EFFECT OF $NaNO_3$, $NaClO_3$ AND TiO_2 ON MECHANICAL PROPERTIES AlSi7Mg ALLOY

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Abstract

Hypo-eutectic silumins are used in a wide range of industrial applications, but their properties are continuously studied to improve the quality of cast products. The initial structure of AlSi9Mg alloy is composed of granular and acicular β phase, with α phase as matrix. The hard, irregular, often pointed β phase is responsible for the poor mechanical properties of said alloy. This composition is responsible for the alloy's low strength parameters, and it limits the extent of practical applications. The properties of alloys may not only depend on the chemical composition, modifiers, but may also depend on the conditions of the modification effect. Chemical elements and compounds, both added to the alloy and formed as a result of exothermic reactions, “pass” into the alloy, changing the course of its crystallization. Selection of the mixture components allows – to a degree – to decide about the starting moment of crystallization and change the range of alloy solidification or its individual phases. In the present study, the microstructure and technological properties of silumins were improved through modification with the use a chemical mixture as an exothermic modification. It was found that the exothermic modifier containing $NaNO_3$ $NaClO_3$ and TiO_2 exerted the strongest multidirectional refining effect on the studied alloys.

Keywords: Aluminum alloy, exothermic mixtures, modifications, tensile strength, elongation

1. INTRODUCTION

Modern industry requires high quality casting alloys. Foundry alloys are often improved to increase their performance. Experimental methods are not always used. Computer technology is often used to simulate expensive research. Non-inoculated alloy AlSi7Mg is characterized by coarse-grained structure, consisting of grains and acicular precipitates of phase β, contrasted with dendritic phase α. Such microstructure is responsible for its poor uses properties for example tensile strength, elongation, hardness. The mechanical properties of alloys are determined primarily by the structure of hard eutectic β phase whose needles and grains form natural notches which decrease both the strength and plasticity of silumins. Silumins eutectic are usually modified with Na, Sr and Sb or their compounds and other e.g. Ti, Ca, B and other elements [1]. There are other methods modified microstructure of Al-Si alloys as homogeneous modifiers produced by fast cooling [2], directional crystallization [3], technological processes [4].

An interesting method of Al-Si treatment is exothermical method, mainly by treatment method known as Inmold. The degree of ‘assimilation’ of the components added is of primary importance while employing this method in alloy treatment. When the Inmold method is applied, individual alloy additions may undergo dissolution in the alloy treated (if their melting point is lower than or the same as the temperature of the alloy and the process lasts long enough), enrich its composition as solid particles (if their melting point is higher than the temperature of the alloy or the process does not last long enough), or do both (if the mixture consists of particles whose melting point is lower and higher than the temperature of the alloy). The effect intensity is connected with the velocity of flow (i.e. the velocity of casting and dimensions of the reaction chamber), as well as the chemical compounds from the mixture [5].

Such methods for enhancement of silumins properties may be interested for many branches of industry i.a. corrosion problems [6,7], machine design [8,9], LNG control design [10,11], biotechnology [12,13] or waste management [14-16]. The observed interactions between controlled factors should be also taken into consideration in a methodology of future similar designed experiments [17,18], especially involving mixtures [19,20] or – focused on observed microstructure changes – image analyses [21-23] of modified surface layer [24-26]. The obtained dataset may also inspiring source for parametric [27,28] and non-parametric [29,30] uncertainty analysis.

2. METALLOTHERMY PROCESS

Metallothermy allows to obtain metals on the base of reactions proceeding between a given metal – reducing agent and some compounds, mainly oxygen ones. The procedure of metallothermy, which is part of 'out-of-furnace' treatment, may be applied while producing ferrous and non-ferrous alloys. Enriching elements, both added to the alloy and formed as the result of exothermic reactions, 'pass' into the alloy, changing the course of its crystallization, microstructure and properties. According to professional literature [31,32], the energy condition of a spontaneous course of reactions is assuming the minimum enthalpy gain by –300 kJ/mol of the reducer. If the thermal effect caused by the reaction course is too low, the missing amount of heat should be supplied. In the case of 'out-of-furnace' treatment, the missing amount of enthalpy may be supplied in the form of heat of liquid alloy. Reactions of metal oxides with Al as a redactor may be presented on the example of the following reaction (1), (2) and (3):

$6NaNO_3 + 10Al \rightarrow 5Al_2O_3 + 3Na_2O + 3N_2$ and $\Delta H = -623.9$ kJ/mol (1)

$NaClO_3 + 2Al \rightarrow Al_2O_3 + NaCl$ and $\Delta H = -783$ kJ/mol (2)

$3/4TiO_2 + Al \rightarrow 3/4Ti + 1/2Al_2O_3$ and $\Delta H = -129.4$ kJ/mol (3)

3. MATERIALS AND METHODS

The aim of the research presented in this paper was to evaluate the influence of chemical compositions producing an exothermic effect on the mechanical properties (tensile strength and elongation) of AlSi7Mg alloy (**Table 1**). An improvement in the functional properties of alloys may be achieved by adding to silumin compounds containing elements which after reduction affect the process of crystallization and increase the strength of solution α - phase and eutectic (α+β).

Founding, that studied proprieties are continuous functions considered variables and its can be with sufficient exactitude represented in figure of polynomial in investigations planning experiences was applied active, applying complete factorial experiment (2^3) for three independent variables: $NaNO_3$, $NaClO_3$, TiO_2 (**Table 2**). The results were analyzed mathematically, which enabled to formulate the factor equation for three variables, for the studied parameters, at the level of significance α = 0.05. The adequacy of the above mathematical equation was verified using the Fischer criterion.

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (4)$$

The real chemical composition of the tested AlSi7Mg alloy is presented in **Table 1**.

The alloy was obtained from industrial piglets. The alloy was melted in an Al_2O_3 crucible in an electric furnace, and the modification process was carried out. Chemical additions were introduced to the crucible. The alloy was modified at a temperature of 850 °C for 8 minutes. Cylindrical samples, 8 mm in diameter and 75 mm in length, were poured into a mold made of molding sand. Upon the completion of each modification stage, specimens were collected for mechanical tests. Samples for mechanical tests were obtained from the upper part of the casting. A elongation test was performed according to the standard ISO 6892-1:2016 metallic materials - tensile testing - part 1: method of test at room temperature, using a universal strength testing machine (W.P.M. Germany), determining tensile strength *Rm* and elongation *A*.

Table 1 Real mean chemical composition of the AlSi7Mg alloy (wt%)

Si	Cu	Mg	Mn	S	Cr	Fe	Ti	Zr
7.2	0.05	0.32	0.36	0.02	0.01	0.15	0.02	0.05

Table 2 Component of mixture

Variable	**Primary level** (wt %)	**Range of changes** (wt%)	**Higher level** (wt%)	**Lower level** (wt%)
$NaNO_3$	0.5	0.2	0.7	0.3
$NaClO_3$	0.5	0.2	0.7	0.3
TiO_2	0.5	0.2	0.7	0.3

4. RESULTS AND DISCUSSION

The tensile strength (*Rm*) of the AlSi7Mg alloy after chemical treatment is presented in **Figures 1-6** and percentage elongation (*A*) is shown in **Figures 7-12**. The tensile strength of AlSi7Mg alloy after modification with modifier contents with: 0.3 % $NaClO_3$ + 0.3 % TiO_2 and 0.3 % $NaNO_3$ was 138 MPa (**Figure 2**) and elongation *A* = 2.8 % (**Figure 10**). An increase in the quantity of $NaNO_3$ to 0.7 % *Rm* increased to 161 MPa (**Figure 1**) and *A* = 3.6 % (**Figure 7**). Next with the identical increase in the share of $NaClO_3$ and TiO_2, *Rm* grew to 183 MPa (**Figure 1**) and elongation to 6.4 % (**Figure 6**). It was the highest tensile strength and elongation for analyzed components.

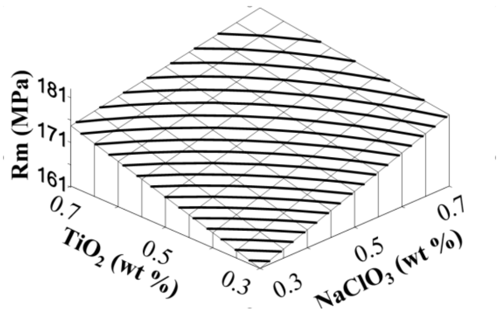

Figure 1 Tensile strength of AlSi7Mg alloy with: $NaClO_3 \in <0.3, 0.7>$ wt%, $TiO_2 \in <0.3, 0.7>$ wt%, for 0.7 wt% $NaNO_3$

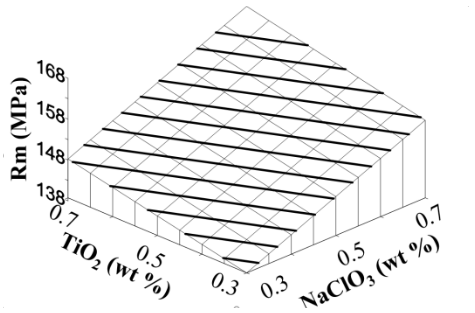

Figure 2 Tensile strength of AlSi7Mg alloy with: $NaClO_3 \in <0.3, 0.7>$ wt%, $TiO_2 \in <0.3, 0.7>$ wt%, for 0.3 wt% $NaNO_3$

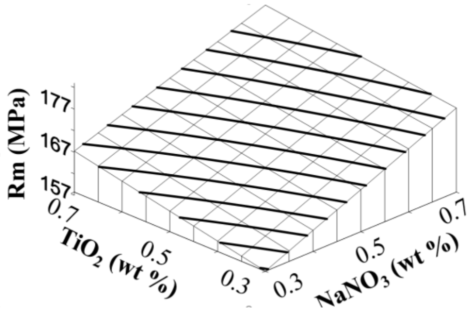

Figure 3 Tensile strength of AlSi7Mg alloy with: $NaNO_3 \in <0.3, 0.7>$ wt%, $TiO_2 \in <0.3, 0.7>$ wt%, and 0.7 wt% $NaClO_3$

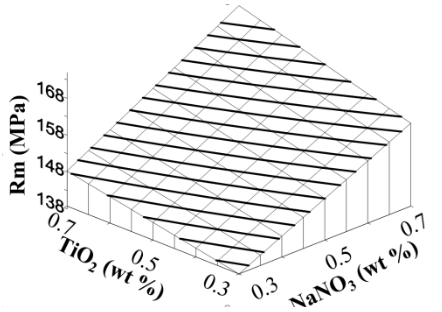

Figure 4 Tensile strength of AlSi7Mg alloy with: $NaNO_3 \in <0.3, 0.7>$ wt%, $TiO_2 \in <0.3, 0.7>$ wt%, and 0.3 wt% $NaClO_3$

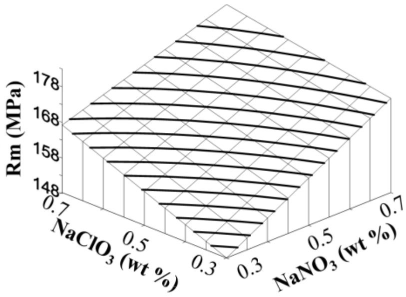

Figure 5 Tensile strength of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%, $NaClO_3$ ∈ <0.3, 0.7> wt% and 0.7 wt% TiO_2

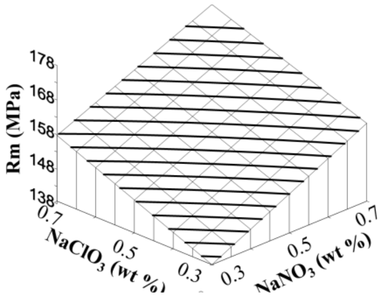

Figure 6 Tensile strength of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%,$NaClO_3$ ∈ <0.3, 0.7> wt% and 0.3 wt% TiO_2

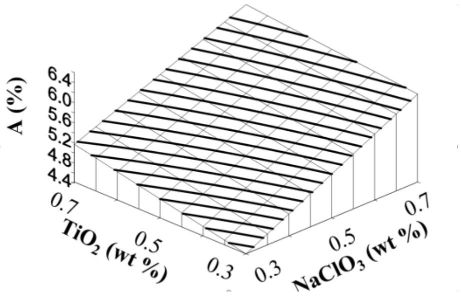

Figure 7 Elongation of AlSi7Mg alloy with: $NaClO_3$ ∈ <0.3, 0.7> wt%, TiO_2 ∈ <0.3, 0.7> wt% for 0.7 wt% $NaNO_3$

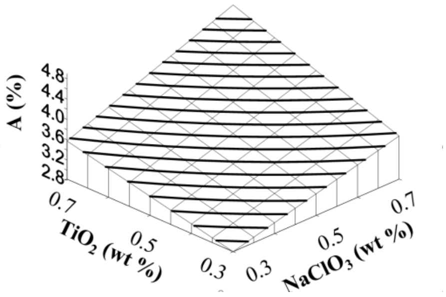

Figure 8 Elongation of AlSi7Mg alloy with: $NaClO_3$ ∈ <0.3, 0.7> wt%, TiO_2 ∈ <0.3, 0.7> wt% for 0.3 wt% $NaNO_3$

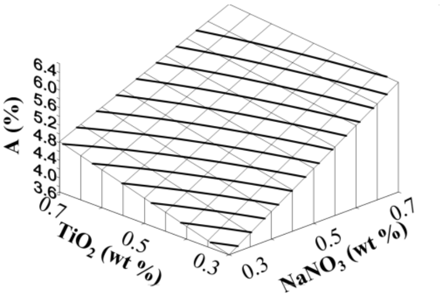

Figure 9 Elongation of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%, TiO_2 ∈ <0.3, 0.7> wt% and 0.7 wt% $NaClO_3$

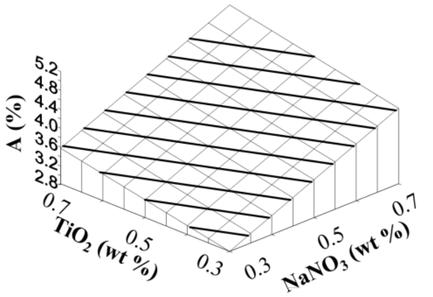

Figure 10 Elongation of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%, TiO_2 ∈ <0.3, 0.7> wt% and 0.3 wt% $NaClO_3$

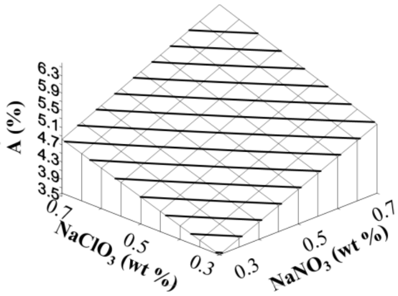

Figure 11 Elongation of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%,$NaClO_3$ ∈ <0.3, 0.7> wt% and 0.7 wt% TiO_2

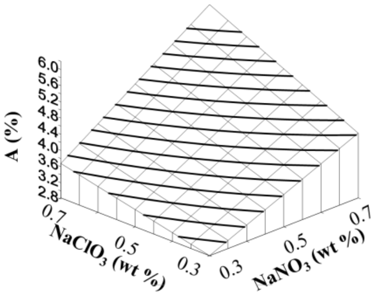

Figure 12 Elongation of AlSi7Mg alloy with: $NaNO_3$ ∈ <0.3, 0.7> wt%,$NaClO_3$ ∈ <0.3, 0.7> wt% and 0.3 wt% TiO_2

With the participation of 0.7 wt% $NaNO_3$ for changes in *Rm* and 0.3% for changes in *A*, $NaClO_3$ and TiO_2 are similar (**Figure 1** and **Figure 8**). A large gradient of contour lines indicates intensive changes in the analyzed parameters. For 0.7 wt% $NaClO_3$, the TiO_2 component interacts more intensively on *Rm* than $NaNO_3$ (**Figure 3**), similarly with 0.3 wt% $NaClO_3$, but in this system the influence of the remaining components of the mixture is more intense, although the *Rm* obtained is lower (**Figure 4**). Generally, the influence of $NaNO_3$ on the analyzed mechanical properties is more intensive than NaClO3, regardless of the share of TiO_2 (**Figures 5, 6, 11, 12**). The intensity of the TiO_2 interaction depends on the proportion of the other two components in the mixture. It is generally higher with the participation of at least one of them at a higher level (0.7 %) (**Figures 1-4** and **7-10**).

5. CONCLUSION

Based on the results of the research, it was found that:

- the interaction of individual components of the mixture depends on the share of the other two (it is correlated),
- the interaction intensity can be ordered into $NaNO_3$, $NaClO_3$ and TiO_2,
- ingredients based on Na independently affect the strength parameters of the alloy, while the ability of TiO_2 to cause changes is strongly influenced by components containing sodium,
- the mechanical parameters were higher after treatment the alloy with a higher energy mixture (equations 2-4).

REFERENCES

[1] MICHNA, S., LUKAC, I., OCENASEK, V., KORENY, R., DRAPALA, J., SCHNEIDER, H., MISKUFOVA, A. *Encyclopaedia of aluminium*. Adin s.r.o. Presov, 2005.

[2] LIPINSKI, T. Microstructure and mechanical properties of the AlSi13Mg1CuNi alloy with ecological modifier. *Manufacturing Technology*. 2011, vol. 11, pp. 40-44.

[3] WOŁCZYŃSKI, W. Concentration micro-field for lamellar eutectic growth. *Defect and Diffusion Forum*. 2007, vol. 272, pp. 123-138.

[4] NOVÁ, K., NOVÁK, P, VANKA, T., PRŮŠA, F. The effect of production process on properties of FeAl20Si20. *Manufacturing Technology*. 2018, vol. 18, pp. 295-298.

[5] LIPINSKI, T., SZABRACKI, P. Modification of the hypo-eutectic Al-Si alloys with an exothermic modifier. *Arch. Metall. Mater*. 2013, vol. 58, pp. 453-458.

[6] SZABRACKI, P., LIPINSKI, T. Influence of sigma phase precipitation on the intergranular corrosion resistance of X2CrNiMoN25-7-4 super duplex stainless steel. In *METAL 2014: 23rd Int. Conf. on Metallurgy and Materials*. Ostrava, TANGER, 2014, pp. 476-481.

[7] LIPINSKI, T., KARPISZ, D. Corrosion rate of 1.4152 stainless steel in a hot nitrate acid. In *METAL 2019: 28th Int. Conf. Metallurgy and Materials*. Ostrava, TANGER, 2019, pp. 1086-1091.

[8] DOMAGALA, M. Simulation of cavitation in jet pumps. *Technical Transactions*. 2013, vol. 110, pp. 51-58.

[9] DOMAGALA, M., MOMENI, H., DOMAGALA-FABIS, J., FILO, G., KWIATKOWSKI, D. Simulation of cavitation erosion in a hydraulic valve. *Mater. Res. Proc*. 2018, vol. 5, pp.1-6.

[10] FILO, G. Computer monitoring and control system of a local LNG supply station. *Technical Transactions*. 2013, vol. 110, pp. 105-112.

[11] FILO, G. Asynchronous buffer read method in development of DAQ application for supporting research of hydraulic systems. *Technical Transactions*. 2015, vol. 112, pp. 77-82.

[12] SKRZYPCZAK-PIETRASZEK, E., HENSEL, A. Polysaccharides from Melittis melissophyllum L. herb and callus. *Pharmazie*. 2000, vol. 55, pp. 768-771.

[13] PIETRASZEK, J., SKRZYPCZAK-PIETRASZEK, E. The optimization of the technological process with the fuzzy regression. *Adv. Mater. Res-Switz*. 2014, vol. 874, pp. 151-155.

[14] BROZOVA, S., INGALDI, M., SPERLIN, I. Economical aspects of high-temperature heating utilization for industrial waste treatment. In *METAL 2013: 22nd Int. Conf. on Metallurgy and Materials*. Ostrava, TANGER, 2013, pp. 1735-1739.

[15] INGALDI, M. Management of the packaging waste in companies in Poland. In *15th Int. Multidiscip. Sci. GeoConf. SGEM*. vol.3. Albena: Bulgarian Acad. Sci., 2015, pp. 385-392.

[16] DZIUBA, S.T., INGALDI, M. Segragation and recycling of packaging waste by individual consumers in Poland. In *15th Int. Multidiscip. Sci. Geoconf. SGEM, vol. 3*. Albena: Bulgarian Acad. Sci., 2015, pp. 545-552.

[17] PIETRASZEK, J. Response surface methodology at irregular grids based on Voronoi scheme with neural network approximator. In *Rutkowski L., Kacprzyk J. (eds) Neural Networks and Soft Computing*. Advances in Soft Computing, vol 19. Physica, Heidelberg: 2003, pp. 250-255.

[18] PIETRASZEK, J., GADEK-MOSZCZAK, A. The smooth bootstrap approach to the distribution of a shape in the ferritic stainless steel AISI 434L powders. *Solid State Phenomena*. 2012, vol. 197, pp. 162-167.

[19] SKRZYPCZAK-PIETRASZEK, E., REISS, K., ZMUDZKI, P., PIETRASZEK, J. Enhanced accumulation of harpagide and 8-O-acetyl-harpagide in Melittis melissophyllum L. agitated shoot cultures analyzed by UPLC-MS/MS. *PLOS One*. 2018, vol. 13, art. e0202556.

[20] SKRZYPCZAK-PIETRASZEK, E., PISKA, K., PIETRASZEK, J. Enhanced production of the pharmaceutically important polyphenolic compounds in Vitex agnus castus L. shoot cultures by precursor feeding strategy. *Engineering in Life Sciences*. 2018, vol. 18, pp. 287-297.

[21] GADEK-MOSZCZAK, A., KUCIEL, S., WOJNAR, L., DZIADUR, W. Application of computer-aided analysis of an image for assessment of reinforced polymers structures. *Polimery.* 2006, vol. 51, pp. 206-211.

[22] GADEK-MOSZCZAK, A., RADEK, N., WRONSKI, S., TARASIUK, J. Application the 3D image analysis techniques for assessment the quality of material surface layer before and after laser treatment. *Advanced Materials Research-Switz*. 2014, vol. 874, pp.133-138.

[23] WOJNAR, L., GADEK-MOSZCZAK, A., PIETRASZEK, J. On the role of histomorphometric (stereological) microstructure parameters in the prediction of vertebrae compression strength. *Image Analysis and Stereology*. 2019, vol. 38, pp.63-73.

[24] ZORAWSKI, W., CHATYS, R., RADEK, N., BOROWIECKA-JAMROZEK, J. Plasma-sprayed composite coatings with reduced friction coefficient. *Surface & Coatings Technology*. 2008, vol. 202, pp. 4578-4582.

[25] DUDEK, A. Investigations of microstructure and properties in bioceramic coatings used in medicine. *Arch. Metall Mater*. 2011, vol. 56, pp. 135-140.

[26] MARUSZCZYK, A., DUDEK, A., SZALA, M. Research into morphology and properties of TiO_2-NiAl atmospheric plasma sprayed coating. *Adv. Sci. Technol. Res. J.* 2017, vol. 11, pp. 204-210.

[27] KORZEKWA, J., BARA M., PIETRASZEK, J., PAWLUS, P. Tribological behaviour of Al_2O_3/inorganic fullerene-like WS2 composite layer sliding against plastic. *Int. J. Surf. Sci. Eng*. 2016, vol. 10, pp. 570-584.

[28] PIETRASZEK, J., GADEK-MOSZCZAK, A., TORUNSKI, T. Modeling of errors counting system for PCB soldered in the wave soldering technology. *Advanced Materials Research*. 2014, vol. 874, pp. 139-143.

[29] PIETRASZEK, J., KOLOMYCKI, M., SZCZOTOK, A., DWORNICKA, R. The fuzzy approach to assessment of ANOVA results. *Lecture Notes in Artificial Intelligence*. 2016, vol. 9875, pp. 260-268.

[30] SKRZYPCZAK-PIETRASZEK, E., KWIECIEN, I., GOLDYN, A., PIETRASZEK, J. HPLC-DAD analysis of arbutin produced from hydroquinone in a biotransformation process in Origanum majorana L. shoot culture. *Phytochemistry Letters*. 2017, vol. 20, pp. 443-448.

[31] LYAKISHEV, N.P., KLINER, YU.L., IGNATIENKO, G.S., LATTO, S.I. *Aluminothermy*, Moscow, 1978.

[32] LIPINSKI, T. Use Properties of the AlSi9Mg alloy with exothermical modifier. *Manufacturing Technology*. 2011, vol.11, pp. 44-49.