ARPN Journal of Engineering and Applied Sciences

PRODUCTION OF ALUMINUM ALLOYS MODIFICATOR FROM LIGATURE

E. H. Ri[1], Hosen Ri[1], S. N. Khimukhin[2], Ermakov M. A.[3] and T. S. Khimukhin[4]
[1]Foundry and Metal technology Chair, Pacific National University, Khabarovsk, Russia
[2]Construction and Instrumental Materials Laboratory, Institute of Materials Science of Khabarovsk Scientific Center of Far-Eastern Branch of Russian Academy of Sciences, Khabarovsk, Russia
[3]Engineering, Pacific National University, Khabarovsk, Russia
[4]Department of Foreign Languages, Pacific National University, Khabarovsk, Russia
Email: ermakovma@yandex.ru

ABSTRACT

The paper presents the research results of obtaining aluminum alloys modificators. Complex ligature AKCe (wt.%: 30 Al, 28 REM, 4 Ca, the rest is Ni), which is a traditional additive in cast irons, was used as a metallurgical charge for obtaining new modifying alloys. The melting point of the master alloy used in the experiments is 1400 °C. Modifying alloys from ligature were obtained in two ways. In the first way, aluminum (A7) was melted, and then different amounts of AKCe powder were added to the superheated (1400 °C) aluminum melt. In the second method different amounts of aluminum (A7) were added to the molten (1400 °C) master alloy. The melting was carried out in Tamman furnace where a protective atmosphere of technically pure argon was created. In both methods of producing the modifier, the component was added in the amount of 20% to 70% by weight. The element composition analysis of the resulting alloys showed that, when adding 60 wt. % (AKCe or A7) the element composition and melting point were not significantly different, regardless of the production method having been used. The micro-X-ray spectral analysis showed that the initial ligature alloy consisted of intermetallides Al-Ni-RZM, Al-Ni and Al-Ca. The obtained alloys, regardless of the method of their production, consisted of an α-solid solution of Ni in Al and intermetallides of Al-Ni, where instead of the intermetallic compound AlNi the intermetallide Al3Ni was formed which appeared to have a lower melting point and better plastic properties.

Keywords: ligature, nickel aluminide, REM aluminide, solid solution, eutectic, atomic percentage, stoichiometry, melting point.

INTRODUCTION

The production of aluminum-based alloys in the world ranks second after the production of iron-based alloys. The wide use of aluminum alloys in all spheres of human life is due to a good combination of its functional properties such as density, strength, plasticity and corrosion resistance. The production of aluminum alloys ingots of high quality is directly determined by the ligatures used in the process of synthesis. At present a large number of newly created ligatures contain elements intended not only for alloying, but also for modification. The advantage of modification process lies in the fact that small amounts of additives are introduced to produce alloys where the limits of content of chemical elements do not exceed the regulated ones for a given brand.

It is necessary to note that the main trend in obtaining ligatures now is the use of rare-earth metals (REM). The use of REM makes it possible to obtain a number of alloys properties that cannot be achieved by using conventional ligatures. Scientists and metallurgists have known for a long time the unique modifying possibilities that are provided by the introduction of REM into alloys [1], but some time ago high cost of REM often held back their widespread use. At present the situation has been changed. Due to the increased REM production in China their cost has been lowed and the production of REM containing ligatures is going to be increased. Traditionally the most types of REM containing ligatures, which are produced now are intended for iron-carbon alloys [2, 3] and much smaller - for aluminum alloys. However the number of recent research works studying the influence of REM additives on the structure and properties of aluminum alloys has increased. The use of REM additives in aluminum alloys is caused by the need to modify the Si phase in the eutectic [4-6]. The REM addition allows enhancing the properties in fatigue tests [7]. The REM addition also is known to increase the tensile strength at heating temperatures to 350°C [8]. For improving strength of aluminum alloys modifying additives containing Ni present great interest.

This paper considers the issues of obtaining REM containing nickel-based ligatures for aluminum alloys from the ligature that has been intended for cast irons.

METHODS AND MATERIALS

REM containing complex modifier AKCe (Russia) [9] intended for cast iron as the initial charge and aluminum of technical purity A7 have been used (the total amount of Fe and Si impurities <0.3 mass .%, that is similar in composition to the USA brand Aluminum 1070) [10]. The elemental composition of the AKCe ligature is given in Table-1.

ARPN Journal of Engineering and Applied Sciences

Table-1. The elemental composition of the AKCe ligature (wt %).

Al	Ca	Fe	Ni	La	Ce	Nd
35,31	4,57	0,27	31,52	9,38	15,45	3,49

Experimental meltings were carried out using a Tamman furnace and BeO crucibles in the argon protective atmosphere. The ligature for further adding into aluminum alloys was obtained in two ways. According to the first method A7 was first melted and then different amount of AKCe powder was added to the aluminum melt. The powder (fraction <0.63 mm) was wrapped in aluminum foil before introducing it into the aluminum melt; that increased the solubility of the powder and prevented its slagging. In accordance with the second method, the ligature was melted and the pieces of A7 were added thereto. Regardless of the method used to produce the master alloy none of the parameters such as speed of heating or cooling changed. After heating the melt (AKCe or A7) at the rate of 50 ° C / min and overheating to 1400° C, it was stirred and held for 5 minutes, and then the second component (AKCe or A7) was added; after stirring and subsequent second soaking (5 minutes) the resulting alloy was cooled at the rate of 35 °C/min. Having been cooled the ingots of the ligature were extracted from the crucible and cut into longitudinal and transverse samples for studying defects and homogeneity of the macro and microstructure of the ingots. Macro-microstructure of the ingots was investigated using digital (SUPEREYES 3.2) and metallographic (Micro 200) microscopes. To determine the concentration of the structure components of the modifier, the method of micro-X-ray spectral analysis was used on the SU-70 Hitachi raster electron microscope with the corresponding attachments to the device (EDX and WDX) [11].

THE RESULTS AND DISCUSSIONS

The work was carried out in two stages. At the first stage, the structure and composition of the intermetallide phases of the original ligature were investigated. The purpose of the second stage was to establish changes in the structure and composition of intermetallic phases with the addition of various amounts of pure aluminum to the initial ligature.

Macrostructural analysis of the initial ligature showed a homogeneous character of the distribution of structural components, the absence of pores and nonmetallic inclusions (Figure-1, a). Micro-X-ray spectral analysis was carried out on three samples made from different pieces of ligature. Figure-1, b, c, d shows the tested sections on which the composition of the intermetallide phases were studied. Basing on the results of micro-X-ray spectral analysis, three different groups of intermetallides were identified in the ligature. At the same time, no significant differences in the composition of intermetallic compounds in the groups were found. Table-2 presents the generalized results for the three groups of intermetallic compounds.

As follows from the above given results, the crystals of Ni and REM aluminides contain calcium in all cases. The approximate stoichiometric composition of this compound corresponds to: $Al_{5.65}Ni_{2.26}REM= (Al,Ni)_{7.91}REM \approx (Al, Ni)_8REM$ (Table-2).

Fe impurity in the amount of 0.5 at, % was found in the aluminides of nickel AlNi. The maximum amount of impurities (Mn; Ni; Cu; REM) is concentrated in calcium aluminide $Al_{1.79}Ca \approx Al_{1.8}Ca$.

At the second stage smelting of the modifiers was carried out according to the two methods having been mentioned in the method procedure chapter. The comparative analysis of the chemical compositions of the alloys obtained by different methods of smelting showed that, regardless of the method (with additives of 50-60% wt. % AKCe or A7), the content of the main alloying elements of Al, Ni and REM did not change significantly (Figure-2). Thus (at additive weight% 60) the average concentration values of the chemical elements correspond to mass%: 68.1 Al; 1.15 Ca; 20.0 Ni; 3.82 La; 7.43 Ce (11.25 REM).

ARPN Journal of Engineering and Applied Sciences

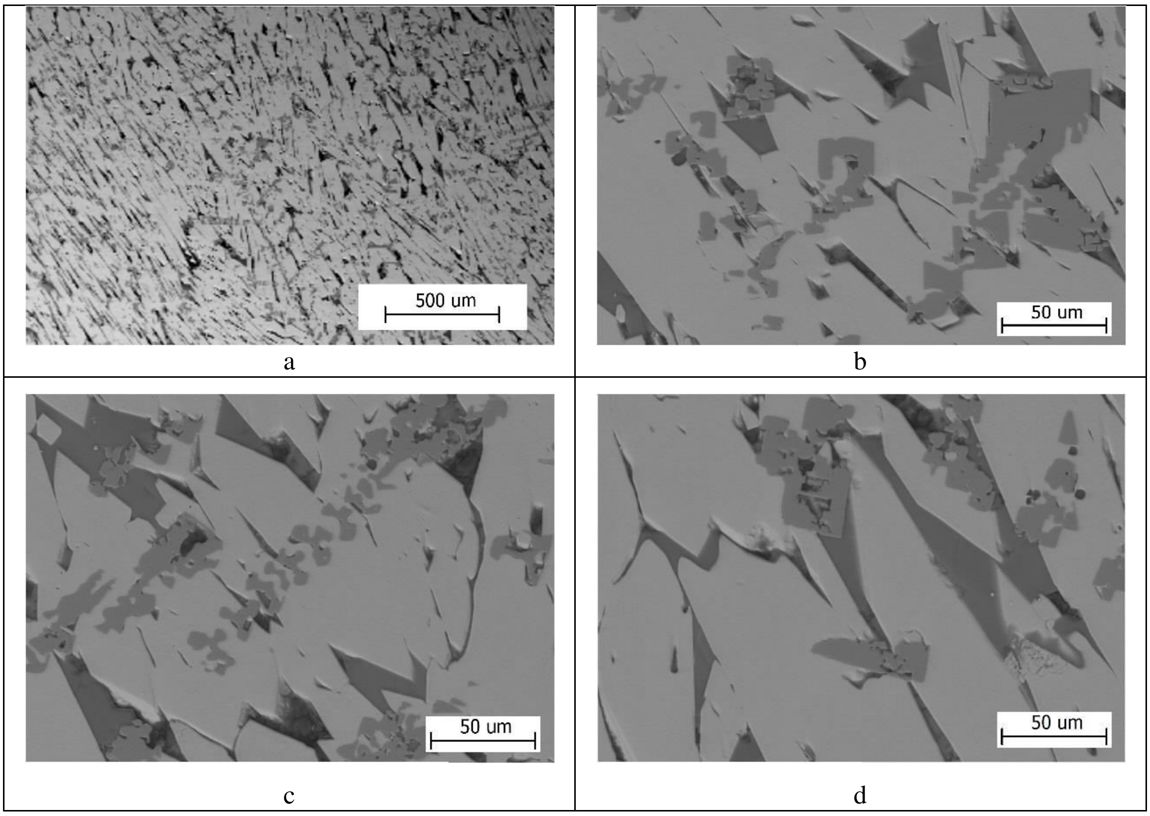


Figure-1. Microstructure of the ligature AKCe: a - macrostructure; b, c, d - segments under analysis by points on samples 1 - 3 respectively.

Table-2. The elements content in the intermetallides of the AKCe ligature.

Sample	Element content, % ат									
	Al	**Ca**	**Mn**	**Fe**	**Ni**	**Cu**	**La**	**Ce**	**Nd**	**REM**
1	62,6	0,93	-	-	25,23	-	3,79	6,27	1,16	11,3
2	62,6	0,92	-	-	24,97	-	3,74	6,25	1,17	11,07
3	62,85	1,24	-	-	25,15	-	3,7	6,16	1,06	10,93
Average value	62,76	1,03			25,12		3,74	6,23	1,13	11,1
$Al_{62,76}Ni_{25,12}REM_{11,1} = Al_{5,65}Ni_{2,26}REM$ (impurity - 1,03 Ca)										
1	53,41	-	-	0,47	46,12	-	-	-	-	-
2	53,36	-	-	0,5	46,14	-	-	-	-	-
3	53,07	-	-	0,53	46,4	-	-	-	-	-
Average value	53,26			0,5	46,22					
$Al_{53,26}Ni_{46,22} = Al_{1,15}Ni$ (impurity 0,5 Fe)										
1	62,77	34,64	0,33		0,73	0,72	0,22	0,59		0,81
2	62,0	35,1	0,29		0,88	0,7	0,24	0,5		0,98
3	62,46	34,69	0,36		1,1	0,68	0,24	0,48		0,72
Average value	62,41	34,81	0,33		0,9	0,70	0,23	0,52		0,83
$Al_{62,41}Ca_{34,81} = Al_{1,79}Ca$ (impurities - 0,33 Mn; 0,9 Ni; 0,7 Cu; 0,83 REM)										

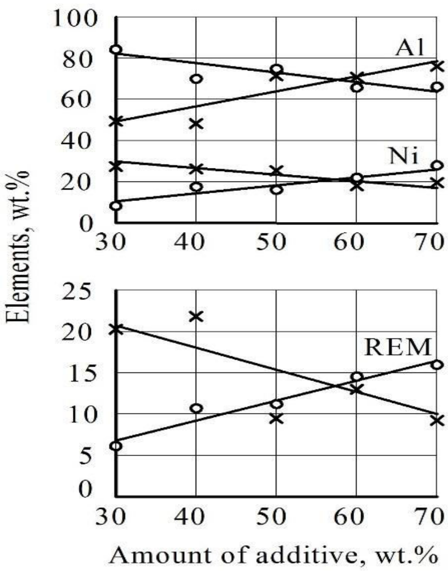
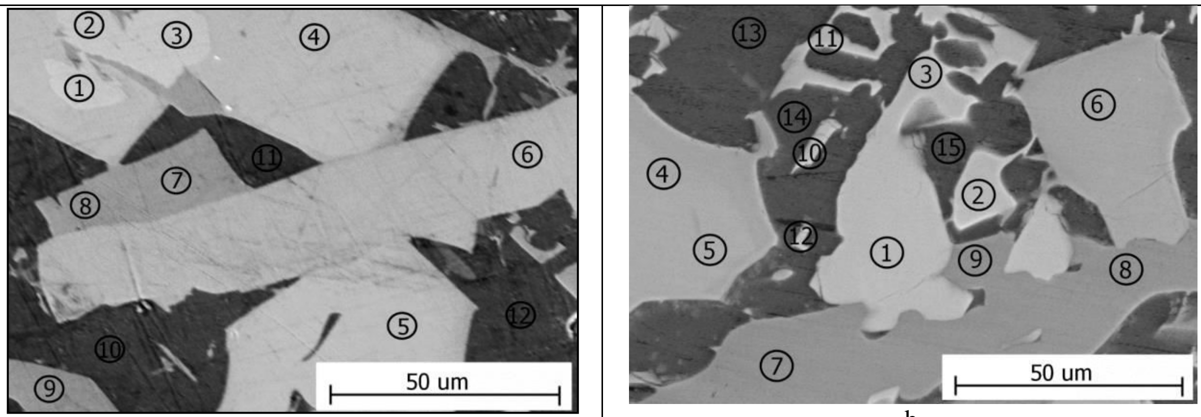


Figure-2. Comparative elements analysis of the alloys depending on the method of smelting. -o- Al base and AKCe additive; -x- AKCe base and A7 additive.

The alloys with 60% wt.% additives were used for comparative studies to determine the influence of the production method on the elements content in the structural constituents of the alloys. The melting point of the alloys obtained – 720 - 740° C. Figure-3 shows the microstructure of the alloys fused in the regime of reflected electrons [11], which makes it possible to distinguish phases by contrast. Table-3 presents the results of micro-X-ray spectral analysis of the intermetallide phases (Figure-3, a) contained in the alloy having been obtained with the addition of AKCe to the aluminum melt.

As follows from the analysis of the research results, the alloy obtained by the first method contains three types of intermetallics and an α-solid solution based on Al. Nickel aluminide corresponds approximately to the known stoichiometric composition ($Al3_{,17}Ni \approx Al_3Ni$). Rare-earth elements (~ to at. % 10) contain nickel aluminide and REM aluminide (~ 19 at.%). At the same time, Si is a part of REM aluminide, where Ca is also found.



a b

Figure-3. Microstructure and points of elements analysis of structural constituents of the alloy:
a - Al + 60% wt.% AKCe; b- (AKCe + 60 wt.%).

In Figure-3, b and in Table-4 the results of analysis of the alloy obtained by the second method are presented. In contrast to the alloy obtained by the first method, the formation of another REM intermetallide with a higher (by factors 4-5) Ca concentration was revealed. It should be noted that there is a higher content of REM in the corresponding intermetallics.

Table-3. Distribution of elements in different phases of synthesized alloys A7 +60% wt.% AKCe.

Points of analysis	Element content, at. %							
	Al	Si	Ca	Fe	Ni	La	Ce	Nd	∑REM
1	76,38	-	-	-	23,53	-	-	-	-
2	76,01	-	-	-	23,76	-	-	-	-
3	75,59	-	-	0,33	23,94	-	-	-	-
4	76,31	-	-	-	23,44	-	-	-	-
5	75,69	-	-	-	24,18	-	-	-	-
6	75,30	-	-	-	24,61	-	-	-	-

Average value	75,88	-	-	0,06	23,91	-	-	-	-
Nickel aluminide: $Al_{75,88}Ni_{23,91} = Al_{3,17}Ni \approx Al_3Ni$									
7	74,70	-	1,03	-	16,42	1,87	4,97	0,99	7,85
8	71,28	-	0,87	-	17,39	2,15	6,39	0,91	9,45
9	73,41	-	3,14	1,23	17,33	1,96	2,42	0,77	4,88
Average value	73,13	-	1,68	-	17,05	1,91	4,59	1,22	7,39
Nickel aluminide with REM:$Al_{73,13}Ni_{17,05}{\cdot}REM_{7,39} = Al_{9,89}Ni_{2,3}{\cdot}REM$									
10	74,53	0,29	3,55	-	0,05	5,44	9,41	2,51	18,54
11	75,12	-	3,79	-	0,31	6,15	9,03	1,85	17,45
12	74,13	1,96	4,97	-	0,34	4,40	10,0	2,39	18,21
Average value	74,66	1,13	3,8	-	0,24	5,33	9,50	2,25	18,01
REM aluminide: $Al_{74,66}REM_{18,01} = Al_{4,12}REM \approx Al_4REM$									
13	99,58	-	0,07	-	0,26	-	-	-	-
14	99,78	-	-	-	0,14	-	-	-	-
15	99,50	-	0,13	-	0,19	-	-	-	-
16	99,80	-	-	-	-	-	-	-	-
17	99,70	-	-	-	0,26	-	-	-	-
Average value	99,76	-	0,04	-	0,17	-	-	-	-
α-solid solution based on Al									

Table-4. Distribution of elements in different phases of synthesized alloys AKCe +60 wt. % A7.

Points of analysis	Element content, at. %								
	Al	**Si**	**Ca**	**Fe**	**Ni**	**La**	**Ce**	**Nd**	**∑REM**
1	73,94	-	-	0,28	25,77	-	-	-	-
2	73,94	-	-	0,28	25,77	-	-	-	-
3	74,04	-	-	-	25,96	-	-	-	-
4	73,99	-	-	0,13	25,88	-	-	-	-
5	73,86	-	-	0,30	25,84	-	-	-	-
Average value	73,95	-	-	0,20	25,84	-	-	-	-
Nickel aluminide: $Al_{73,95}Ni_{25,84} = Al_{2,86}Ni \approx Al_3Ni$									
6	71,70	-	2,40	1,38	18,70	1,84	3,38	0,61	5,83
7	71,87	-	2,34	1,35	18,76	1,69	3,28	0,69	5,66
8	71,36	-	3,94	2,30	17,80	1,14	2,78	0,69	4,61
Average value	71,64	-	2,89	1,68	18,42	1,56	3,15	0,66	5,37
Nickel aluminide with REM: $Al_{71,64}Ni_{18,42}REM_{5,37} = Al_{13,34}Ni_{3,43}REM$									
9	77,64	0,28	1,40	-	0,46	7,06	11,12	2,04	20,22
10	77,09	0,16	1,48	-	0,57	6,94	11,48	2,27	20,69
11	77,37	0,26	1,40	-	0,54	6,69	13,73	-	20,42
12	77,86	0,13	1,50	-	0,43	6,49	13,60	-	20,09
Average value	77,49	0,21	1,45	-	0,50	6,80	12,48	1,08	20,36
REM aluminide: $Al_{77,49}REM_{20,36} = Al_{3,81}REM$									
13	99,89	-	-	-	0,11	-	-	-	-

ARPN Journal of Engineering and Applied Sciences

14	99,66	-	-	-	0,34	-	-	-	-
15	99,75	-	-	-	0,25	-	-	-	-
16	99,85	-	-	-	0,15	-	-	-	-
Average value	99,79	-	-	-	0,21	-	-	-	-
α-solid solution based on Al									

Table-5. Continuation.

Points of analysis	Element content, at. %								
	Al	Si	Ca	Fe	Ni	La	Ce	Nd	∑REM
17	77,54	0,53	5,09	-	0,42	4,99	9,34	2,09	16,42
18	78,43	0,44	6,23	-	0,33	4,25	8,30	2,02	14,57
19	77,73	0,46	7,36	-	0,41	3,91	8,15	1,98	14,04
20	77,85	0,54	5,33	-	0,36	4,84	8,98	2,11	15,93
Average value	77,89	0,49	6,00	-	0,38	4,50	8,69	2,05	15,24
REM aluminide: $Al_{77,89}REM_{15,24} = Al_{4,73}REM$									

For convenience of carrying out a comparative analysis and evaluation of the content of elements in the structural constituents of the alloys obtained by the two methods, the results are summarized in Table-5. As follows from the results received, nickel aluminides obtained by the two methods have approximately the same stoichiometric composition corresponding to Al_3Ni, whereas in the initial ligature the intermetallic compound corresponds to AlNi. In accordance with the phase diagram [12], the intermetallide Al_3Ni has a lower melting point (~ 500 ° C) as compared to AlNi, which is preferable when using a modifier in aluminum alloys.

In addition, the initial ligature contains calcium aluminide ($Al_{62.41}Ca_{34.81}$=$Al_{1.79}Ca$), which forms nickel aluminide with REM and REM aluminide in the modifier.

Table-6. Comparative results of the elements content in various structural components of the resulting alloys, at. %.

No	Phases	Alloys	
		A7 + 60 wt.% AKCe	AKCe + 60 wt.% A7
1	Nickel aluminide Al_3Ni	75,88 Al; 23,913 Ni; 0,104 REM	73,99 Al; 23,86 Ni; 0,01 Si; 0,03 Ca; 0,14 REM; 0,22 Fe
2	REM aluminide ($Al_{11}REM_3$ = $Al_{3,66}REM$)	74,66 Al; 18,01 REM; 1,0 Ca; 0,24 Ni	77,41 Al; 18,62 REM; 0,35 Si; 3,08 Ca; 0,02 Fe;0,51 Ni
3	Nickel aluminide with REM	73,13 Al; 17,05 Ni; 7,396 REM	71,36 Al; 18,02 Ni; 5,50 REM; 1,53 Si; 1,69 Ca; 1,87 Fe
4	Solid solutions	99,68 Al; 0,053 Ca; 0,19 Ni	99,79 Al; 0,21 Ni

Having compared the two methods of obtaining modifiers from the ligature, it should be marked that the first one is more preferable from the point of view of the possibility of carrying out the smelting process without using a protective atmosphere, which makes the production cheaper. In this case, the role of the protective ligature is performed by the aluminum melt.

CONCLUSIONS

a) The initial ligature intended for using as an additive in cast irons consists mainly of high-temperature aluminides AlNi, (Al, Ni) REM and calcium AlCa.

b) Regardless of the method for obtaining the modifier, when adding ligatures to aluminum or aluminum to a ligature (60% by weight), the elemental composition and the melting temperature of the alloys are not significantly different, thus making it possible to use both methods of smelting.

c) The modifiers obtained for aluminum alloys contain Al3Ni in their composition instead of high-temperature intermetallides AlNi, as it is in case of the initial ligature alloy.

ACKNOWLEDGEMENT

Studies were carried out on the equipment of Joint Use Center "Applied Material Science" at Federal State Educational Institution of Higher Professional Education "Pacific National University" with financial support from the Russian Ministry of Education and Science in accordance of the state order (state registration 11.3014.2017/4.6).

REFERENCES

[1] Gorbunov Jury A. 2015. The Role and Prospects of Rare Earth Metals in the Development of Physical-Mechanical Characteristics and Applications of Deformable Aluminum Alloys. In J. Sib. Fed. Univ. Eng. technol. 8(5): 636-645. DOI: 10.17516/1999-494X-2015-8-5-636-645.

[2] Gao Jinzhu; Fu Paixian; Liu Hongwei; Li Dianzhong. 2015. Effects of Rare Earth on the Microstructure and Impact Toughness of H13 Steel. In Metals. 5(1): 383-394. DOI: 10.3390/met5010383.

[3] Li, Juan; Cai, Yu; Chen, Qiang; Zhang, Hang; Liu, HuaShan; Jin, ZhanPeng. 2012. Thermodynamic modeling of Fe-Ce-Bi system and explanation of interfacial reaction in Fe-45at%-Ce/Bi couple. In Calphad. 38, pp. 133-139. DOI: 10.1016/j.calphad.2012.05.004.

[4] Li Qinglin; Xia Tiandong; Lan Yefeng; Li Pengfei; Fan Lu. 2013. Effects of rare earth Er addition on microstructure and mechanical properties of hypereutectic Al–20% Si alloy. In Materials Science and Engineering: A 588, pp. 97-102. DOI: 10.1016/j.msea.2013.09.017.

[5] Li Qinglin; Xia Tiandong; Lan Yefeng; Zhao Wenjun; Fan Lu; Li Pengfei. 2013. Effect of rare earth cerium addition on the microstructure and tensile properties of hypereutectic Al-20%Si alloy. In Journal of Alloys and Compounds 562, pp. 25-32. DOI: 10.1016/j.jallcom.2013.02.016.

[6] SONG Xianchen; YAN Hong; ZHANG Xiaojun. 2017. Microstructure and mechanical properties of Al-7Si-0.7Mg alloy formed with an addition of (Pr+Ce). In Journal of Rare Earths. 35(4): 412-418. DOI: 10.1016/S1002-0721(17)60927-X.

[7] Bai Song; Liu Zhiyi; Li Yuntao; Hou Yanhui; Chen Xu. 2010. Microstructures and fatigue fracture behavior of an Al–Cu–Mg–Ag alloy with addition of rare earth Er. In Materials Science and Engineering: A. 527(7-8): 1806-1814. DOI: 10.1016/j.msea.2009.11.011.

[8] Xiao D. H.; Wang J. N.; Ding D. Y.; Yang H. L. 2003. Effect of rare earth Ce addition on the microstructure and mechanical properties of an Al–Cu–Mg–Ag alloy. In Journal of Alloys and Compounds. 352(1-2): 84-88. DOI: 10.1016/S0925-8388(02)01162-3.

[9] TU #0865-01-94634068-2006 (RF Technical Requirements) Complex ligatures without silica.

[10] ISO. 2007. 209 Aluminium and aluminium alloys - Chemical composition.

[11] Goldstein J., Newbury D., Joy D., Lyman C., Elchlin P., Lifshin E., Sawyer L., Michael J. 2003. Scanning electron microscopy and X-ray microanalysis. Kluwer Academic/Plenum Publishers, New York/Boston/Dordrecht/London/Moscow.

[12] 1990. Binary Alloy Phase Diagrams–Second edition. T. B. Massalski, Editor-in-Chief; H. Okamoto, P. R. Subramanian, L. Kacprzak, Editors. ASM International, Materials Park, Ohio, USA. xxii, 3: 3589.