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MODIFICATION OF THE HYPO-EUTECTIC Al-Si ALLOYS WITH AN EXOTHERMIC MODIFIER

MODYFIKACJA PODEUTEKTYCZNYCH STOPÓW Al-Si MODYFIKATOREM EGZOTERMICZNYM

Results of studies on the modification of AlSi7Mg alloy with an exotherimc modifier are presented in the paper. MgO, Cr_2O_3, Na_2O_2, $NaNO_3$, Na_2MoO_4 were used as modifiers in the amount of 0.05, 0.10, 0.15, 0.20 and 0.25%, and Cr_2O_3+Al, $NaNO_3$+Al, Na_2MoO_4+Al were applied as exothermic modifiers with Al as the reducing agent in the amount of 0.04-0.3%. The analyzed modifiers were incorporated in line with factorial design 2^3. The Inmold modification method was applied. The microstructure of selected modified alloys was presented, and their tensile strength, percentage elongation and Brinell hardness number were given in graphic form. The results of the study indicate that the use of modifiers delivering an exothermic effect influences the effectiveness of silumin modification.

Keywords: Al alloys, modification, silumin, exothermic modifier

W pracy przedstawiono wyniki badań nad modyfikacją stopu AlSi7Mg modyfikatorem egzotermicznym. Do badań użyto, jako modyfikatorów związków MgO, Cr_2O_3, Na_2O_2, $NaNO_3$, Na_2MoO_4 wprowadzanych w ilości 0.05, 0.10, 0.15, 0.20 and 0.25% oraz w postaci modyfikatora egzotermicznego z Al jako reduktorem Cr_2O_3+Al, $NaNO_3$+Al i Na_2MoO_4+Al w ilości 0.04-0.3% wprowadzanych zgodnie z planem czynnikowym 2^3. Modyfikację prowadzono metodą Inmold. Przedstawiono wybrane mikrostruktury stopu po modyfikacji oraz w postaci graficznej wytrzymałość na rozciąganie, wydłużenie procentowe i twardość Brinella. Wykazano, że zastosowanie modyfikatora w postaci mieszanki dającej efekt egzotermiczny wpływa na efektywność modyfikacji siluminu.

1. Introduction

Microstructural changes aiming to improve the functional, mainly mechanical, properties of subeutectic silumins have been researched extensively for many years. Various methods of enhancing silumins' mechanical attributes have been proposed [1-7]. Chemical modifiers are usually applied in the production of Al alloy casts. Various chemical elements and compounds are incorporated into the process to enhance alloy properties [8-10]. The applied modifiers contain several elements or compounds. Different methods for adding modifiers have been proposed, including introduction into the crucible or the Inmold technique, to increase the effectiveness of silumin modification. There is a general scarcity of information, however, about the impact of exothermic reactions on alloy modification.

In the Inmold method, the reaction is initiated in the reaction chamber, but there are no grounds to believe that this is where the process ends. Liquid alloy carries the modifier from the reaction chamber to the mold cavity. It is modified during flow and crystallization, and heat produced in that reaction also affects solid phase formation. The chemical reaction and its effects can last until the alloy solidifies.

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 [11].
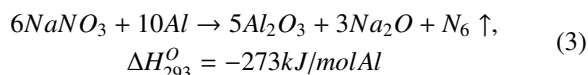
$$Me'O + Me'' \rightarrow Me' + Me''O \qquad (1)$$
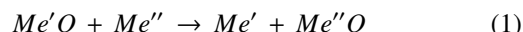
The reaction (1) may occur if the value of enthalpy is equal to:

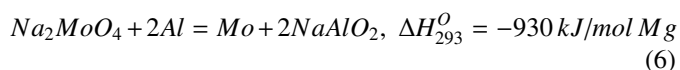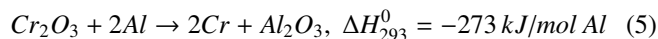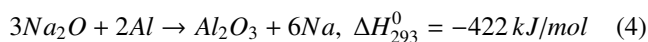$$\Delta H^O_{298Me''O} > \Delta H^O_{293Me'O} \qquad (2)$$

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 literature [11], 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 aluminum may be presented

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on the example of the following reaction (3) and next (4) or (5) or (6).

$$6NaNO_3 + 10Al \rightarrow 5Al_2O_3 + 3Na_2O + N_6 \uparrow,$$
$$\Delta H_{293}^O = -273 kJ/molAl \qquad (3)$$

and next (4)

$$3Na_2O + 2Al \rightarrow Al_2O_3 + 6Na, \ \Delta H_{293}^0 = -422 \, kJ/mol \quad (4)$$

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3, \ \Delta H_{293}^0 = -273 \, kJ/mol \, Al \quad (5)$$

$$Na_2MoO_4 + 2Al = Mo + 2NaAlO_2, \ \Delta H_{293}^O = -930 \, kJ/mol \, Mg \qquad (6)$$

3. Aim of the study and methods

The objective of this study was to investigate whether the use of a modifier delivering exothermic effects influences the effectiveness of hypo-eutectic silumin modification.

Reducing agents were aluminum (Al) (3) and magnesium (Mg) (5). Modifiers content of the alloy is given as weight in weight concentration (mass fraction) 0.05, 0.10, 0.15, 0.20 and 0.25%. Exothermic modifiers: Cr_2O_3, $NaNO_3$, Na_2MoO_4 content of the alloy is given as weight in weight concentration 0.04, 0.17 and 0.3%. The experiments were conducted on alloy AlSi7Mg (Tab. 1), following a factor design for 3 independent variables.

TABLE 1

Chemical compositions of AlSi7Mg alloy

Alloy	Chemical composition (wt%)							
	Si	Mg	Mn	Fe	Cu	Ti	Ni	Al
AlSi7Mg	7.11	0.34	0.32	0.42	0.10	0.1	0.006	balance

Tab. 2 shows the basic composition and range of changes in modifiers.

TABLE 2

Contents of the chemical compounds of exothermic modifiers

Alloy number	Chemical compounds, wt%		
	Cr_2O_3	$NaNO_3$	Na_2MoO_4
1	0.04	0.04	0.04
2	0.3	0.04	0.04
3	0.04	0.3	0.04
4	0.3	0.3	0.04
5	0.04	0.04	0.3
6	0.3	0.04	0.3
7	0.04	0.3	0.3
8	0.3	0.3	0.3

The adequacy of the above mathematical dependence was verified using the Fischer criterion. The significance of coefficients was determined employing the Student's t-test at a level of α =0.05. The adequacy of the above mathematical

equation was verified using the Fischer criterion. The mixtures were made of powders in the right proportions. After special preparation, they were placed in a reaction chamber, under the down-gate (Inmold method). The alloy temperature was 1123 K. The modifier content of the alloy is given as weight in weight concentration (mass fraction). For comparative purposes, two castings were produced (without additions), at the beginning and at the end of the study. Hand molding was carried out. Fig. 1 presents section of the casting mold.
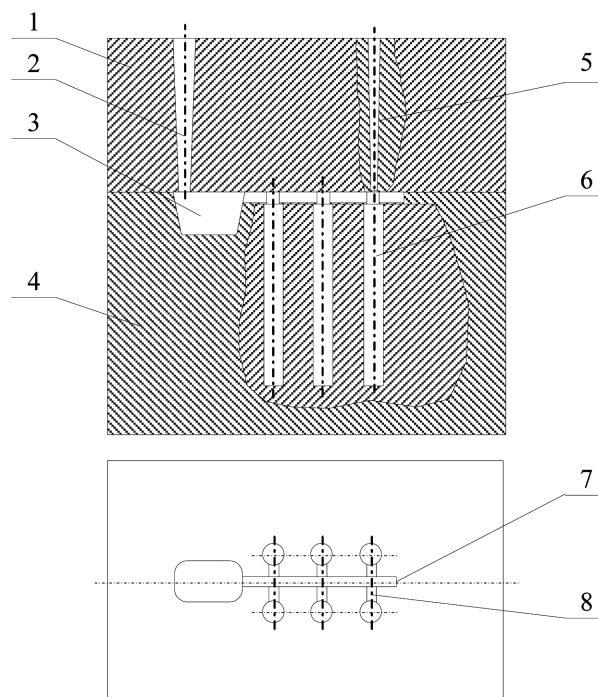

Fig. 1. Section of the casting mold for exothermic modifier: 1 – top moulding box, 2 – down-gate, 3 – reaction chamber, 4 – down moulding box, 5 – strain relief, 6 – sample for strength testing and probe for thermal analysis, 7 – cross-gate, 8 – running gate

The face of cut served as metallographic specimen for microstructure analysis. Samples for mechanical tests were obtained from the upper part of the casting. Samples for metallographic tests were taken from the lower part of the samples designed for mechanical tests. Hardness tests were performed on the upper parts of strength test samples (six measurements per sample). All measurements were carried out according to the standard PN-EN 6506-1: 2008 Metallic materials – Brinell hardness test Part 1 – Test method, with a standard ball, 2.5 mm in diameter, at a load of 612.9 N. A tensile strength test was performed, on six samples for every one with plan point, according to the Polish Standard PN-EN 6892-1: 2010 Metallic materials – Tensile testing – Part 1: Method of test at room temperature, using a universal strength testing machine, determining tensile strength R_m and percentage elongation A.

4. Results

The microstructure of AlSi7Mg silumin without modifying additives consists of a solid solution of silicone in aluminum (phase α) and a solid solution of aluminum in silicone (phase β) (Fig. 2). The eutectic is composed of

irregular-shaped grains of phase β. As a result, the mechanical properties of the alloy are poor. The introduction of 0.15-0.25% MgO into the silumin's microstructure resulted in a gradual increase in grain refinement of eutectics $(\alpha + \beta)$. The microstructure was partially modified with the addition of 0.25% MgO (Fig. 3). Similar changes were reported following the introduction of 0.15-0.25% Cr_2O_3. The addition of up to 0.1% MgO or Cr_2O_3 did not lead to observable microstructural changes. Microstructural alterations were manifested by changes in the alloy's mechanical properties after modification with the above compounds. The incorporation of 0.05% and 0.1% MgO and Cr_2O_3 did not lead to variations in tensile strength R_m or percentage elongation A (Fig. 4 and Fig. 5, respectively). When the share of MgO and Cr_2O_3 modifiers was increased to 0.15-0.25%, a gradual increase was noted in the values of R_m and A. When the AlSi7Mg alloy was modified with Na_2O_2 or $NaNO_3$ or Na_2MoO_4, microstructural changes were also determined by the applied quantity of modifier, and modification effects were noted already at 0.1% modifier content (Fig. 6). Grain refinement was observed when the content of every modifier was increased to 0.25%. Alloy microstructure modified with 0.25% Na_2MoO_4 is presented in Figure 7. In comparison with the microstructures resulting from treatment with 0.25% MgO (Fig. 3) and with 0.1% Na2MoO4 (Fig. 6), it is characterized by more intensive eutectic grains $(\alpha + \beta)$ modified. The values of R_m and A for the tested modifiers are presented in Fig. 8 and 9. When the impact of each additive (Na_2O_2, $NaNO_3$, Na_2MoO_4) was compared separately, the greatest modification effects were delivered by Na_2MoO_4, followed by Na_2O and $NaNO_3$ (Fig. 8 and 9).

increased tensile strength to 160 MPa and percentage elongation – to 4%. Despite this increase, the noted values are not satisfactory.

Fig. 4. Tensile strength (R_m) of AlSi7Mg alloy with MgO or Na_2O_2

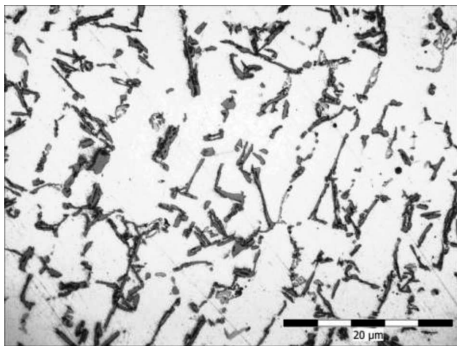Fig. 5. Percentage elongation (A) of AlSi7Mg alloy with MgO or Na_2O_2

Fig. 2. Microstructure of AlSi7Mg without modifying additives
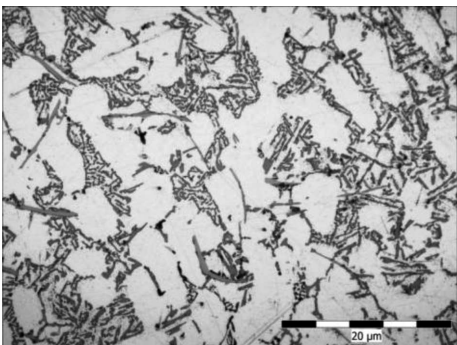
Fig. 3. Microstructure of AlSi7Mg with 0.25% MgO

Fig. 6. Microstructure of AlSi7Mg with 0.1% Na_2MoO_4
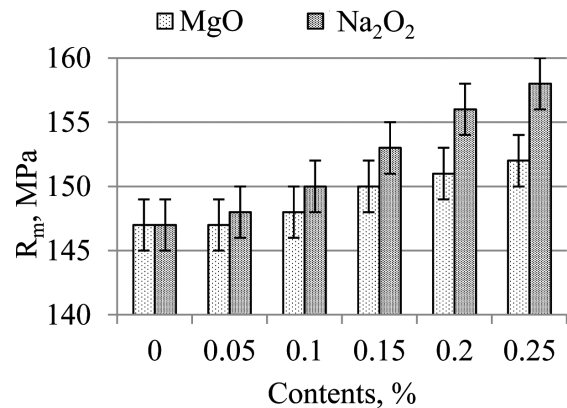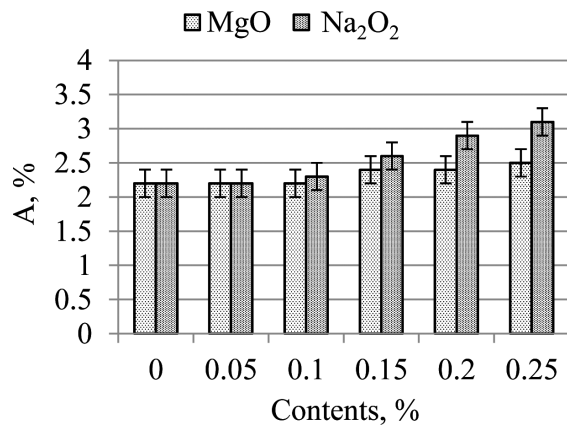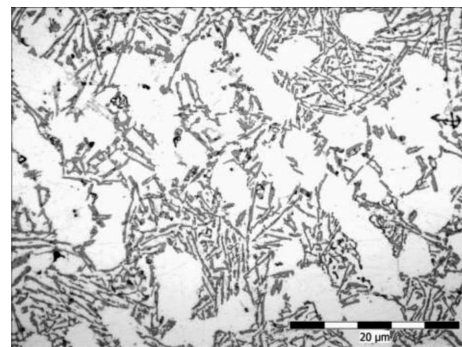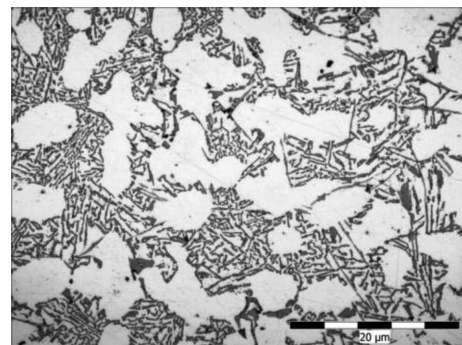

Fig. 7. Microstructure of AlSi7Mg with 0.25% Na_2MoO_4

Following the incorporation of MgO or Cr_2O_3, maximum tensile strength reached 155 MPa and maximum elongation percentage – 3%. The use of Na-containing modifiers
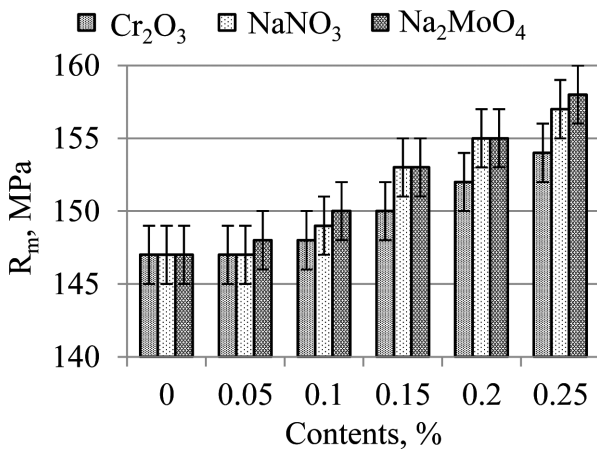
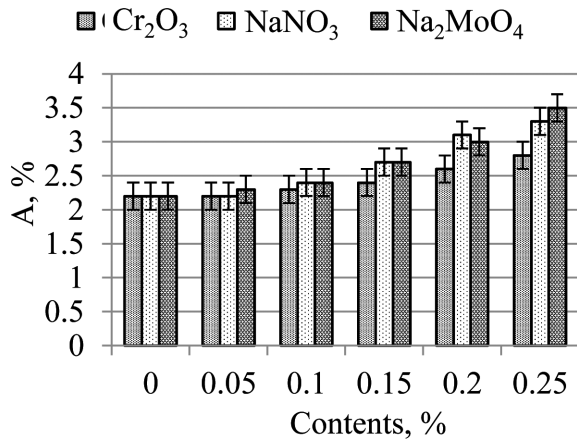Fig. 8. Tensile strength (R_m) of AlSi7Mg alloy with Cr_2O_3, Na_2O_2 and Na_2MoO_4

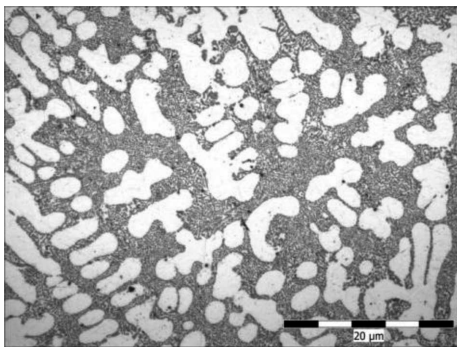Fig. 9. Percentage elongation (A) of AlSi7Mg alloy with Cr_2O_3, Na_2O_2 and Na_2MoO_4

Fig. 10. Microstructure of AlSi7Mg with 0.3% Cr_2O_3+ 0.3% $NaNO_3$+ 0.3% Na_2MoO_4

Higher modification effectiveness was reported for the exothermic modifier with Al reducing agent. Higher degree of grain refinement was observed, and eutectic silicon had oval morphology. Alpha phase dendrites were refined (Fig. 10). Silumin's mechanical properties were enhanced as the result of microstructural modification (Fig. 11-19).

The results of a tensile strength (R_m), percentage elongation (A) and Brinell hardness (HB) of AlSi7Mg alloy with exothermic modifier containing $NaNO_3$+Al$\in$<0.06, 0.2>[%] and Na_2MoO_4+Al $\in$<0.04, 0.3>[%] and Cr_2O_3+Al =0.04%

are shown in Tab. 3 and at Fig. 11a, 12a, 13a, and for Cr_2O_3+Al =0.3% are shown at Fig. 11b, 12b, 13b.

TABLE 3

Mechanical properties (mean value) of AlSi7Mg alloy with exothermic modifiers

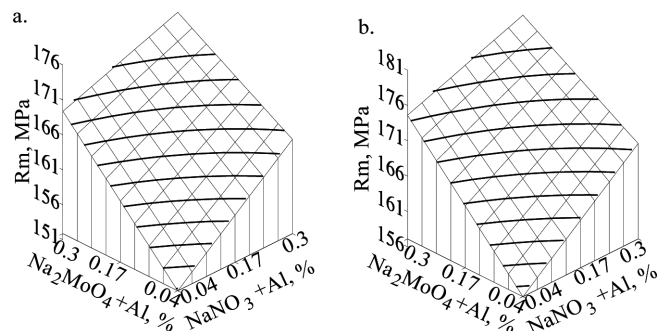| Alloy number	Tensile strength R_m	Percentage elongation A	Brinell hardness HB
	MPa	%	HB
1	152±2	2.5±0.2	52±2
2	157±2	3.3±0.2	60±2
3	164±2	3.9±0.2	56±2
4	172±2	5.6±0.2	59±2
5	169±2	4.2±0.2	66±2
6	175±2	6.0±0.2	64±2
7	177±2	6.3±0.2	60±2
8	179±2	6.8±0.2	62±2

Fig. 11. Tensile strength (R_m) of AlSi7Mg alloy with $NaNO_3$+Al$\in$<0.06, 0.2>[%] and Na_2MoO_4+Al $\in$<0.04, 0.3>[%] for a. Cr_2O_3+Al =0.04%, b. Cr_2O_3+Al =0.3%
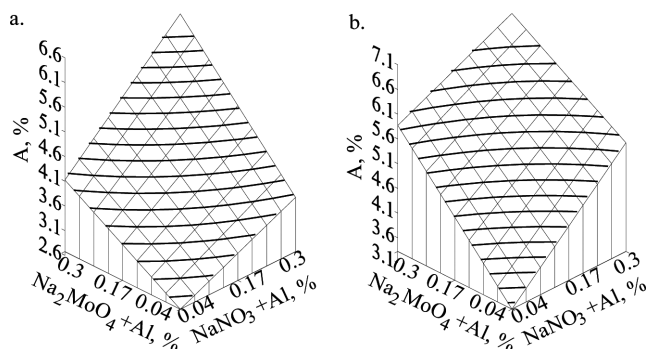

Fig. 12. Percentage elongation (A) of AlSi7Mg alloy with $NaNO_3$+Al$\in$<0.06, 0.2>[%] and Na_2MoO_4+Al $\in$<0.04, 0.3>[%] for a. Cr_2O_3+Al =0.04%, b. Cr_2O_3+Al =0.3%

The results of a R_m, A and HB of AlSi7Mg alloy with exothermic modifier containing Cr_2O_3+Al $\in$<0.06, 0.2>[%] and Na_2MoO_4+Al $\in$<0.04, 0.3>[%] and $NaNO_3$+Al =0.04% are shown at Fig. 14a, 15a, 16a, and for $NaNO_3$+Al =0.3% are shown at Fig. 14b, 15b, 16b.
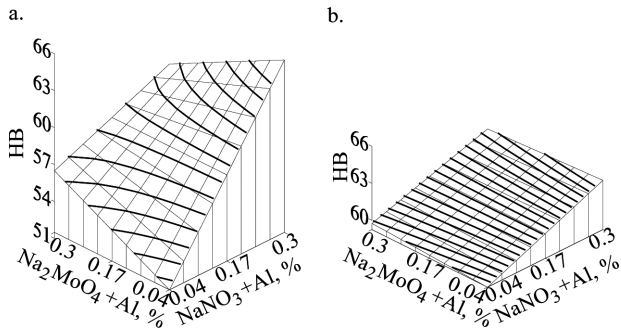
Fig. 13. Brinell hardness (HB) of AlSi7Mg alloy with $NaNO_3+Al \in <0.06, 0.2>$[%] and $Na_2MoO_4+Al \in <0.04, 0.3>$[%] for a. $Cr_2O_3+Al =0.04\%$, b. $Cr_2O_3+Al =0.3\%$
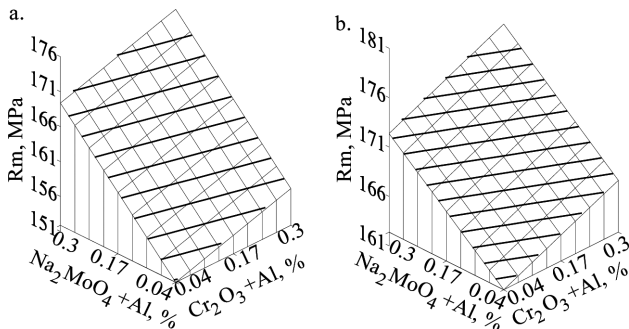
Fig. 14. Tensile strength (R_m) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $Na_2MoO_4+Al \in <0.04, 0.3>$[%] for: a. $NaNO_3+Al =0.04\%$, b. $NaNO_3+Al =0.3\%$
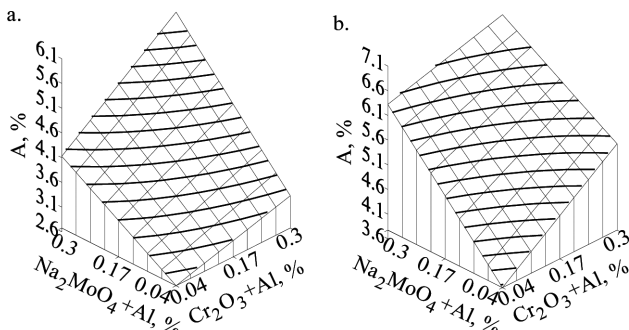
Fig. 15. Percentage elongation (A) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $Na_2MoO_4+Al \in <0.04, 0.3>$[%] for: a. $NaNO_3+Al =0.04\%$, b. $NaNO_3+Al =0.3\%$
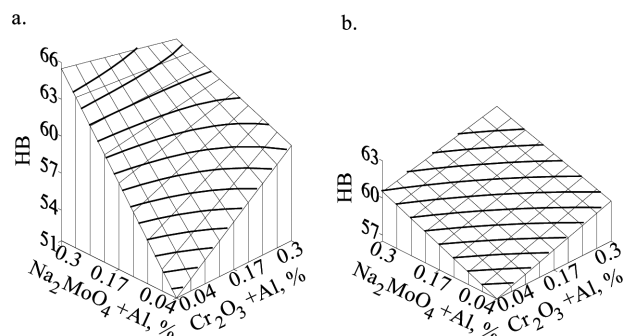
Fig. 16. Brinell hardness (HB) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $Na_2MoO_4+Al \in <0.04, 0.3>$[%] for: a. $NaNO_3+Al =0.04\%$, b. $NaNO_3+Al =0.3\%$

The results of a R_m, A and HB of AlSi7Mg alloy with exothermic modifier containing $Cr_2O_3+Al \in <0.06, 0.2>$[%]

and $NaNO_3+Al \in <0.04, 0.3>$[%] and $Na_2MoO_4+Al =0.04\%$ are shown at Fig. 17a, 18a, 19a and for $Na_2MoO_4+Al =0.04\%$ are shown at Fig. 17b, 18b, 19b.
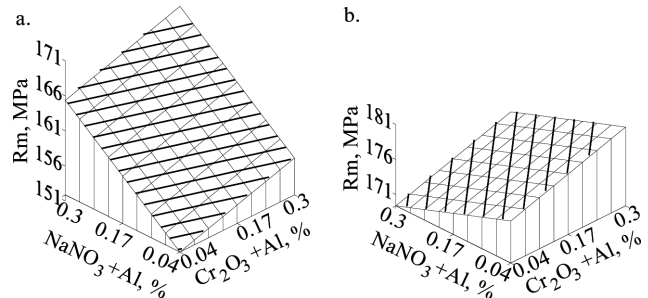

Fig. 17. Tensile strength (R_m) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $NaNO_3+Al \in <0.04, 0.3>$[%] for: a. $Na_2MoO_4+Al =0.04\%$, b. $Na_2MoO_4+Al =0.04\%$
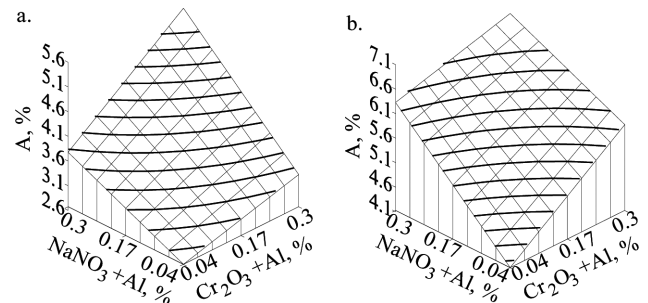
Fig. 18. Percentage elongation (A) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $NaNO_3+Al \in <0.04, 0.3>$[%] for: a. $Na_2MoO_4+Al =0.04\%$, b. $Na_2MoO_4+Al =0.04\%$
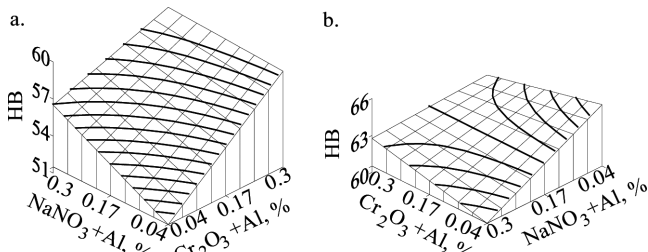
Fig. 19. Brinell hardness (HB) of AlSi7Mg alloy with $Cr_2O_3+Al \in <0.06, 0.2>$[%] and $NaNO_3+Al \in <0.04, 0.3>$[%] for: a. $Na_2MoO_4+Al =0.04\%$, b. $Na_2MoO_4+Al =0.04\%$

An analysis of changes in R_m, A and HB values in alloys with a different share of modifiers delivering exothermic effects indicates that the tested additives were characterized by different intensity. The most effective compound was Na_2MoO_4, followed by $NaNO_3$ and Cr_2O_3 (Fig. 11 and 14). The tested compounds' effectiveness was correlated with the energy of exothermic reactions produced by modifiers (3), (4), (5) and (6). The products of the above reactions should also be taken into account. A modifier that produces a typical beta phase modifier (such as Na) will be characterized by greater effectiveness than, for example, Al_2O_3 or Cr_2O_3.

The mechanical properties of an AlSi7Mg alloy enhanced with a combination of exothermic modifiers were satisfactory. The highest tensile strength ($R_m =180$ MPa) was achieved by enriching the alloy with a mixture of 0.3% Cr_2O_3+ 0.3% $NaNO_3$+ 0.3% Na_2MoO_4, the highest percentage elongation

(A=6.8%) was achieved by enriching the alloy with a mixture of 0.3% Cr_2O_3 + 0.3% $NaNO_3$ + 0.3% Na_2MoO_4 and the highest Brinell hardness (HB=66 HB) was achieved by enriching the alloy with a mixture of 0.04% Cr_2O_3 + 0.04% $NaNO_3$ + 0.3% Na_2MoO_4.

5. Conclusions

The modification of the AlSi7Mg alloy with one of the applied compounds (MgO, Cr_2O_3, Na_2O_2, $NaNO_3$ or Na_2MoO_4) improved its mechanical properties (R_m, A and HB) proportionally to the quantity of incorporated modifier. The noted improvement was visible in the alloy's microstructure.

The use of modifiers delivering exothermic effects increased the intensity of the modification process. The values of the analyzed mechanical properties (R_m, A and HB) increased proportionally to the quantity of introduced modifier. Since all of the applied mixtures were characterized by proportional effectiveness (the improvement in mechanical properties was proportional to the amount of incorporated modifier), a synergistic effect can be ruled out. The values of the analyzed parameters were shaped by each modifier as if it were introduced separately, but the effect of the analyzed mixtures on the final values of R_m, A and HB represents the overall effectiveness of every modifier's share in the mixture. The analysis of the process of hypo-eutectic Al-Si alloy modification with exothermic modifiers shows that modifying additions affected mechanical properties of AlSi7Mg alloy.

The following conclusions can be formulated based on the results of the study:
- modifiers introduced in the form of exothermic mixtures are more effective in altering the microstructure of silumin and improving its mechanical properties,
- modifiers created in an exothermic reaction during silumin modification are more effective than analogous external modifiers,
- it can be assumed that the exothermic modification process itself leads to silumin modification, and in combination with compounds that can alter silumin microstructure, it clearly enhances their effectiveness.

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