REFINING OF BIOSOLUBLE ALLOY OF Mg-Nd-Zr SYSTEM FOR MANUFACTURE OF IMPLANTS

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Abstract

Currently, biosoluble materials are widely used for the manufacture of implants, among which the most promising are magnesium alloys. Magnesium is a natural element of the body - it is contained in bone and muscle tissue, is involved in various metabolic processes. In addition, magnesium and its biocorrosion products have excellent biocompatibility. The main advantage of magnesium alloys is the positive effect of magnesium on the human body, but their quality does not meet the requirements for their use in the human body. It is possible to increase the properties of magnesium alloys as a result of improving the processes of refining and modification of liquid melt. The technology of modification of cast magnesium alloys of Mg-Zr-Nd system by dispersed graphite powder is proposed. It is shown that the optimal carbon additive in the amount of 0.05 - 0.1 wt% C improves the mechanical properties due to grain grinding and additional strengthening of structural components. A complex filter containing equal amounts of magnesite, graphite and limestone is proposed, which provides an increased level of refining of the melt to obtain high quality casting. It is shown that the use of a complex carbon-containing filter provides not only efficient refining of the melt, but also its additional modification. In the structure of the alloy there is an increased amount of intermetallic γ-phase, which increases the microhardness of the structural components of the alloy and improves its physical and mechanical characteristics.

Keywords: Magnesium alloy, carbonaceous materials, filtration, modification, refining

1. INTRODUCTION

Currently, biosoluble materials are widely used for the manufacture of implants, among which the most promising are magnesium alloys. Their main advantage is the positive effect of magnesium on the human body. Magnesium is a natural element of the body - it is contained in bone and muscle tissue, is involved in various metabolic processes. In addition, magnesium and its biocorrosion products have excellent biocompatibility.

The main requirements for modifiers of magnesium alloys for medical purposes are the ability to form insoluble centers of crystallization, stable modification effect, low cost, non-deficiency and non-toxicity. The most suitable for these conditions is carbon [1,2], the main advantage of which is its ability to contaminate the metal with oxide inclusions and reaction products in contact with the melt [3,4]. Given that carbon is insoluble in magnesium [5,6] and its particles or carbides can be additional centers of crystallization, the use of carbonaceous materials, in particular graphite, to modify magnesium alloys is a promising direction to improve their quality.

Various fluxes are widely used to protect and refine the liquid magnesium alloy, however, in this case there is a risk of contamination of the metal with flux and its refining products [7-9], which leads to flux corrosion and reduces the quality of implants. To improve their quality, melt filtration is used before pouring it into the mold [10,11] using materials capable of adsorbing flux, non-metallic inclusions [12,13] and providing high quality metal and improved mechanical properties [14-16]. It is obvious that different carbonaceous materials will have different refining and modifying ability due to their chemical composition and physicochemical properties [17,18]. Therefore, the correct choice of filter material, which provides increased refining capacity, maximum grinding of metal grains and, as a consequence, increased complex properties of the metal, is an urgent task.

2. MATERIALS AND METHODS OF RESEARCH

The magnesium alloy of the Mg-Zr-Nd system (wt%: 0.1 - 0.7 Zn; 0.4 - 1.0 Zr; 2.2 - 2.8 Nd; Mg residue) was smelted in the induction furnace of crucible type IPM-500. Refining of the alloy was carried out in a dispensing furnace with batch selection of the melt and introduced growing additives of dispersed graphite powder (wt%: 99.1 C; 0.9 ash) fraction of 0.071 mm, mixed thoroughly and poured standard samples for mechanical tests. The samples were heat treated in Bellevue and PAP-4M furnaces according to T6 mode: heating to 540 ± 5 °C, holding for 15 hours, cooling in air and aging at 200 ± 5 °C, holding for 8 hours, cooling in air.

The efficiency of purification of the melt by filtration materials was compared by the method of determining the characteristics of the surface interaction in different systems. The method of "lying drop" was used for this [19]. Samples from the alloy system Mg-Zr-Nd (Ø 7.5 mm × 7.5 mm) were placed in a graphite heater, which was located in a quartz glass furnace in the middle of the inductor on substrates of magnetite, limestone and graphite. Surface tension ($\sigma_{p.r.}$), cohesion (A_k), adhesion (A_a) and wetting edge angle (K_p), as well as the efficiency of removal of inclusions from the melt during its filtration ($W_{fi.}$) were determined [20]. After melting a drop of metal and subsequent crystallization, hardened metal samples were cut in half and made sections. The microstructure of the metal on the metal-substrate contact surface was studied by optical microscopy after etching in 7% alcoholic nitric acid solution. The micro-hardness of the metal was determined on a micro-hardness tester from Buehler at an indenter load of 10 g.

The filtration efficiency through different materials was investigated on a magnesium alloy, after refining with VI-2 flux (wt%: 38-46 MgCl; 32 - 43 KCl; 8-10 $CaCl_2$; 5-9 $BaCl_2$; 3-5 CaF_2). Pre-heated to a temperature of 500 °C, filter materials with a granularity of 10 - 50 mm alternately poured on the grid of a removable gutter bowl 100 mm high, mounted above the mold riser, and poured cast samples with a working diameter of 12 mm to determine mechanical properties and metallographic control.

The temporary tensile strength (σ_B) and relative elongation (δ) of samples with a working diameter of 12 mm were determined on a rupture machine "P-5" at room temperature. The microstructure of the castings was studied by light microscopy ("Neophot 32") on heat-treated samples after etching with a reagent consisting of 1% nitric acid, 20% acetic acid, 19% distilled water, 60% ethylene glycol.

The chemical composition of castings from magnesium alloys was monitored using optical emission spectrometers "SPECTROMAXx" and "SPECTROMAXxF", photoelectric spectrometers MFS-8 and TFS-36.

3. RESEARCH RESULTS

The effect of growing additives of fine graphite powder (0.05 wt%, 0.1 wt%, 0.3 wt%). On the structure and mechanical properties of the magnesium alloy was studied. The microstructure of the alloy of the Mg-Zr-Nd system, cast by standard technology, was a δ-solid solution with the presence of eutectoid (δ + γ phase) spherical shape and individual intermetallics γ-phase (**Figure 1, a**).

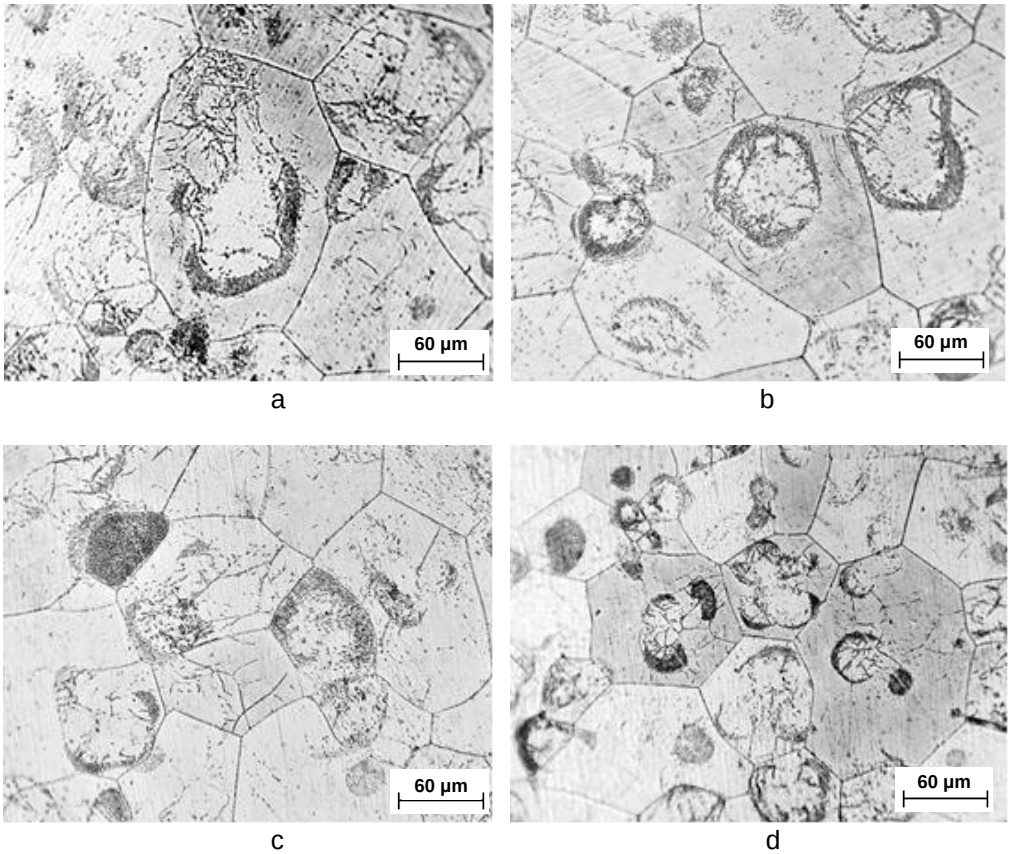


Figure 1 The microstructure of the magnesium alloy after heat treatment
a – the source metal; b – additive 0.05 wt% C; c – additive 0.1 wt% C; d – additive 0.3 wt% C

The introduction and increase in the concentration of the graphite modifier in the alloy helped to reduce the size and amount of eutectoid secretions (**Figures 1, c-d**). The value of the micro grain decreased by 1.5 times, however, the size of the structural components by 2 times (**Table 1**).

Table 1 Dimensions of structural components and their micro hardness in magnesium alloy samples

Additive modifier C (wt%)	Dimensions of structural components (µm)		Microhardness HV (MPa)	
	Eutectoid	Micrograin	Matrix	Eutectoid
without modif.	60 - 330	160 - 280	772 - 899	1012 - 1119
0.05	60 - 240	100 - 210	985 - 1045	1293 - 1387
0.1	60 - 200	80 - 200	1015 - 1054	1296 - 1622
0.3	50 - 180	60 - 180	1065 - 1269	1357 - 1788

It was found that the micro hardness of eutectoid alloys of the cast alloy was significantly higher in terms of matrix δ-solid solution. In the heat-treated alloy there was an increase in the micro hardness of the matrix and a decrease in the hardness of the eutectoid, which indicates an increase in the homogeneity of the heat-treated alloy. The addition of carbon from 0.05 wt% to 0.3 wt% helped to increase the micro hardness of the structural components (**Table 1**) and, as a consequence, increases the strength of the alloy (**Table 2**).

Based on the above, it can be noted that the modification of the magnesium alloy with carbon content up to 0.1 wt% contributed to the increase of its mechanical properties due to the additional strengthening of the structural components of the alloy and grain grinding. Heat treatment increased the homogeneity of the alloy

due to the redistribution of elements between the axes and axial spaces of the dendrites, which led to the alignment of properties along the cross section of the metal.

Table 2 Mechanical properties of samples of magnesium alloy with the addition of graphite powder

Additive modifier C (wt%)	**Mechanical properties**			
	without heat treatment		**after heat treatment**	
	σ_B (MPa)	δ (%)	σ_B (MPa)	δ (%)
without modif.	153	1.9	223	2.9
0.05	163	2.5	231	4.9
0.1	178	3.1	240	4.8
0.3	173	3.0	236	3.5

Addition to the melt of more than 0.1 wt% of carbon led to contamination of the metal with films, increasing the porosity of the material and, as a consequence, reducing its mechanical properties.

Analysis of research results (**Table 3**) showed that the surface tension ($\sigma_{p.r.}$) at the "alloy - gas" boundary in the systems "alloy - carbonate substrate" and "alloy - oxide" was at the level of 71 - 80 MJ/m^2.

The flux spread on carbonate materials and practically did not wet the oxide, which caused different values of surface tension ($\sigma_{p.r.}$) on substrates of oxides and carbonates. Adhesion (A_a) at the interface "flux - substrate of $CaCO_3$, $MgCO_3$ and graphite" was 131 MJ/m^2, 127 MJ/m^2 and 124 MJ/m^2, respectively, which is 2 - 3 times more than the adhesion at the boundary "flux - substrate of oxides ".

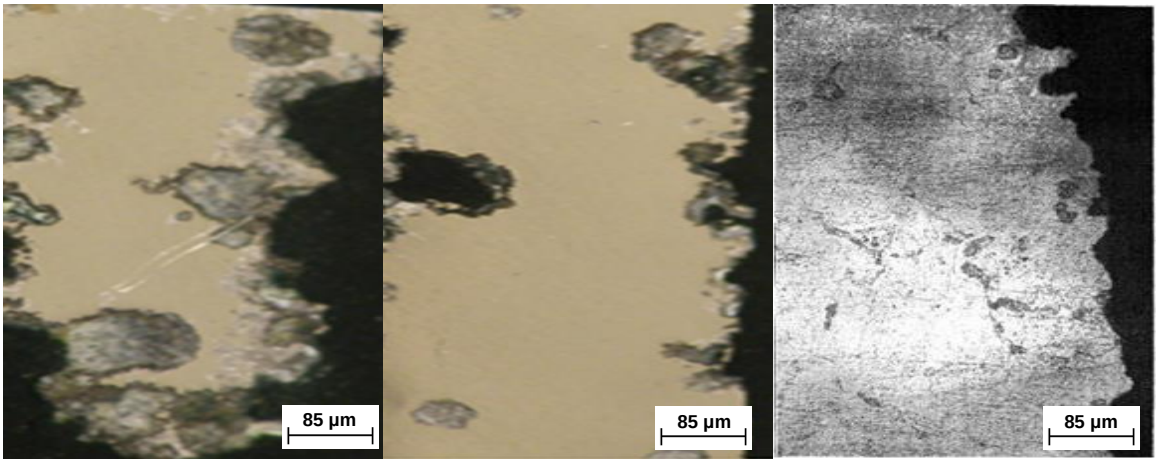
In the systems "alloy - substrate of carbonates" and "alloy - oxide" lower wetting angle and correspondingly high adhesion work were obtained for the material with $CaCO_3$.

Table 3 Characteristics of surface interaction between alloy, flux and substrate material (average values)

Material substrates	$\sigma_{p.r.}$	σ	A_a	A_k	K_p
	(MJ/m^2)	(°)	(MJ/m^2)	(MJ/m^2)	(MJ/m^2)
	alloy / flux	**alloy / flux**	**alloy / flux**	**alloy / flux**	**alloy / flux**
$CaCO_3$	80/79	128/49	32/131	158/155	-126/-25
$MgCO_3$	71/78	141/53	17/127	141/156	-125/-31
graphite	73/76	155/50	9/124	143/152	-138/-26
SiO_2	72/103	131/132	24/35	139/204	-116/-170
Al_2O_3	75/100	138/144	21/20	149/200	-129/-183
MgO	71/102	149/138	12/29	141/203	-130/-174

The depth of interaction between the alloy and the filter material was assessed by metallographic analysis. It was found that the magnesium melt penetrated into the filter material with $CaCO_3$ to a depth of 180 μm, which significantly exceeded the action of graphite (10 mm) and magnesite (12 mm) (**Figure 2**).

An increased number of intermetallics, compared to the rest of the droplet volume, was observed in the surface zone of contact of the investigated drops with the substrate material. It was found that more intermetallics were found in the surface zone of the drop in contact with the magnesite substrate. The size of intermetallics reached 25 μm, which is 3 - 4 times more than in drops in contact with limestone and graphite. The size of the micrograin in the material of all investigated drops was at the same level (**Table 4**).



a b c

Figure 2 Microstructure of the limit of interaction of metal with the filter: a – of limestone; b – from graphite; c – from magnesite

Table 4 Structural components of melt droplets Inc.

Material substrates	**Interaction depth** (µm)	**Micrograin size** (µm)	**γ phase size** (µm)
limestone	unto 180	80 – 155	2.0 – 5.0
graphite	unto 12	80 - 185	3.0 – 7.0
magnesite	unto 10	75 - 150	3.0 – 20.0

Thus, the best properties of the magnesium alloy are achieved by filtration through a complex filter containing limestone, magnesite and graphite. The use of a complex filter [7] in the production of castings from magnesium alloys can improve their quality, physical and mechanical properties and increase the yield of suitable castings.

4. CONCLUSION

1) Additives to the magnesium alloy of dispersed graphite powder up to 0.1 wt% C help to improve the mechanical properties of the metal due to the additional strengthening of both solid solution and eutectoid. This changes the parameters of the eutectic transformation and reduces the eutectoid δ + γ. Heat treatment helps to increase the homogeneity of the metal between the axes and axial spaces of the dendrites.

2) It is established that in the process of filtration of magnesium melt through carbonaceous materials (magnesite, limestone and graphite) its effective refining was provided. The use of a filter containing equal amounts of magnesite, graphite and limestone when pouring magnesium alloy provided a reduction in the size of the structural components of the metal by 1.5 times, increased its strength by 20% and ductility almost twice.

3) It is established that when the filter materials interact with the magnesium melt, it is effectively modified. In the structure of the alloy there is an increased amount of intermetallic γ-phase, which increases the microhardness of the structural components of the alloy and improves its physical and mechanical characteristics.

4) The use of carbon-containing materials for the modification and refining of magnesium-based alloys is quite effective for improving the quality of medical casting and improving its physical and mechanical properties.

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