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INFLUENCE OF SAND-CASTING PARAMETERS ON MICROSTRUCTURE AND PROPERTIES OF MAGNESIUM ALLOYS

WPŁYW PARAMETRÓW ODLEWANIA GRAWITACYJNEGO NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI STOPÓW MAGNEZU

The paper present the influence of modifying process on chemical composition, microstructure, and selected properties of Mg alloys. Two sand-casting creep-resistant alloys, Elektron 21 and WE43, were analyzed in various forms: without modifiers, with the amount of modifier suggested by the producer, and with this amount increased by 50% and 100%. The volume fraction of eutectic areas, tensile strength, and yield strength were measured and the fluidity and linear contraction were analyzed. The research shows that, in contrast to what is widely assumed to be a positive influence of rare-earth elements on Mg alloys properties, a large increase in the amount of modifiers does not always lead to an improvement in the alloy properties. However, the results are tentative because they may have been influenced by the melting technology used, which can be improved. Rare-earth elements tend to react with fluxes, which could lead to a decrease in mechanical properties and fluidity. More research is planned wherein the alloys are melted under a protective atmosphere.

Keywords: Mg alloys, sand casting, modification, Elektron 21, WE43, properties, fluidity

W artykule zaprezentowano wpływ modyfikacji odlewniczych stopów magnezu na skład chemiczny, mikrostrukturę i wybrane właściwości. Badano 2 stopy odlewane do form piaskowych, przeznaczone do pracy w podwyższonej temperaturze: Elektron 21 i WE43 w czterech wariantach: bez modyfikacji, z ilością modyfikatorów dodaną zgodnie z procedurą zalecaną przez producenta, powiększoną o 50 i 100%. Wykonano ilościową analizę udziału objętościowego eutektyk, zmierzono wytrzymałość na rozciąganie, granicę plastyczności, wykonano próbę lejności oraz skurczu liniowego. Wykazano, że mimo powszechnie uznanego za pozytywny wpływu metali ziem rzadkich na właściwości stopów Mg dodawanie zwiększonych ilości modyfikatorów w stosunku do zaleceń producentów nie zawsze ma dobry wpływ na wyniki. Prawdopodobnie duży wpływ na wyniki badań miała technologia odlewania, wymagająca poprawy – zastosowane topniki mogą reagować z pierwiastkami stopowymi i powodować obniżenie właściwości mechanicznych i lejności. W przyszłości planowane są podobne badania dla stopów topionych w atmosferze gazowej.

1. Introduction

Magnesium is the lightest metal used for constructional alloys. Magnesium alloys are characterized by low density and good mechanical properties [1], which are the primary reasons that they find widespread use in the motor vehicle and aircraft industries. The disadvantages of these alloys are their poor properties at elevated temperature [2] and their high reactivity [1]. A range of alloys are commercially available, from Mg-Al alloys to the highest strength, high-temperature Mg-Zr alloys with the addition of yttrium. However, alloys that contain are expensive due to difficulties in casting. Therefore, a need exists for an alternative alloy with properties similar to Mg-Y alloys, but with foundry handling and associated costs similar to that of non-yttrium-containing alloys [3].

The basic function of rare-earth (RE) chemical elements is formation of reinforcing intermetallic phases that remain stable at elevated temperature [4]. Simultaneously, they limit the range of crystallization temperature, which in turn decreases hot cracking susceptibility, improving its welding properties [5]. Alloys containing gadolinium are characterized by their substantial age-hardening properties. Neodymium creates phases both within the solid-solution grains as well as at the boundary of the solid solution of α -Mg, influencing the reinforcing effect of age hardening by minimizing the range of solubility of gadolinium in an α -Mg solid solution. This facilitates the process of age hardening with a lower content of gadolinium [6,7], which is expensive. However, gadolinium tends to segregate (and this tendency increases with increasing content), which decreases the alloy's ductility [8].

In sand-casting magnesium alloys, the one of the basic alloy additions is zirconium (it is absent only in Mg-Al alloys). Its basic task is to refine α -Mg solid solution. This effect is attributed to the similar crystal lattices of Mg and Zr [4]. Zinc is another element that is added to magnesium alloys to improve their mechanical properties during heat treatment. In addition, it increases the resistance to corrosion caused by impurities such as Fe and Ni [4, 9]. In magnesium alloys

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containing Nd and Gd, the addition of Zn inhibits the ageing effect [10]. The addition of yttrium increases creep resistance, thereby enabling age hardening, which stems from the fact that the Mg-Y intermetallic phases are characterized by a low diffusion rate and good coherence with the alloy's matrix [11].

To obtain the appropriate chemical composition, fine-grained structure and good properties, a process of modification is introduced. This paper presents the results of research into the amounts of casting modifiers that should be introduced into the alloy and the influence of these modifiers on the chemical composition, microstructure, and mechanical and technological properties of WE43 and Elektron 21 alloys.

2. Research material

Two sand-casting magnesium alloys were investigated: WE43 and Elektron 21. The modifier used in this case goes under the commercial name of Zirmax, with the addition of a gadolinium and neodymium hardeners for Elektron 21 and a WE hardener for the WE43 alloy. The chemical compositions of the alloys used are presented in Table 1, with a list of modifiers presented in Table 2.

3. Methodology of research

The alloys were melted in a gas furnace using a steel St3S melting crucible with a capacity of 30 kg. The sequence of testing stages was as follows:

- 1. Load ingots into the crucible;
- 2. Heat alloy to 740-780°C until melting is complete;
- 3. Remove oxides from the surface, add Zirmax modifier and appropriate hardeners. The options or variations used in the modification process are presented in Tables 3 and 4.
- 4. Heat alloy to 780 to 800°C, mix, and cast into molds.

 TABLE 1

 Chemical composition of WE43 and Elektron 21 alloys [wt%]

Alloy		RE (Dy, Ib)	Nd	Y	Zr	Zn	Gd	Mn	Fe	Ag	Mg
WE43	-	1.12	2.3	4.1	0.49	0.01	-	0.01	0.001	< 0.01	
Elek- tron 21	0.12	-	2.8	-	0.45	0.35	1.2	-	0.002	<0.01	rest

Chemical composition of modifiers and hardeners [wt%]

TABLE 2

Modifier/ Hardener	RE (Dy, Ib)	Nd	Y	Zr	Zn	Gd	Mg
Zirmax	-	-	-	35	-	-	65
Gd Hardener	-	-	-	-	-	21	79
WE Hardener	-	0.8	20	-	-	-	79.2
Nd Hardener	0.1	12.4	-	-	-		87.5

TABLE 3

Amount of modifier [kg] added per 100 kg of alloy (following producer specifications)

	Nd Hardener	Zirmax	Gd Hardener	WE hardener
WE43	0.5	3	-	2
Elektron 21	3	6	1	-

TABLE 4

Modification option symbols

Option	А	В	C	D
Amount of modifiers in relation to producers' suggestion [%]	0	100	150	200

Research into the mechanical properties of alloys that were subjected to various degrees of modification was conducted in accordance with the PN-91/H-88052 norm on samples, presented in Fig. 1, and according to linear casting contraction following the TGL (103-2011) norm (Fig. 2). Castability was tested in accordance with the BN-65/4051-08 norm (Fig. 3).



Fig. 1. Model (a) and example cast (b) of sample with gating system used to test mechanical properties



Fig. 2. Model (a) and example cast (b) of sample with gating system used to test linear casting contraction



Fig. 3. Model (a) and example cast (b) of sample with gating system used to test castability

The chemical composition was deduced from a wavelength-dispersive analysis of the x-ray fluorescence spectrum (WDXRF) using a Bruker S4 EXPLORER. Typical etchants for Mg alloys were used. The microstructure of the magnesium alloys was observed with an OLYMPUS GX 71 metallographic microscope and a HITACHI S-3400N scanning electron microscope equipped with the Thermo Noran energy-dispersion spectrometer. Phase composition was analyzed using JEOL JDX-7S diffractometer equipped with a copper anode ($\lambda_{CuK\alpha} = 1.5406$ Å). Phases were indentyfied with the help of pcpdfwin, version 2.1 (JCPDS-ICDD). Quantitative analysis of the microstructure was done with the Met-Ilo program.

4. Results and discussion

4.1. Microstructure of WE43 and Elektron 21 in as-cast condition

WE43 alloy

After sand casting, α -Mg solid-solution matrix and β eutectic areas were observed in the structure of the WE43 alloy (Fig. 4a). The intermetallic β phase is isomorphic to the Mg₅Gd phase. In addition, precipitations containing yttrium (Fig. 4b) occur close to the eutectic areas-most probably Mg₂Y or MgY phases.



Fig. 4. Microstructure of WE43 magnesium alloy in as-cast condition: (a) scanning electron microscope, (b) scanning transmission electron microscope

Elektron 21 alloy

The Elektron 21 alloy is characterized by an α -Mg solid-solution structure with eutectic areas at the grain boundaries of the α -Mg solid solution (Fig. 5a) and regularly shaped precipitates of a phase containing gadolinium (Fig. 5b). The phase that, together with the solid solution, forms the eutectic areas is the Mg₃Gd phase, whereas the minor precipitates are the MgGd₃ phase.



Fig. 5. Microstructure of Elektron 21 alloy in as-cast condition: (a) scanning electron microscope, (b) transmission electron microscope

4.2. Microstructure of introduced modifiers and hardeners

The microstructure of hardeners consists of the α -Mg solid solution with one or more intermetallic phases. In the Nd hardener (Fig. 6), the intermetallic phase precipitate at the α -Mg solid-solution grain boundary and within grains. It contains about 30% neodymium. The phase was identified as Mg₁₂Nd. Moreover, singular precipitates containing 55% neodymium were also observed.



Fig. 6. Diversified morphology of $Mg_{12}Nd$ phase precipitates within microstructure of Nd hardener: (a) Light microscope, (b) Scanning Electron Microscope, back-scattered electron image

The gadolinium hardener includes phase precipitates containing approximately 50% Gd, which forms the eutectic with the α -Mg solid solution. This is a type of Mg₅Gd phase. Moreover, small amounts of phase precipitates containing approximately 65% Gd were present (Fig. 7).



Fig. 7. Mg_5Gd phase precipitates in microstructure of Gd hardener: (a) LM, (b) SEM – BSE image

Phase precipitates containing approximately 30% Y and 10% REs were observed in the α -Mg solid-solution matrix of the WE hardener. Further small precipitates containing almost pure yttrium were also observed (Fig. 8). The phase containing Y and REs was identified as Mg₂₄Y₅ phase, and the precipitates containing almost pure yttrium was identified as the α -Y solid solution.

The Zirmax modifier is characterized by a dual-phase microstructure composed of α -Mg solid solution and α -Zr solid solution (Fig. 9). The proportional mass of the α -Mg attains 69.5%, with α -Zr levels at 30.5%.



Fig. 8. $Mg_{24}Y_5$ phase precipitates in microstructure of WE hardener: (a) LM, (b) SEM – BSE image



Fig. 9. Zirmax microstructure. Nonetched metallographic specimen, (a) SEM – BSE, (b) etched metallographic specimen, LM

4.3. Chemical composition of magnesium alloys after modification

Tables 5 and 6 show the chemical composition of investigated alloys after modification.

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	WE43 – A	WE43 – B	WE43 – C	WE43 – D			
Y	3.35	3.17	2.97	2.74			
Nd	1.46	2.65	3.04	3.16			
Gd, Ib	0.532 + 0.33	0.49 + 0.36	0.65 + 0.35	0.54 + 0.38			
Zr	0.46	0.61	0.62	0.65			

Chemical composition of WE43 allov after modification (wt%)

TABLE 5

 TABLE 6

 Chemical composition of Elektron 21 alloy after modification (wt%)

	Elektron	Elektron	Elektron	Elektron
	21 – A	21 – B	21 – C	21 – D
Nd	2.22	2.9	2.65	2.79
Gd	1.03	1.27	1.26	1.25
Zn	0.321	0.366	0.347	0.335
Zr	0.413	0.613	0.617	0.643

The investigations of the chemical composition of both alloys show that there is no direct correlation between the amount of modifiers added and the amount of certain alloy elements in the cast. We attribute this result to the segregation of the alloying elements and the high affinity with oxygen of certain elements forming this composition. The most disadvantageous tendency occurs for yttrium in the WE43 alloy. Despite the addition of increasing doses of yttrium in the form of a WE hardener, the yttrium content in the alloy decreases proportionally. What is more, even for maximum yttrium content (option A), the alloy fails to meet the requirements of the ASTM norm. The amount of RE elements generally increases in proportion to the amount of hardener. Exceptions to this rule may be found in gadolinium. The content of neodymium in the WE43-A alloy – also very low in comparison with other variations – can most likely be attributed to the inhomogeneous composition, because the Nd hardener (introduced at the rate of 0.5 kg per 100 kg of alloy) cannot increase the amount of Nd that much. The amount of Zr increases with the amount of hardener for all tested variations.

For Elektron 21, the amount of neodymium increases in consecutive variations. The maximum amount for option B is most likely due to the segregation of alloying elements. Gadolinium levels rise solely for option B. The content of this element did not increase as a consequence of the increased dose of hardener. This tendency proved similar to that for Zr. Even though Zr amount rised for all optional variations, the most significant difference remains between options A and B. The increase in Zr content for option D is small and is quite insignificant for option C. None of the modifiers introduced in the course of testing included Zn, so any changes in concentration of Zn are attributed to segregation.

4.4. Influence of modification process on volume fraction of eutectic areas

As initially forecast, the volume fraction of eutectic areas in the WE43 alloy increases with subsequent modification options (Fig. 10).



Fig. 10. Volume fraction of eutectic areas in WE43 and Elektron 21 magnesium alloys after modification

Volume fraction of eutectic areas increase, despite a decrease of RE levels (Gd, Ib) for options B and D. Note that the highest increase in volume fraction of eutectic areas is found between A and B. The addition of hardeners in amounts exceeding the recommendations made by the MEL does not produce a significant increase in the number of eutectic areas.

In contrast to the WE43 alloy, the volume fraction of eutectic areas in the total volume of the Elektron 21 alloy decreased proportionally to the increase in hardeners. However, this decrease is linear, which is most likely an effect of refinement of the grain in the solid α -Mg solution.

4.5. Influence of modification process on mechanical properties

The tensile strength of WE43 alloy (Fig. 11) is greatest for an alloy without hardeners (option A). Smaller addition of hardener decreases tensile strength (options B and C). A significant increase occurs for the maximum amount (option D), reaching the value similar to option A. The reason for such behavior is attributed to the insufficient protection of the molten metal and to the presence of impurities in the gating system. The presence of impurities and the consequent unpredictability of the results suggest a need for technological improvement; for example, the use of a protective atmosphere instead of the fluxing material.



Fig. 11. Mechanical properties of WE43 alloy after modification

In the Elektron 21 alloy (Fig. 12), the tensile strength in subsequent options decreases linearly. From this result, it may be deduced that this decrease in mechanical properties is associated with the decrease in volume fraction of the eutectic areas. In both alloys, the decrease in tensile strength was accompanied by an increase in yield strength.



Fig. 12. Mechanical properties of Elektron 21 alloy after modification

4.6. Influence of modification on castability and linear casting contraction of alloys

The influence of chemical composition on alloy castability is difficult to explain because the content of alloying elements significantly influences a variety of factors that in turn influence the metal's fluidity (such as viscosity, surface tension, range of crystallization temperatures, presence of impurities [12], latent heat, and thermal conductivity). The influence of RE elements on castability is quite a complex issue. On the one hand, a more narrow range of crystallization temperatures, the formation of eutectic areas, and the possibility to degas the cast all improve castability. On the other hand, REs react with oxygen and with fluxing materials, producing impurities and decreasing castability. The results of castability research of the WE43 and Elektron 21 alloys for the various options of modification are presented in Fig. 13.



Fig. 13. Castability of WE43 and Elektron 21 alloys after modification

WE43 alloy demonstrates the best castability for option C. The chemical composition of this option included the highest level of Gd. Nd and Ib amount was close to those for option D. Castability increases linearly for options A, B, and C, which we tentatively attribute to the positive influence of REs on castability. Castability decreases after adding the maximum amount of hardeners (option D), which may be due to impurities in the molten metal bath inhibiting the metal's flow.

The Elektron 21 alloy behaves in the completely opposite manner. For options A, B, and C, castability decreases linearly. Yet, after adding a greater amount of hardeners, it increases dramatically, reaching a maximum for option D. In comparison with WE43, the Elektron 21 alloy presumably owes its castability to a higher concentration of REs in the three cases A, B, and D. For option B, both alloys produce similar results. The different results for option C once again stem from insufficient protection of the molten metal and the formation of impurities.



Fig. 14. Linear casting contraction uninhibited by modifier variant

The results of the linear casting contraction are presented in Fig. 14 We certified that the increase in alloying elements that results from the introduction of hardeners causes an increase of linear contraction. The lowest values for linear casting contraction for both alloys are noted in modification B, which are the casting conditions suggested by the producer.

5. Conclusions

This research leads to the following conclusions:

- 1. The microstructure of the WE43 alloy is composed of α -Mg+ β eutectic areas within the matrix of the α -Mg solid solution-independent of the level of modification. Likewise, the Elektron 21 alloy is characterized by an α -Mg solid-solution matrix, with eutectic areas forming at the grain boundaries.
- 2. The volume fraction of eutectic areas in subsequent variations of the modification process for the WE43 alloy suggests that the optimum amount of modifiers and hardeners is that of option B (as suggested by the producer). For Elektron 21, the results also demonstrate that the addition of modifiers and hardeners in excessive amounts is unnecessary.
- 3. The castability of the WE43 alloys increases linearly with the increase in the level of modification. This is linked with the positive impact of RE elements. The Elektron 21 alloy demonstrates a greater castability than the WE4 alloy, which we attribute to a higher RE content in the former.
- 4. Due to the lack of compliance with the demands concerning yttrium levels in WE43, the effectiveness of melting and casting technologies for this alloy needs to be increased, and special attention should be dedicated to protecting the metal's surface against oxidation.
- 5. The unpredictability of the results regarding the mechanical properties and castability and the presence of impurities in the test samples means the test results need to be verified in more stable conditions; namely, under a protective atmosphere. This is the subject of further research.

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