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Mg–Bi–X (X = Ca, Mn, Zn) Alloys Microstructure in the As-Solidified Condition

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Magnesium alloys are promising candidates for many structural applications in automotive and aerospace industry. However, due to the low service temperature of the majority of magnesium alloys, huge efforts are made in order to develop the high temperature systems with maximum exploitation temperature of up to 300 °C. Nevertheless, the increase of high temperature properties of magnesium alloys is connected with application of expensive rare earth elements (RE). In the paper the microstructure of Mg–XBi (X = 2, 5, 10) alloys has been investigated. The Mg–Bi system may be an effective substitute of Mg–RE alloys, due to the ability of formation of fine precipitates, strengthening the alloy, resulting from the limited solid solubility of Bi in Mg. Moreover the influence of ternary additions of Ca, Mn, and Zn on the microstructure and morphology of eutectic compound has been analysed. It has been found that Ca and Mn alters the microstructure of Mg–Bi alloys, resulting in refinement of eutectic compound precipitates, when Zn addition has no influence on the microstructure of investigated alloys.

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1. Introduction

Magnesium alloys are promising material for the structural elements in automotive and aerospace industries. With the density equal to about 1.8 g/cm³ and the ultimate tensile strength (UTS) reaching 400 MPa in wrought alloys [1], their specific strength is comparable to aluminium alloys and even some groups of steels. As the magnesium has a hexagonal close-packed crystal structure, magnesium alloys are hardly workable in ambient temperature. Hence, the majority of the elements produced from magnesium alloys are manufactured by casting — usually sand casting or high pressure die casting. Currently, one of the most widely applied cast magnesium alloys are these with aluminium addition (Mg–Al–Mn, Zn). They exhibit good technological properties and acceptable mechanical properties (UTS = 270 MPa, YS = 170 MPa, A₅ = 4.5%) [2]. However, their main disadvantage is low maximum working temperature, justified by the low thermal stability of main intermetallic phase present in the microstructure of these alloys — Mg₁₇Al₁₂ phase [3]. With the melting point slightly above 450 °C, such phase quickly undergoes morphological changes at elevated temperature, resulting in significant decrease of material's properties. Therefore, the Mg–Al based alloys may be applied up to 150 °C. Magnesium alloys could be applied for the elements in transportation industry such as engine housings and engine blocks, successfully decreasing total mass of the vehicle. However, these applications demand better stability of properties at higher temperature. This led to development of the alloys with

the addition of rare earth elements [3, 4]. Such modification of the chemical composition of Mg–Al alloys results in the formation of thermally stable Al–RE phases.

Further increase of maximum working temperature of magnesium alloys has been achieved by replacing aluminium with rare earth elements. Mg–RE alloys may be successfully applied for elements operating up to 250 °C or even 300 °C [5]. Magnesium and rare earth elements form thermally stable phases with the melting point exceeding 800 °C [6], resulting in stability of the alloy's properties at high temperature. However, rare earth elements are expensive and hardly available. Thus, many researches are conducted to replace rare earth elements with other, cheaper elements.

The high mechanical properties of magnesium alloys are usually obtained after age hardening. The majority of magnesium alloys is designed to receive a potential to ageing heat treatment. There are two crucial factors, which have to be exhibited by the system to exhibit significant response for the age hardening treatment. Firstly, the solubility of the alloying element in the magnesium solid solution has to increase with increasing temperature. Secondly, its maximum solubility has to be high enough to form significant number of strengthening precipitates during the ageing treatment. Both of these factors are found in the Mg–Bi system. Maximum solubility of bismuth in magnesium at the eutectic temperature (553 °C) is equal to 1.12 at.% and decreases to nearly 0% at the ambient temperature. Moreover the melting point of Mg₃Bi₂ intermetallic phase is equal to 821 °C [7], which indicates its high thermal stability, similar to the one, exhibited by Mg–RE intermetallic phases.

Strengthening phases formed during the ageing treatment may have various morphologies and may precipitate at various planes and in various directions in the magnesium crystal lattice. These are mainly: rods

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or needles precipitating in the [0001] direction of α -Mg, plates precipitating at the basal planes, plates precipitating at the prismatic planes, and spherical particles. It has been evaluated that with constant density of shear-resistant particles per unit volume, plates precipitating at the prismatic plates of magnesium crystal lattice bring the highest increment to yield strength among all strengthening particles [8, 9]. So far, phases with such a morphology and precipitation direction have been found only in the alloys of Mg–RE system [10, 11]. However, some literature data present the results of the research on potential formation of the prismatic plates in Mg–Bi system [12]. High thermal stability of Mg–Bi phases as well as possibility to form significantly strengthening particles, indicates that alloys of this system may be prospective substitute of the expensive Mg–RE alloys.

Although many Mg-containing systems exhibit possibility of age hardening, the efficiency of this process in the binary alloys is rather poor, due to the low density of the precipitates formed during the ageing treatment (sometimes one magnitude smaller in age-hardenable aluminium alloys) [13]. It is believed that vacancies in the supersaturated α -Mg solid solution weakly interacts with the alloying elements. This leads to slow precipitation of new phases, resulting in small density of coarse precipitates after the process [14, 15]. The most strengthening particles should be fine and the distances between them should also be small. Such particles are known to effectively block the dislocations movement and strengthening the material.

Addition of ternary alloying elements to the binary magnesium-based alloys is known to significantly increase their age hardening response. Transition metals and elements such as Ca or Ba were introduced to binary Mg–Zn alloys [13, 14, 16–18], which led to the increase of the number of strengthening precipitates. Additions of Bi or Sb led to increased age hardening response of Mg–Al alloys [19, 20]. Al has been found to increase the mechanical properties of binary Mg–Sn alloys after heat treatment [21]. Although many researchers investigated the phenomena occurring during ageing treatment of the magnesium alloys, there is still lack of information on the mechanisms resulting in their increased age hardening response. It is believed that transition elements may increase the number of vacancies in the supersaturated α -Mg solid solution, thus increasing the number of precipitating particles [15]. Ca addition may also lead to the formation of more complex phases, increasing mechanical properties of the Mg-based alloys [18]. Such particles, besides strengthening the alloys itself, may act as a nuclei for the formation of other phases. Moreover, strengthening phases nucleating at particles present in the alloy's microstructure may grow in different directions, activating new precipitation systems.

There are many similarities between the Mg–Bi and Mg–RE systems. These are: high thermal stability of the intermetallic phases, age hardening response and possibility to form plate-like precipitates at the prismatic

planes of magnesium crystal lattice. These similarities indicate that alloying of magnesium with expensive rare earth elements could be successfully substituted with cheaper bismuth. In the present work the microstructural investigations of as-solidified Mg–Bi alloys with ternary additions of Ca, Mn, and Zn are presented. The conducted research is a basis for the further investigation of precipitation sequence in Mg–Bi system and may help in understanding of strengthening mechanisms in age hardenable magnesium alloys.

2. Research material and methodology

The material for the research comprises binary Mg–XBi and ternary Mg–XBi–0.5Me alloys, where X = 2, 5, 10 and Me = Ca, Mn, Zn. The investigated alloys were prepared from ingots and powders of pure elements. The materials were melted and homogenised at 700 °C for 1 h in a resistance furnace. The melting and solidification of the alloys were conducted under the protective atmosphere of Ar. The alloys were investigated in the as-solidified condition.

Microsections preparation included grinding on SiC abrasive papers with grades 120–1200, followed by polishing on diamond suspensions with a mean grain size equal to 6, 3, and 1 μm . Final polishing has been conducted on SiO₂ suspension with grain size equal to 0.05 μm . The microstructures were observed both on unetched microsections and samples etched in 3% solution of HNO₃ in ethanol. Images of microstructure were registered using the Olympus GX71 light microscope (LM) as well as Hitachi S3400N and Hitachi S4200 scanning electron microscopes (SEM). The chemical composition of the microstructure constituents was analysed with energy dispersive spectrometers (EDS) attached to the SEM.

3. Research results

The binary Mg–XBi alloys microstructure consists of α -Mg solid solution dendrites and intermetallic phases located in the interdendritic regions (Fig. 1). With the increasing Bi content, the volume fraction of the intermetallic phases increases, while the α -Mg solid solution dendrites cells size decreases. α -Mg solid solution in the interdendritic regions is strongly etched with the etching reagent. This indicates that the solid solution in these regions is enriched in soluted elements.

The backscattered electrons (BSE) SEM observations of the binary Mg–Bi alloys microstructure revealed that the interdendritic regions are brighter than the dendrites cores (Fig. 2a, arrow). This indicates that these areas are enriched in heavy elements — in this case Bi. Moreover, the closest vicinity of the grain boundaries is depleted in Bi (Fig. 2b, arrow). This is probably the effect of the higher vacancies density in these regions. High vacancy density leads to increased rate of diffusion of soluted elements. Thus, during slow cooling after solidification, the soluted elements might diffuse to the grain boundaries, forming intermetallic phases.

The intermetallic phases located in the interdendritic regions in low Bi alloys have bulky morphology and form

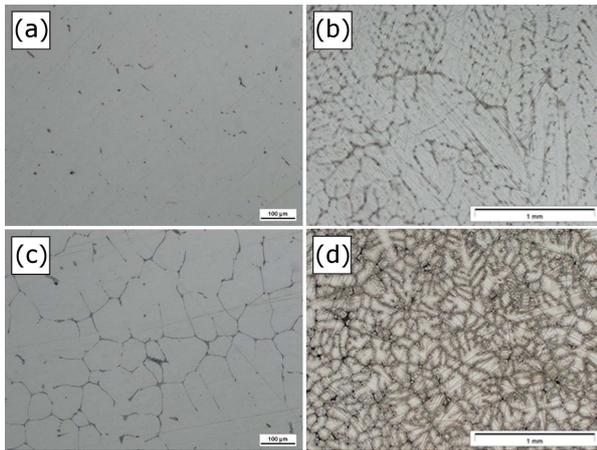


Fig. 1. Microstructure of the hypoeutectic Mg–Bi alloys, LM: (a, b) Mg–2Bi, (c, d) Mg–10Bi alloy.

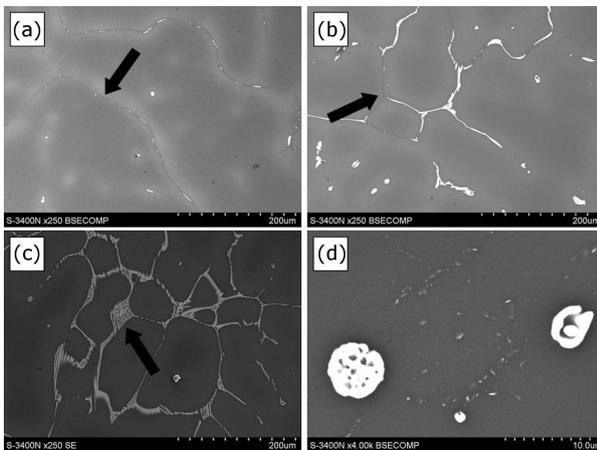


Fig. 2. Microstructure of the hypoeutectic Mg–Bi alloys, SEM: (a) Mg–2Bi alloy, (b) Mg–5Bi alloy, (c, d) Mg–10Bi alloy.

discontinuous net of precipitates. When the Bi content is increased up to 10 wt%, they begin to form more complex morphologies with islands of α -Mg solid solution within them (Fig. 2c). In the interdendritic α -Mg solid solution, very fine precipitates of intermetallic phases were observed (Fig. 2d). EDS chemical composition analysis of the intermetallic phases revealed that they consist of Mg and Bi (Fig. 3), with the atomic ratio of 3:2. The only equilibrium intermetallic phase in Mg–Bi alloys is Mg_3Bi_2 compound. The intermetallics observed in the alloys microstructure are probably Mg_3Bi_2 phases formed in the eutectic reaction $L \rightarrow \alpha\text{-Mg} + \text{Mg}_3\text{Bi}_2$.

The addition of ternary alloying elements has led to some significant changes in the microstructure. Introduction of 0.5 wt% of Ca has led to formation of much higher number of fine, intermetallic phases particles in the interdendritic α -Mg solid solution (Fig. 4a). They are probably characterized by needle-like or hexagonal-platelet-like morphology (Fig. 4b). Such phases were observed also in binary Mg–Bi alloys, however, their density was much smaller. Addition of Mn has led to the change in eu-

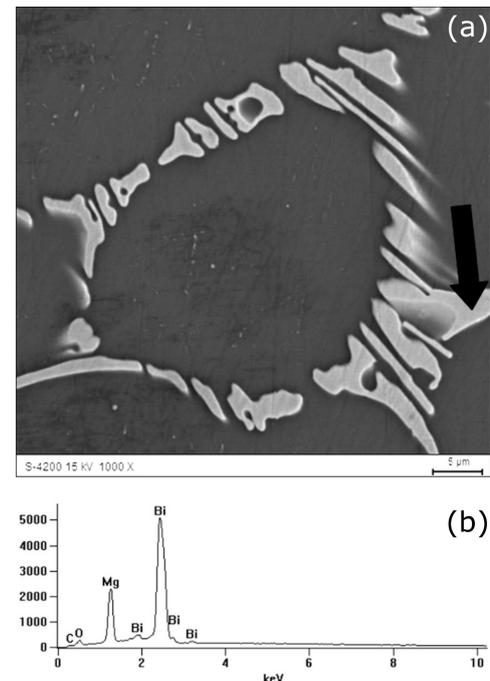


Fig. 3. Mg–10Bi alloy microstructure (a) and the EDS analysis (b) obtained from the region indicated with the arrow.

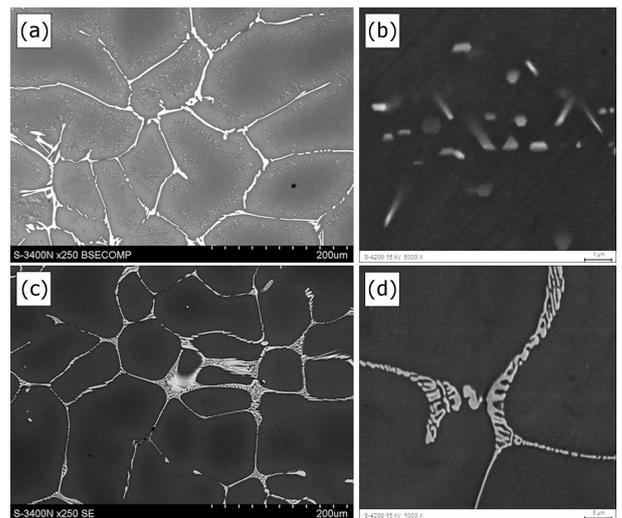


Fig. 4. The microstructure of the Mg–10Bi–0.5Ca (a) and Mg–10Bi–0.5Mn (b) alloys, SEM.

tectic phases morphology. The eutectic in Mg–Bi–Mn alloys has semi-divorced morphology, with large number of α -Mg solid solution islands within the Mg_3Bi_2 eutectic phases precipitates (Fig. 4c,d). The fine precipitates within the α -Mg solid solution have not been observed. Also the trace amounts of Mn were found in the intermetallic phases chemical composition. The Zn addition has no influence on the microstructure and morphology of the precipitated intermetallic phases.

The analyses of the α -Mg solid solution chemical composition were conducted on all samples. 10 regions within

TABLE I

Results of the EDS analyses of α -Mg solid solution dendrite cores (at.%).

Alloy	Mg		Bi		Ca		Mn		Zn	
	\bar{X}	σ								
Mg-2Bi	100	0	0	0	–	–	–	–	–	–
Mg-2Bi-0.5Ca	100	0	0	0	0	0	–	–	–	–
Mg-2Bi-0.5Mn	99.9	0.1	0.1	0.1	–	–	0	0	–	–
Mg-2Bi-0.5Zn	99.7	0.3	0	0	–	–	–	–	0.3	0.3
Mg-5Bi	99.9	0.1	0.1	0.1	–	–	–	–	–	–
Mg-5Bi-0.5Ca	99.9	0.1	0.1	0.1	0	0	–	–	–	–
Mg-5Bi-0.5Mn	99.9	0.1	0.1	0.1	–	–	0	0	–	–
Mg-5Bi-0.5Zn	99.6	0.4	0.2	0.2	–	–	–	–	0.2	0.2
Mg-10Bi	99.9	0.1	0.1	0.1	–	–	–	–	–	–
Mg-10Bi-0.5Ca	100	0	0	0	0	0	–	–	–	–
Mg-10Bi-0.5Mn	99.7	0.1	0.3	0.2	–	–	0	0	–	–
Mg-10Bi-0.5Zn	99.7	0.2	0.1	0.1	–	–	–	–	0.2	0.2

TABLE II

Results of the EDS analyses of α -Mg solid solution in the interdendritic regions (at.%).

Alloy	Mg		Bi		Ca		Mn		Zn	
	\bar{X}	σ								
Mg-2Bi	99.2	0.2	0.8	0.2	–	–	–	–	–	–
Mg-2Bi-0.5Ca	99.2	0.2	0.8	0.2	0	0	–	–	–	–
Mg-2Bi-0.5Mn	99	0.2	0.9	0.1	–	–	0.1	0.1	–	–
Mg-2Bi-0.5Zn	98.2	0.6	0.8	0.1	–	–	–	–	1	0.6
Mg-5Bi	99	0.1	1	0.1	–	–	–	–	–	–
Mg-5Bi-0.5Ca	98.9	0.1	1.1	0.1	0	0	–	–	–	–
Mg-5Bi-0.5Mn	98.9	0.1	1.1	0.1	–	–	0	0	–	–
Mg-5Bi-0.5Zn	98.2	0.5	1	0.1	–	–	–	–	0.8	0.5
Mg-10Bi	98.9	0.2	1.1	0.2	–	–	–	–	–	–
Mg-10Bi-0.5Ca	98.8	0.1	1.2	0.1	0	0	–	–	–	–
Mg-10Bi-0.5Mn	98.8	0.1	1.2	0.1	–	–	0	0	–	–
Mg-10Bi-0.5Zn	98.4	0.4	1	0.2	–	–	–	–	0.6	0.4

the dendrite cores and 10 regions in the interdendritic regions were analysed. The results of the analyses are given in Tables I and II. It can be found that in dendrite cores, no more than 0.3 at.% of Bi is soluted in the as-solidified condition. Also neither Ca, nor Mn were found in dendrite cores. However, up to 0.3 at.% of Zn was soluted in the α -Mg solid solution dendrites.

EDS analyses of the supersaturated α -Mg solid solution in the interdendritic regions revealed that up to 1.2 at.% of Bi may be soluted in the as-solidified condition. The content of soluted Bi in the interdendritic α -Mg solid solution increased with the increasing content of Bi in the alloy's chemical composition. Similarly to the previous case, mainly Zn was found to be soluted in α -Mg solid solution. In this case, up to 1 at.% of Zn was found.

4. Discussion and final conclusions

The microstructure of the hypoeutectic Mg–Bi alloys in the as-solidified condition consists of α -Mg solid

solution dendrites with up to 0.3 at.% of Bi soluted and α -Mg+Mg₃Bi₂ eutectic compound. With the increasing Bi content, the alloys microstructure undergoes refinement. According to Mg–Bi phase diagram, with increasing Bi content, the liquidus temperature decreases. Thus, when the alloys are solidified from the same temperature, the overcooling increases, leading to grain refinement.

The addition of the ternary alloying elements has a significant effect on the alloys microstructure. However, it might not change the alloys phase composition. Addition of calcium has led to significant precipitation of the fine phases within the α -Mg solid solution. The precipitates are formed probably during prolonged cooling of the alloys after solidification. The supersaturated α -Mg solid solution in the interdendritic regions undergoes decomposition. Similar phenomenon is observed in Mg–Al alloys during the precipitation of platelet-like Mg₁₇Al₁₂ phase within the α -Mg. The precipitation of the phases is similar to this, observed during ageing of the solution treated alloys. Previous researches [17, 18] revealed that Ca addition has an effect on the precipitation sequence of Mg-based alloys by changing the mechanism of phases nucleation or by formation of new, ternary strengthening phases.

Addition of Mn has led to the change in the eutectic Mg₃Bi₂ intermetallic phase morphology. Also the traces of Mn were found in the intermetallic phases chemical composition. It may indicate that Mn influences Mg–Bi eutectic compound solidification. Buha [14] has found that addition of V to the Mg–Zn influences the alloy's solidification, leading to significant grain refinement. Mn also belongs to the transition elements group and may have similar effect on the alloys solidification and structure.

Modification of the binary Mg–Bi alloys with Zn did not change the alloys microstructure. As the solubility of Zn in Mg is quite high, even in ambient temperature [22], all of the alloyed Zn was soluted in the α -Mg solid solution dendrites, which is clearly indicated by the EDS investigations.

The addition of the ternary alloying elements may significantly influence the alloys' microstructure and phase composition after the heat treatment consisting of soluting and ageing. Calcium, which influences precipitation of fine intermetallic phases, will probably influence also the precipitation of phases during the ageing treatment. Zn atoms soluted in the α -Mg dendrites may change the vacancies density, thus influence the precipitation processes, as well. The researches revealed that Mn influence the solidification of Mg–Bi alloys. However, if it will be soluted in the matrix during solution treatment, it may also change the precipitation phenomena.

1. The hypoeutectic Mg–Bi and Mg–Bi–X (X = Ca, Mn, Zn) alloys microstructure in the as-solidified condition consists of α -Mg solid solution dendrites and α -Mg+Mg₃Bi₂ eutectic compound located in

the interdendritic regions. Addition of the ternary alloying elements does not influence the alloys phase composition.

2. The addition of Ca leads to the formation of the significant amount of fine intermetallic phases within the α -Mg solid solution. This is caused probably by the modification of precipitation sequence during the decomposition of supersaturated α -Mg solid solution.
3. The Mn addition leads to the modification of eutectic phases morphology. Mn affects the solidification of the eutectic compound in the Mg–Bi alloys.
4. Addition of 0.5 wt% of Zn does not influence the microstructure of the Mg–Bi alloys. Due to high solubility of this element in the α -Mg solid solution, all of the introduced Zn was soluted in the matrix.

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