For this reason, implements modifying these alloys causing substantial change in the structure, and the exclusion of the eutectic silicon in the form of substantial change in the structure, and the exclusion of eutectic silicon in the form of rods to fiber in the plane of the metallographic sectioning appear rounded grains [1]. Being under modified and hardened condition the alloy reaches tensile strength of 200 MPa. Strength properties of Al-Si-Mg silimin alloy can be positively influenced by vaccination, which provides grain softening, when we can reach the value approaching 300 MPa.

A lot of research projects have been focused on aluminium alloys modifying. However, until now the modification mechanism has not been known exactly and has not been analysed in detail. The modification effect among Al-Si alloys for all elements of groups IA and IIA in the periodic table of elements (alkali metals and alkaline earth metals) is demonstrated, but the only modification of sodium, strontium and antimony has practical importance. The elements added as the modifier, which include calcium, are used less often and their influence on Al-Si modification is currently investigated [3]. Some researches consider calcium as a modifier, other researches take it as a harmful element, because the structure modified calcium is worse quality as in the case of modifying strontium or sodium. With the growing content of calcium (about 0,01 wt%) are together manifested alloys tend to increased oxidation. At the higher calcium content (over 0,14 wt%) forms intermetallic phases $CaSi_2$ and other, yet unidentified composition. These phases increase homogeneity of the structure and reduce the mechanical properties. To reduce the calcium content has proved to be the addition of phosphorus. In addition, calcium strontium cancels the effects of the modifier [2, 3, 5]. In the past calcium was used for finding impurities in aluminum alloys, although the results were not stable. Calcium was also offered to improve electrical conductivity of commercial aluminum.

The information and identification capacity of the structures may by greatly widened by the colour contrast which can by obtained by the surface treatment of metallographic specimens (color etching, vapor deposition) or by treatment of the surface of specimens (anodic oxidation) with the subsequent use of additional attachments of optical microscope (polarized light). The reaction of the surface of the metallographic section and the colour etching agent results in the formation of a transparent film playing the role of an interference coating. The thickness of this coating depends mainly on the chemical compositon of the material of the section and on the etching conditions. If there are significant changes in the chemical composition of the individual microlocations, the thickness of the resultant coating will also change and, consequently, there will be changes in the colour of the individual microlocations already during illumination in the light field [6].

This paper deals with structural analysis AlCa10 addition alloys, its influence on the properties of Al alloys and the analysis possible structural alloys AlCa10. Furthermore, also deals with the process of alloying hypereutectic silumin AlSi7Mg0,3 with different calcium content in terms of structure.

Fluidity testing for different types of alloys

For experimental purposes aluminum alloy from the group of hypereutectic AlSi7Mg0,3 silumins was used. It is a ternary alloy with the initial chemical composition as listed in Tab. 1. Alloying was carried out using calcium in the form of master alloy AlCa10. There was a total of 4 cast melts. The first one was without the addition of master alloys AlCa10 and the other three were with graded amounts of calcium (0,1%, 0,5% and 1% Ca).

Table 1

Entrance chemical composition of alloys AlSi7Mg0,3

Alloy	Chemical composition in % by weight								
	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
AlSi7Mg0,3	7,09	0,105	0,001	0,017	0,230	0,001	0,001	0,003	0,118
	Chemical composition in % by weight								
	B	Be	Ca	Cd	Ga	Li	Na	V	Hliník
	<0,0001	<0,0000	<0,0002	0,0036	0,0131	<0,0000	0,0004	0,0031	<92,41

Alloy fluidity is the ability to fill the form perfectly; it depends on the ratio between the alloy flow speed and its cooling speed. Fluidity test was performed on the shortened Curry spiral. The form was made of sand mixture used by the company Unitherm Ltd. from Jablonec nad Nisou (this company is engaged into the production of standard aluminum alloy castings in sand molds). There was silica sand material, betonies cement, coal powder and 3,5% water. The melt for the experiments was prepared from AlSi7Mg0,3 material, which contained 0%, 0,1%, 0,5% and 1% Ca. Melting took place in a graphite crucible in electrical furnace PEK-1 under 750 °C. After melting the treated melt was always refined from salt, and skimming was removed from the melt surface. After temperature measurement, 720 °C melt was casted into a casting mold with the shortest delay. The casting time which did not exceed 5 seconds was kept. In the Fig. 1 there are casting spirals and in the Tab. 2 there are Curry spiral measured values for each alloy.

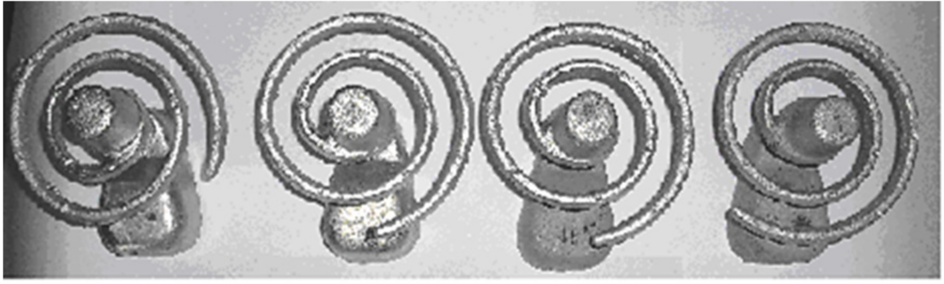

Fig. 1. Casting spirals for Curry fluidity test

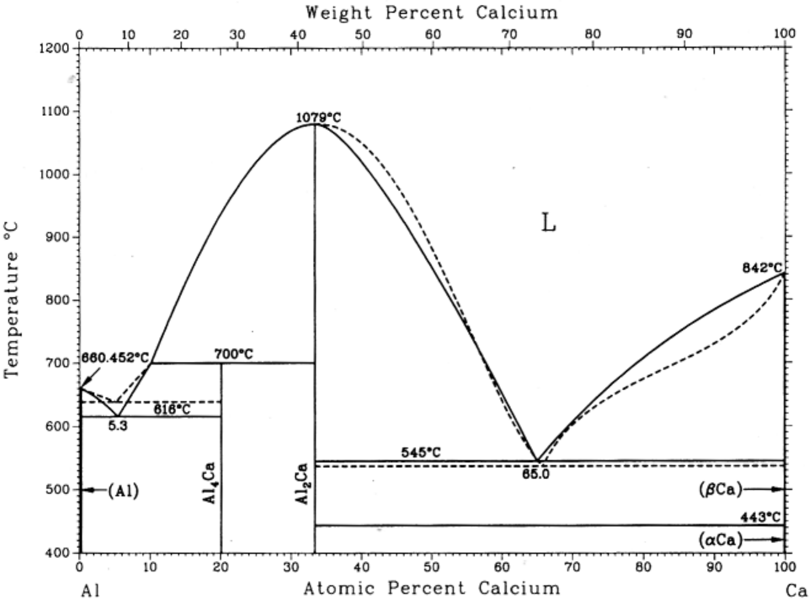

Fig. 2. The binary diagram Aluminium – Calcium

Table 2

Curry spiral measured values for each alloy AlSi

Alloy	Curry spiral values [cm]			
AlSi7Mg0,3	A = 0% Ca	B = 0,1% Ca	C = 0,5% Ca	D = 1,0% Ca
	80,1	70,0	88	93

Metallographis analysis of the addition alloys AlCa10

In terms of a binary Al-Ca diagram (Fig. 2) and the observation of the structure of the addition alloys AlCa10 it can be stated, it is hypoeutectic alloy, the eutectic point of 7,6% Ca. Structure of master alloys containing eutectic (α + $CaAl_4$) and coarse plates phase $CaAl_4$ [7].

Examination of the master alloys AlCa10 showed the presence of the metallurgical defects in the structure to the form of large pore, the material also shoes considerable structural heterogeneity, in the distribution of the $CaAl_4$ plates plates (Fig. 3).

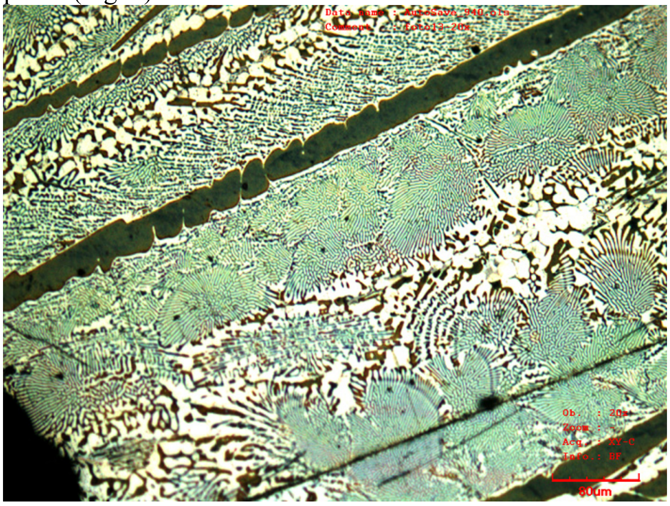

Fig. 3. The microstructure of master alloys AlCa10 with (200x magnification)

Preparation and metallographic analysis AlSi7Mg0,3 new alloys, with different Ca

Preparation of alloy melts AlSi7Mg0,3 with different Ca. For experimental purposes hypereutectis AlSi7Mg0,3 silumins was used, with the initial chemical composition as listed in Tab. 1 Alloying was carried out using calcium in the form of master alloy AlCa10. There was a total of 4 cast melts, the first one was without the addition of master alloy AlCa10 and the other three were with graded amounts of calcium 0,1%, 0,5% and 1% Ca. The individual operations of melting refining and allowing were carried out in an oven at 720°C. At each melt was treated with purified salt melt and the melt surface was withdrawn smear. The melt was purified into a metal way gravity molds preheated to a temperature of 220°C.

Metallographic analysis of different type sof alloys AlSi7Mg0,3 with different Ca. Metallographic thin sections were prepared to evaluate the microstructure of AlSi7Mg0,3 (0%, 0,1%, 0,5% and 1% Ca) alloy casting. The microstructure of the prepared casts was analyzed using color contrast method after etching potassium permanganate solution in alkaline medium of sodium hydroxide. These prepared samples were observed by the means of laser confocal microscope OLYMPUS LEXT OLS 3100.

The first set of sample cast was without addition the calcium is the starting microstructure hypereutectic unmodified silumin, which is composed of α-phase grains and eutectic silicon eutectic formed platelets distributed in solid solution α, that metallographic sectioning needles appear dark gray color, even with the addition of calcium is seeing considerable between dendrites porosity (Fig. 4).

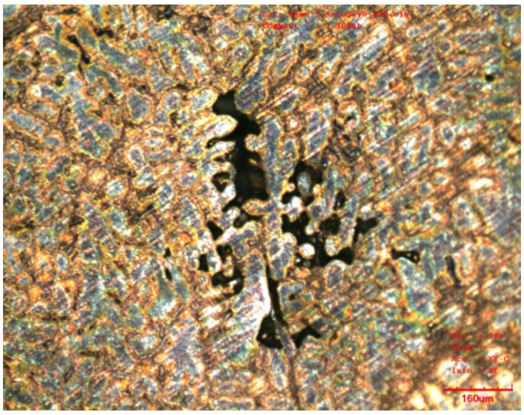

Fig. 4. The microstructure of alloys AlSi7Mg0,3 without the addition of Ca (100x magnifycationt)

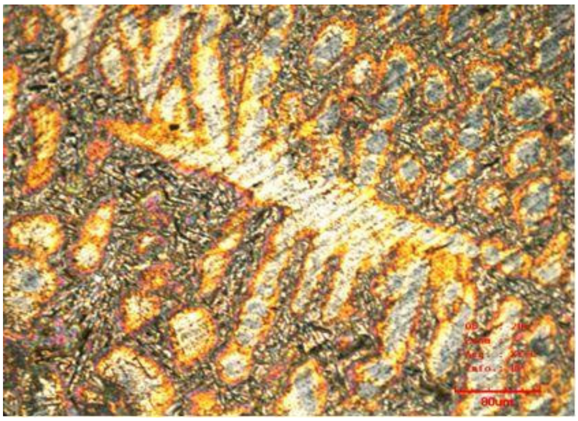

Fig. 5. The microstructure of alloy AlSi8Mg0,3 with addend amount of calcium 0,1% Ca (200x magnification)

The amount of calcium contained in the second cast was 0,1% Ca. A substantial modification effect of calcium on the resulting structure is noticed. The structure shows rounded Si particles of granular or elongated shapes (Fig. 5). On the whole, it is very fine-grained structure.

The amount of calcium addend in the third cast was 0,5% Ca. The increase in porosity in the shape of local clusters and the presence of granular particles of eutectic silicon is evident. The separate coarse dark needles (spatial plates) of intermetallic compounds are also noticed in the structure (Fig. 6).

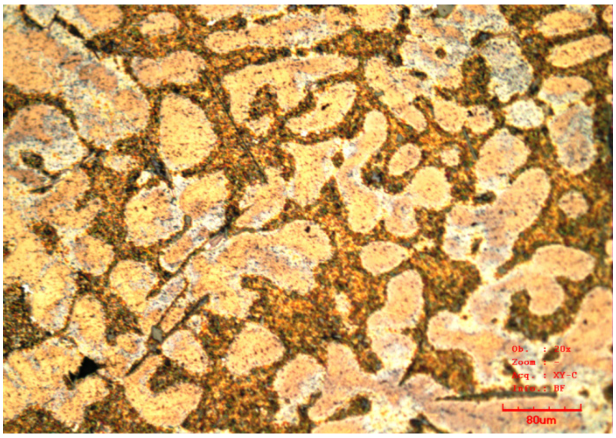

Fig. 6. The microstructure of alloy AlSi8Mg0,3 with addend amount of calcium 0,5 % Ca (200x magnification)

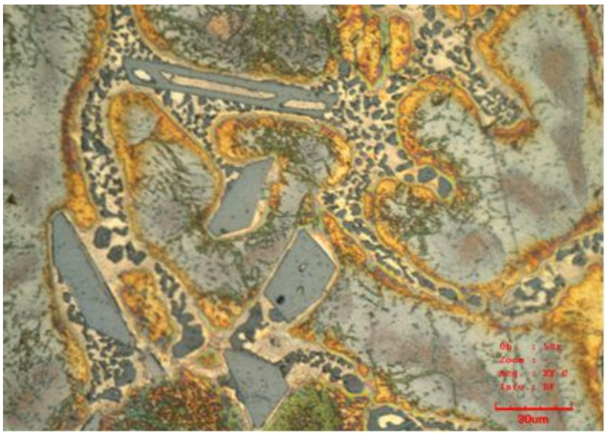

Fig. 7. The microstructure of alloy AlSi8Mg0,3 with addend amount of calcium 1 % Ca (200x magnification)

The amount of calcium contained in the last fourth cast was 1% Ca. The local appearance of coarsen eutectic silicon particles and further increase in the appearance of intermatallic compounds $CaSi_2$ in the form of dark needles are observed in the analysed microstructure (Fig. 7).

In the terms of research sources [2] intermetallic compound $CaSi_2$ and other intermetallic compounds have been still unidentified compositions, they are analyzed below in EDX spot analysis.

EDX spot analysis of the intermetallic phases containing calcium

The cast samples containing 0,5% calcium and 1% Ca were studied in the view of EDX spot analysis in order to determine the chemical composition of different intermetallic phases containing calcium.

Table 3

Results of chemical analysis of the spectra of alloys AlSi7Mg0, 3 with added amount of calcium 0,5 %Ca

Sp.	Mg	Al	Si	Ca	Mn	Fe	Total
1	0,21	55,76	33,41	10,36	0,01	0,01	100,00
2	0,20	48,75	33,85	8,32	0,70	8,18	100,00
3	0,22	97,48	1,79	0,40	0,02	0,09	100,00
4	0,21	82,50	17,23	0,03	0,00	0,02	100,00
5	0,47	97,98	1,51	0,01	0,03	0,00	100,00
6	0,24	97,87	1,91	-0,02	-0,03	0,02	100,00
7	0,05	11,69	88,30	-0,10	0,01	0,05	100,00
8	0,27	60,85	25,29	10,20	0,27	3,12	100,00
Max.	0,47	97,98	88,30	10,60	0,70	8,18	
Min.	0,05	11,69	1,51	-0,10	-0,03	0,00	
Ø	0,23	69,11	25,41	3,68	0,13	1,44	

Sp.	Mg	Al	Si	Ca	Mn	Fe	Total
1	0,20	72,96	24,71	2,09	0,00	0,05	100,00
2	0,16	51,80	47,93	0,06	0,02	0,04	100,00
3	0,25	92,37	6,33	0,00	0,02	0,04	100,00
4	0,19	68,65	31,17	-0,02	0,02	-0,01	100,00
5	0,18	63,93	35,89	0,02	-0,02	-0,01	100,00
6	0,23	81,76	17,98	0,01	0,02	0,01	100,00
7	0,22	76,80	22,97	0,10	0,01	-0,01	100,00
8	0,27	98,37	1,34	-0,01	0,02	0,01	100,00
Max.	0,28	98,38	47,93	2,09	0,02	0,05	
Min.	0,16	51,80	1,34	-0,02	-0,04	-0,01	
Ø	0,22	78,41	21,11	0,24	0,00	0,02	

Table 4

Results of chemical analysis of the spectra of alloys AlSi7Mg0, 3 with added amount of calcium 1 % Ca

Sp.	Mg	Al	Si	Ca	P	Total
1		28,81	48,90	22,29		100,00
2		29,29	48,17	22,54		100,00
3		28,17	49,19	22,08	0,56	100,00
4		20,07	62,72	16,59	0,62	100,00
5		23,88	55,70	19,56	0,86	100,00
6	0,24	25,15	57,48	16,45	0,65	100,00
7	0,25	68,50	19,67	11,57		100,00
8		47,39	41,87	10,74		100,00
9	2,54	50,80	29,78	15,99		
10		35,19	41,69	23,12		
11	0,38	98,21	1,41			100,00
12.	0,34	33,63	41,77	24,26		100,00
Max.	2,54	98,21	62,72	24,26	0,86	100,00
Min.	0,25	20,07	1,41	10,74	0,56	100,00

Sp.	Mg	Al	Si	Ca	P	Ni	Fe	Total
1	0,06	29,40	45,75	23,67	1,04	0,05	0,01	100,00
2	0,07	31,87	42,64	25,01	0,35	0,01	0,06	100,00
3	0,05	25,95	50,76	22,20	1,07	0,01	-0,04	100,00
4	0,02	26,83	49,40	23,11	0,54	0,10	0,00	100,00
5	0,04	27,29	48,90	22,65	1,13	0,01	-0,01	100,00
6	0,65	80,11	18,12	0,45	0,68	-0,02	0,01	100,00
Max.	0,65	80,11	50,76	25,01	1,13	0,10	0,06	100,00
Min.	0,02	25,95	18,12	0,45	0,35	-0,02	-0,04	100,00
Ø	0,15	36,91	42,59	19,52	0,80	0,03	0,01	100,00

On the basis of spot analysis results (Tab. 3 and Tab. 4) and with the help of stechiometric ratios calculations, separate morphologically diverse intermetallic phases containing calcium in the form of long fine needles $CaAl_6Si_4$ (Fig. 8) and coarse sharp particles of irregular geometric shapes $CaAl_2Si_4$ and $CaAl_2Si_3$ (Fig. 9), which showed the expected presence of various intermetallic phases with calcium observed in a scanning microscope and by a carried out EDX spot analysis, were examined. The presence of phosphorus, which is higher due to the application of refining and salt and phosphorus covering, is apparent among some spectra.

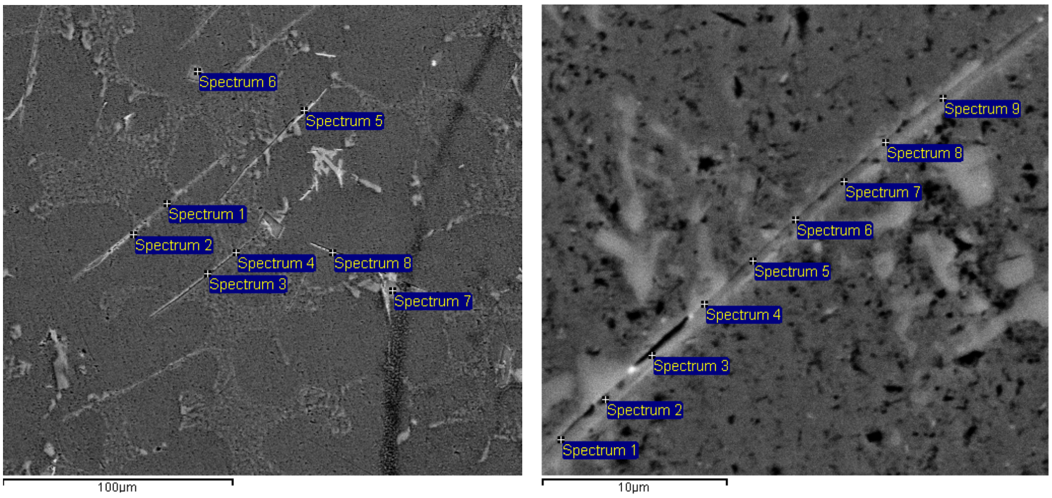

Fig. 8. Image AlSi7Mg0,3 alloy microstructure, with added amount of calcium 0,5 % Ca with marked locations for analysis

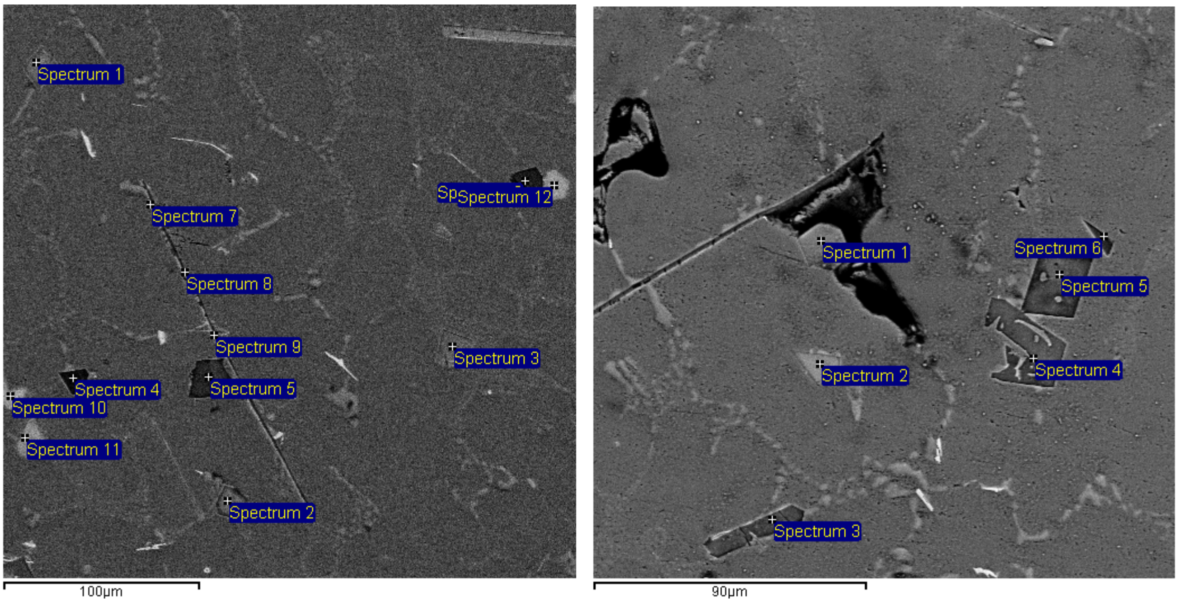

Fig. 9. Image AlSi7Mg0,3 alloy microstructure with added amount of calcium 1 % Ca with marked locations for analysis

Conclusion

On the basis of experiments studying the fluidity of an aluminum alloy which belongs to the group of hypereutectic AlSi7Mg0,3 silumin alloys it can be stated that by the means of adding calcium to the alloy it is possible to improve fluidity. After comparison the castings without the addition of calcium and with addition of 0,5% and 1% Ca an integrated upward trend in calcium influence on the alloy fluidity was demonstrated. The length of castings without the addition of Ca and with 0,5% Ca is about 8cm longer, and after further addition of 1% Ca the length increases at about 5 cm, so it can be stated that the addition of calcium has a positive impact on the alloy fluidity. The process error came during the casting with calcium 0,1%, since it is necessary to follow certain requirements which can effect fluidity and include mold temperature, cast alloy surface, which helps to lose heat, hardening time interval, alloy fluidity speed and the form's property to reduce heat.

The results of metallographic analysis for addition alloys AlCa10 can say that it is a eutectic alloy with hypoeutectic areas of the composition $\alpha+CaAl_4$ with the appearance of rough boards $CaAl_4$ phase. The results of metallographic analysis carried out on samples of the alloy AlSi7Mg0,3 it can be stated that this is a hypereutectic alloy plates consisting of silicon, metallographic cut needles appeal dark gray color and the α-phase dendrites. The modified structure is characterized by the presence of eutectic silicon in the form of sticks, with are cut for metallographic appeal rounded grains. When the modifier content 0,1 %Ca is calcium visible effect on the resulting structure, which is very fine-grained. With further addition of Ca the amount of gas is increasing and it stimulates porosity growth and appearance of coarsen particle of irregular geometric shape on the edge of dendrites and intermetallic compounds of CaSi2 types in the form of dark needles.

With the help of EDX spot analysis and spot values calculated using the stechiometric ratio for each intermetallic phase with calcium, it can be stated about these phase types that:

1. From the morphological point of view, among alloys containing 0,5% calcium there is the presence of long fine needles of intermetallic phases with the stechiometric composition of calcium $CaAl_6Si_4$.
2. According to stechiometric ratio and in terms of morphology, among alloys containing 1% calcium the presence of two types of intermetallic phases with calcium can be observed: a.) dark long fine needles which reveal stechiometric $CaAl_2Si_4$ composition; b.) coarse sharp particles of irregular geometric shapes which reveal stechiometric $CaAl2Si_3$ composition.

Analysis showed a visible effect on the structure of calcium . There is a change in the morphology of eutectic, changing the shape of the excluded silicon eutectic and of different types of intermetallic compounds. From the above it can be concluded that it is possible to color metallographic of aluminum alloys used in various walls. When etching on the surface to produce an optical contrast. This is due to the way in which some parts of the samples surface after etching reflex light. This, we can obtain informatics of diverse nature, acquire next knowledge about the structure, or enhance already acquired knowledge in comparison with black and white contrast.

The advantages of color contrast can be used in particular:

- For color identification of individual types of intermetallic phases with different chemical composition of the aluminum alloys;
- When assessing the quality of homogenizing annealing, the higher quality will be done homogenization annealing, it will be more even and uniform color contrast within individual dendrites cells;
- The identifications of primary and secondary crystallization directions;

- In detecting in homogeneities in the chemical composition of dendrites cells;
- The identification of the undisclosed particles of metal or master alloys;
- The evaluation of recrystallization, the size and shape of the recrystallized grain;
- In assessing the depth marginally coarse recrystallized layer;
- The detection of thermally controllable zones hen entering foreign particles into the material.

Анотація. *Область застосування алюмінію та алюмінієвих сплавів дуже широка і майбутнє алюмінієвих сплавів пов'язано з подальшим розвитком нових сплавів, але в першу чергу з технологією виробництва і переробки. У статті представлено аналіз деяких Ca, вплив яких враховує кількість варіацій, таких як 0,1% на 1% Ca, щоб запропонувати оптимальну кількість для досягнення бажаних технологічних, хімічних і механічних властивостей. Аналіз нових сплавів загального структурного аналізу, ідентифікує окремі структури компонентів нових Ca сплавів використовуючи кольорову металлографію. Застосовуючи кольорову металографію можна диференціювати і визначати наявність частинок інтерметалідів з різним хімічним складом.*

<u>Ключові слова:</u> *сплав Al-Si-Mg, колірний контраст, майстер-сплави, легування.*

Аннотация. *Область применения алюминия и алюминиевых сплавов очень широка и будущее алюминиевых сплавов связанно с дальнейшим развитием новых сплавов, но в первую очередь с технологией производства и переработки. В статье представлен анализ некоторых Ca, влияние которых учитывает количество вариаций, таких как 0,1% на 1% Ca, чтобы предложить их оптимальное количество для достижения желаемых технологических, химических и механических свойств. Анализ новых сплавов общего структурного анализа, идентифицирует отдельные структуры компонентов новых Ca сплавов используя цветную металлографию. Применяя цветную металлографию можно дифференцировать и определить наличие частиц интерметаллидов с различным химическим составом.*

<u>Ключевые слова:</u> *сплав Al-Si-Mg, цветовой контраст, мастер-сплави, легирование.*

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