MICROSTRUCTURE OF CAST MgBi6X0.5 (X = Ca, Mn, Zn) ALLOYS IN PEAK-AGED CONDITION

Cast magnesium alloys are characterised by the lowest density among commercially used structural metals. They are applied mainly in the transportation industry and small, lightweight electronic devices. Due to the low operating temperature of the most widely used alloys from the Mg-Al system, alloys containing rare earth elements with the maximum working temperature reaching 300°C have been developed. However, these alloys are extremely expensive due to the low availability of RE elements. The Mg-Bi system is a promising candidate for the new magnesium-based alloys, as it reveals limited solubility of Bi in Mg enabling precipitation hardening and a high melting point of the Mg3Bi2 phase. The paper presents the results of the analysis of MgBi6 and MgBi6X0.5 (X = Ca, Mn, Zn) alloys’ microstructure in the peak-aged condition. The microstructure of the analysed alloys in the as-cast condition consists of α-Mg solid solution dendrites and Mg3Bi2+α-Mg eutectic compound. Solutionising conducted at 525°C for 8 h, followed by water quenching leads to the dissolution of the intermetallic phases in all of the investigated alloys apart of the MgBi6Ca0.5 alloy. In this case, fine intermetallic phases containing Mg, Bi, and Ca have been found after solutionising. The ageing of the alloys at 200°C results in peak hardness after 120–144 h. The heat treatment leads to the formation of fine strengthening phases within the α-Mg solid solution, characterised by a variety of morphologies – needle, platelet- or lathlike and cuboid. The needle- and platelet- or lathlike phases are found in two sizes – large, with length reaching hundreds of nanometres, and smaller, not exceeding 100 nm. Cuboid particles are found with sizes not higher than 100 nm. The addition of Mn and Zn increases precipitate volume fraction after the heat treatment. Additionally, in the case of the MgBi6Zn0.5 alloy, particles forming an angle of 120° were found, which indicates their presence at the prismatic planes of α-Mg HCP crystal lattice.

Keywords: magnesium alloys, Mg-Bi alloys, heat treatment, casting, cast magnesium alloys, ageing

Odlewnicze stopy magnezu charakteryzują się najniższą gęstością wśród wszystkich komercyjnie stosowanych stopów konstrukcyjnych. Znajdują zastosowanie głównie w przemyśle transportowym oraz małych, lekkich urządzeniach elektronicznych. Z uwagi na niską temperaturę eksploatacji najpowszechniej stosowanych stopów z układu Mg-Al, opracowano stopy, zawierające pierwiastki ziem rzadkich, a zatem mające niską temperaturę topnienia fazy Mg3Bi2, umożliwiając ich umocnienie na drodze utwardzania wydzieleniowego. W artykule przedstawiono wyniki badań mikrostruktury stopów MgBi6 oraz MgBi6X (X = Ca, Mn, Zn) po starzeniu. Mikrostruktura badanych stopów w stanie lamy składa się z dendrytów roztworu stałego α-Mg oraz mieszaniny eutektycznej Mg3Bi2+α-Mg. Przesycanie, przeprowadzone w temperaturze 525°C przez 8 h z chłodzeniem w wodzie, doprowadziło do rozpuszczania faz międzymetalicznych we wszystkich badanych stopach, z wyjątkiem stopu MgBi6Ca0.5. W jego przypadku po przesycaniu zidentyfikowano w strukturze drobne fazy międzymetaliczne, zawierające Mg, Bi i Ca. Maksymalną twardość stopów po starzeniu w temperaturze 200°C osiągnęto po 120-144 h. Zastosowana obróbka cieplna doprowadziła do utworzenia się wewnątrz ziaren roztworu stałego α-Mg drobnych faz umacniających o zróżnicowanej morfologii – od iglastej, przez płatkową, po prostopadłościenistą. Zobserwowano dwa typy wydzielenia iglastych i płatkowych – większe, o długości rzędu kilku set nanometrów oraz mniejsze, nieprzekraczające 100 nm długości. Wydzielenia prostopadłościenne charakteryzowały się rozmiana mi, nieprzekraczającymi 100 nm. Dodatek Mn oraz Zn spowodował wzrost udziału objętościowego wydzielenia po obróbce cieplnej. Dodatkowo, w przypadku stopu MgBi6Zn1,5, wydzielenia tworzyły kąt 120°C, co wskazuje na ich obecność na płaszczyznach przemianowych komórki elementarnej α-Mg.

Słowa kluczowe: stopy magnezu, stopy Mg-Bi, obróbka cieplna, odlewnicze stopy magnezu, odlewniczo, starzenie

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1. INTRODUCTION

Magnesium alloys are characterised by the lowest density among commonly applied structural metallic materials. With high mechanical properties (UTS reaching 400 MPa), their specific strength is comparable to aluminium alloys and some types of steel. Due to the low weight of magnesium alloys’ constituent elements, they are applied mainly in the aerospace and automotive industry, but also as parts of electronic devices. The majority of these parts are produced by means of casting. Currently, one of the most widely applied magnesium alloys are those from the Mg-Al group (e.g. AZ91). Their main drawback is the low melting point of MgBi6 alloys with trace additions of Ca, Mn, and Zn. As many of the potential applications of magnesium alloys require a higher working point, researchers have developed Mg alloys containing rare earth elements. With the high thermal stability of the intermetallic phases forming the microstructure of these alloys, they can be applied up to 300°C. Rare earth elements reveal limited solubility in the α-Mg solid solution, which enables precipitation strengthening [1-3]. Moreover, among all of the commercially applied magnesium alloys, only in Mg-RE system strengthening phases are observed in the form of plates at the prismatic planes of Mg HCP crystal lattice. Such phases are known to have the highest strengthening potential among all of the precipitates formed in the magnesium alloys [4, 5]. Despite many advantages of the Mg-RE alloys (thermal stability, high mechanical properties), they are extremely expensive due to the high price and limited availability of rare earth elements. Therefore, researchers are constantly looking for new, alloying elements that are less expensive than magnesium, resulting in high mechanical properties at elevated temperatures.

One of such elements may be bismuth. This element is characterised by limited solubility in the α-Mg solid solution, enabling precipitation hardening. Moreover, the melting point of the MgBi6 intermetallic phase is equal to 821°C, which indicates similar thermal stability to the phases formed in Mg-RE systems. Also, in the Mg-Bi system, plate-like precipitates was observed at the prismatic planes of Mg crystal lattice, which indicates the possibility of significant precipitation strengthening [6, 7]. The addition of ternary alloying elements may increase the ageing response even further. The introduction of transition metals (Mn, Zn) is known to increase the density of voids in the supersaturated α-Mg solid solution [8-11]. Voids may act as nucleation sites for phases formed during ageing treatment. Thus, the higher density of voids may lead to a greater number of strengthening phases, leading to high mechanical properties after heat treatment. Another element that increases the ageing response of magnesium alloys is calcium. Ca leads to the formation of complex, ternary intermetallic phases, which act as nuclei for the formation of main strengthening phases. Thus, this element may alter precipitation sequence in a different way as compared to Mn or Zn [14].

The following paper presents the results of the research on the influence of heat treatment on the microstructure of cast MgBi6 alloys with trace additions of Ca, Mn, and Zn.

2. METHODOLOGY

The research material consisted of as-cast MgBi6X0.5 (X = Ca, Mn, Zn) alloys. The investigated material was fabricated from magnesium ingots and granules of Bi, Ca, Mn and Zn. Melting was conducted in a resistance furnace at 700°C. The alloys were homogenised for 1 h, followed by casting to sand moulds. The materials were cast in the form of cylinders with a diameter of 25 mm and a length of 120 mm. Melting and casting were conducted under the protective atmosphere of argon. Heat treatment of the materials was performed using a Classic 8013/10013T furnace, also in an argon atmosphere. Solutionising of the alloys was conducted at 525±5°C for 24 h followed by water quenching. Ageing was carried out at 200±5°C for 1-168 h, followed by air cooling.

Vickers hardness of the alloys after heat treatment was tested using a Duramin A300 unit. The alloys’ microstructure was analysed using an Olympus GX71 light microscope (LM) and Hitachi S-3400N scanning electron microscope (SEM) coupled with a Thermo NORDAN System 7 energy dispersive spectrometer (EDS). The preparation of microsections included grinding on a SiC abrasive papers (grade 120-1200) and polishing on water diamond suspension with a grain size of 6, 3, and 1 μm. The final polishing was carried out using an Al2O3 suspension with a grain size of 0.05 μm. The microstructure was observed on both etched and non-etched microsections. A reagent containing 4.2 g picric acid, 10 ml glacial acetic acid, 10 ml distilled water, and 70 ml ethanol was selected as the etching solution. The substructure of the alloys after heat treatment was observed with a Hitachi HD-2300A scanning-transmission electron microscope (STEM) equipped with a Thermo NORDAN System 7 EDS spectrometer. Thin foils for the STEM analysis were electropolished using a Struers A2 reagent with T = -55°C and U = 18-21V.

3. RESULTS

The microstructure of as-cast binary MgBi6 and ternary MgBi6X, where X = Ca, Mn, Zn consists of α-Mg solid solution dendrites and MgBi6 intermetallic phases located within the interdendritic regions [15]. The blocky MgBi6 phase is forming fully divorced eutectic mixture together with α-Mg solid solution supersaturated with Bi. The α-Mg solid solution near the grain boundaries in all of the investigated as-cast alloys is depleted in Bi, which indicates a high density of voids in these areas, increasing diffusion rate of Bi atoms within the solid solution. Moreover, within the α-Mg solid solution, near the interdendritic regions, fine, platelet, or needle-like particles are observed. These are most probably fine MgBi6 precipitates formed due to the decomposition of supersaturated solid solution during slow cooling of the casting in the sand mould.

The addition of Ca to the binary MgBi6 alloy does not change the morphology of intermetallic phases located in the interdendritic regions but leads to the formation of a higher density of fine, platelet- or needle-like particles within the α-Mg solid solution. In the MgBi6Mn0.5 alloy, trace amounts of manganese were detected in the chemical composition of the blocky MgBi6 phase. The addition of Mn leads also to the partial change of the α-Mg+MgBi6 eutectic compound morphology – in some regions it becomes partially divorced, with Chinese script morphology.
of intermetallic compound and α-Mg solid solution islands located within it. In Zn alloyed materials, zinc is found to be dissolved within the α-Mg solid solution dendrites [15].

Solution treatment conducted at 525°C for 24 h, followed by water quenching leads to a complete dissolution of the intermetallic compounds in all of the investigated alloys (Fig. 1a), except for the MgBi6Ca0.5 alloy. In this case, some undissolved intermetallic phases remain in the microstructure (Fig. 1b). Two types of such particles are present: needle- or platelet-like and larger bulky phases. Both types of remaining precipitates contain Mg, Bi, and Ca (Fig. 2). The chemical composition of such particles is given in Table 1. The ratio of Bi:Ca is equal to about 2.18, which indicates that such phases may be of Mg2Bi2Ca type intermetallic compound. The content of magnesium is higher due to a probably larger electron beam excitation volume than the analysed phase itself.

### Table 1. Chemical composition of the particle shown in Fig. 2a [at%]

|     | Mg  | Ca  | Bi  |
|-----|-----|-----|-----|
|     | 54.5| 14.3| 31.2|

The ageing of the alloys at 200°C resulted in two peaks of hardness in all of the alloys besides MgBi6Ca0.5 (Fig. 3). The first peak is observed after 16–24 h of ageing and the second after 120–144 h of ageing. The MgBi6Ca0.5 alloy exhibits peak hardness after 120 h of ageing. In all of the investigated alloys, the highest hardness is observed after long ageing. The maximum hardness for the MgBi6, MgBi6Mn0.5 and Mg6BiZn0.5 alloys is achieved after ageing treatment for 144 hours and is equal to 54±6 HV1, 56±9 HV1, and 55±6 HV1, respectively. The highest hardness for the MgBi6Ca0.5 alloy is measured after 120 h of ageing at 200°C and is equal to 53±9 HV1.

Numerous precipitates with a vast variety of morphologies are observed within the α-Mg solid solution dendrites in all of the investigated materials in peak-aged condition (Fig. 4). In the substructure of aged MgBi6 at least 3 types of strengthening phases’ morphology can be found. The first kind of intermetallics consists of needle-like large particles, with a length reaching hundreds of nanometres (Fig. 4a). The second type consists of large platelet- or lath-like precipitates. The third group of the precipitates is characterised by lower dimensions – reaching dozens of nanometres. They are found in various morphologies – cuboid shape, lath- or platelet-like particles as well as needle-like ones (Fig. 5a). All of the phases are randomly distributed in the matrix and do not exhibit clear orientation.

Similar types of precipitates are present in the structure of the MgBi6Ca0.5 alloy after heat treatment. However, the density of the particles is much lower than in the case of the binary Mg6Bi alloy (Figs. 4b and 5b). Apart from fine precipitates, globular and platelet-like particles with sizes reaching a few micrometres are observed (Fig. 6). They contain Mg, Bi and Ca. Their morphology and chemical
composition indicate, that these are the phases that remained in the microstructure of the alloy after solutionising. The decrease of the precipitates’ density in this alloy may be caused by the bonding of Bi atoms in the intermetallic phase containing calcium. Due to this, such atoms do not participate in the formation of strengthening precipitates formed during ageing treatment. In the case of both MgBi6Mn0.5 and MgBi6Zn0.5 much higher precipitates’ density is observed in peak-aged conditions (Figs 4 c, d, and 5 c, d). The finest precipitates with

Fig. 3. Ageing curves for MgBi6 and MgBi6X0.5 (X = Ca, Mn, Zn) alloys solutionised at 525°C and aged at 200°C

Rys. 3. Krzywe starzenia stopów MgBi6 oraz MgBi6X0,5 (X = Ca, Mn, Zn) przesycanych w temperaturze 525°C i starzonych w temperaturze 200°C

Fig. 4. Substructure of the analysed alloys in peak-aged condition, STEM: a) MgBi6; b) MgBi6Ca0.5; c) MgBi6Mn0.5; d) MgBi6Zn0.5

Rys. 4. Substruktura badanych stopów w stanie starzonym, STEM: a) MgBi6; b) MgBi6Ca0,5; c) MgBi6Mn0,5; d) MgBi6Zn0,5
the cuboid, lath- and needle-like morphologies are distributed within the α-Mg matrix much more evenly than in the MgBi6 and MgBi6Ca0.5 alloys. Moreover, only in MgBi6Zn0.5 alloy, fine, probably needle-like particles are forming at an angle of 120° (Fig. 5d). This indicates the formation of these phases at the prismatic planes of HCP magnesium crystal lattice. In the case of the MgBi6Mn0.5 alloy, fine, bulky particles (Fig. 5c) containing Mg, Bi, and Mn are present within the α-Mg solid solution.

4. DISCUSSION AND CONCLUSIONS

Microstructure of the binary MgBi6 and ternary MgBi6Ca0.5, MgBi6Mn0.5, and MgBi6Zn0.5 alloys after casting consists of α-Mg solid solution dendrites and the Mg, Bi, + α-Mg eutectic compound located within the interdendritic regions. The addition of ternary alloying elements leads to the change of eutectic mixture morphology (Mn), formation of a higher number of fine precipitates near the interdendritic regions (Ca) or dissolution within the α-Mg solid solution (Zn). Solutionising of the alloys at 525°C for 24 h leads to the complete dissolution of intermetallic phases in all investigated alloys, except the MgBi6Ca0.5 alloy. In this case fine bulky and needle- or platelet-like particles, probably Mg, Bi, Ca intermetallic phase precipitates, remain in the microstructure. It is very likely, that the mentioned particles are present in the as-cast microstructure and, due to their thermal stability,
were not dissolved during solution treatment. The peak hardness of the analysed alloys is observed after ageing for 120–144 h at 200°C. Long ageing times needed to obtain the highest hardness indicate that the diffusion rate of bismuth in α-Mg solid solution is low.

Strengthening precipitates with various morphologies are found within the α-Mg solid solution dendrites in the peak-aged condition. The phases were characterised by needle and platelet- or lath-like morphology. Fine, cuboid phases were found, as well. The majority of the phases were not exhibiting clear orientation, which indicates that these precipitates form rather in the last stages of the precipitation process. Only in the alloy with Zn addition, did fine particles form the angle of 120° between them. This can indicate that they are located at the prismatic planes of α-Mg solid solution HCP crystal lattice [7]. The highest density of the strengthening phases can be observed in Mn- and Zn-containing alloys. These elements are known to increase void density in α-Mg solid solution [8–11]. This probably leads to the increased nucleation of strengthening particles during the ageing treatment.

1. The highest hardness of the MgBi6 and MgBi6X0.5 (X = Ca, Mn, Zn) alloys is observed after solutionising at 525°C for 24 h, followed by ageing at 200°C for 120–144 h.
2. Addition of ternary alloying elements to MgBi6 alloys changes the microstructure of the alloys in the peak-aged condition.
3. Mn and Zn additions increase the number of nucleation sites during ageing treatment, leading to increased precipitate density in the peak-aged condition. Zn addition leads to the formation of strengthening precipitates located at the prismatic planes of the α-Mg crystal lattice.
4. Calcium addition to the MgBi6 alloy leads to the formation of thermally stable intermetallic phases containing Mg, Bi, and Ca. These phases are present in the MgBi6Ca alloy after solutionising and do not change their morphology during ageing.

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