ARCHIVES OF METALLURGY AND MATERIALS
Volume 57 2012 Issue 1
DOI: 10.2478/v10172-012-0018-3

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MICROSTRUCTURE, CASTABILITY, MICROSTRUCTURAL STABILITY AND MECHANICAL PROPERTIES OF ZRE1 MAGNESIUM ALLOY

MIKROSTRUKTURA, LEJNOŚĆ, STABILNOŚĆ MIKROSTRUKTURY I WŁAŚCIWOŚCI MECHANICZNE STOPU MAGNEZU ZRE1

The influence of pouring temperature on the microstructure, fluidity and mechanical properties of ZRE1 magnesium alloy was investigated in this paper. The pouring temperature influences on the fluidity, mean area of grain plane section and mechanical properties. The dependence between pouring temperature and volume fraction of the $(Mg,Zn)_{12}RE$ intermetallic phase was not observed. The investigations enabled to determine the optimal pouring temperature of ZRE1 alloy. Moreover, the microstructural stability of ZRE1 alloy during long-term annealing at 150°C, 200°C and 400°C was investigated. ZRE1 magnesium alloy possesses a high microstructural stability up to 200°C, whereas at 400°C magnesium oxides and rare earth metals oxides are observed in the microstructure.

Keywords: Magnesium alloy, ZRE1 alloy, fluidity, microstructure

W pracy przedstawiono wyniki badań wpływu temperatury odlewania na mikrostrukturę, lejność i właściwości mechaniczne stopu magnezu ZRE1. Stwierdzono, że temperatura odlewania wpływa na lejność, średnie pole powierzchni płaskiego przekroju ziarna i właściwości mechaniczne stopu ZRE1. Nie zaobserwowano zależności pomiędzy temperaturą odlewania a udziałem objętościowym wydzieleń fazy międzymetalicznej $(Mg,Zn)_{12}RE$. Przeprowadzone badania umożliwiły określenie najkorzystniejszej temperatury odlewania do form piaskowych dla stopu ZRE1. Przeprowadzono także badania stabilności strukturalnej podczas długotrwałego wygrzewania w temperaturze 150°C, 200°C i 400°C. Stwierdzono, że do temperatury 200°C mikrostruktura jest stabilna, natomiast w temperaturze 400°C stop ZRE1 charakteryzuje się niską stabilnością i skłonnością do tworzenia tlenków magnezu i metali ziem rzadkich.

1. Introduction

Magnesium alloys have a great potential as structural materials in the aerospace and automotive industries due to low density, high specific strength and stiffness, good machinability and superior damping capacity [1]. Magnesium alloys can be divided into Al-containing and Al-free alloy systems. The most commonly used alloys in many branches of industry are those based on the Mg-Al system, like Mg-Al-Zn (AZ), Mg-Al-Mn (AM series). Their poor creep resistance is connected with the presence of low-melting $Mg_{17}Al_{12}$ phase, makes them unsuitable for applications above 120°C [1,2]. The Mg-Al-RE (AE series), Mg-Al-Ca-Sr (AXJ series), Mg-Al-Sr (AJ series) have better creep resistance, because their microstructure is characterized by the second phases from system Al-RE, Al-Sr or Al-Ca at the grain boundaries which are stable line compound with a relatively high melting point. Therefore, the maximum operating temperature of these alloys do not exceed 180°C [2,3]. The basic systems for Al-free magnesium alloys are Zr-containing alloys such as Mg-Zn-Zr (ZK series), Mg-Nd-Y-Zr (WE series), Mg-Ag-Nd-Zr (QE series), Mg-Gd-Nd-Zr (Elektron 21), Mg-Zn-RE-Zr (ZE series), Mg-Th-Zr. These alloys are predicted mainly to gravity casting and their maximum operating temperature is near to 300°C [4-6]. Among these alloys, ZRE1 magnesium alloy exhibits good creep properties up to 200°C. This alloy containing zinc, rare earth metals and zirconium. Zinc is usually used in combination with aluminum, zirconium, rare earths, or thorium to produce precipitation-hardenable magnesium alloys having good strength. Zinc also helps overcome the harmful corrosive effect of iron and nickel impurities that might be present in the magnesium alloy. Rare earth metals are added either as mischmetal to reduce of costs of production.

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Additions of the rare earths increase the strength at elevated temperatures. They also reduce weld cracking and porosity because they narrow the freezing range of the alloys. Zirconium has a powerful grain-refining effect on magnesium alloys. The Elektron ZRE1 alloy exhibits excellent casting characteristics with components being both pressure tight and weldable. Castings are free from microporosity and the tendency to hot cracking in difficult castings is slow [6-9].

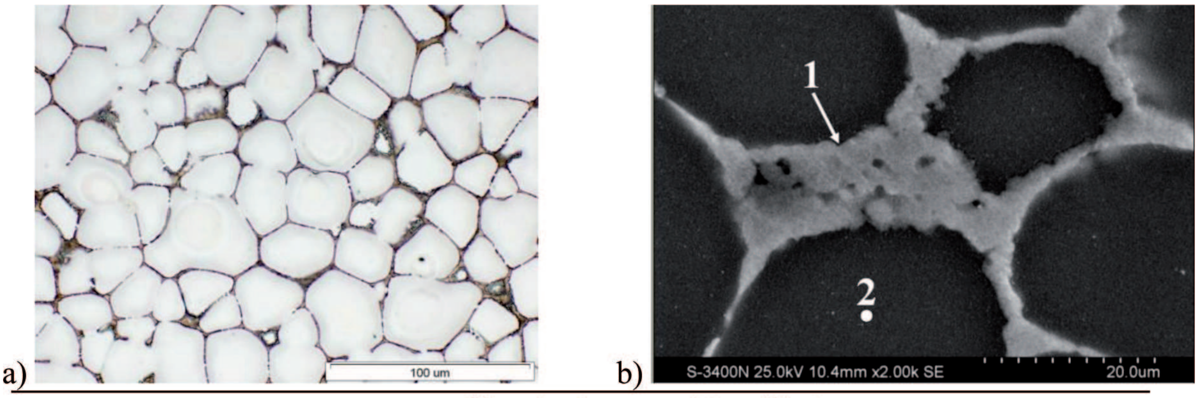
2. Experimental

Sand casts of ZRE1 (Mg-2.7Zn-3.2RE-0.5Zr) alloy were investigated. The rare earth additions were made as mischmetal with the approximate compositions: 50Ce-25La-20Nd-5Pr. Fluidity has been investigated by determination of the flow length with a mould featuring a spiral shaped cavity. Casting in sand moulds has been done at different melt temperature (730, 780, 830°C). Long-term annealing was carried out at temperatures of 150, 200°C and 400°C up to 3000 h in order to determining of microstructural stability of the investigated alloy. Specimens for microstructural studies were mechanically polished using standard methods and etched with a reagent containing of 3 ml HNO_3 and 97 ml H_2O. The microstructure was characterized by optical microscopy (Olympus GX-70) and a scanning electron microscopy (Hitachi S3400) equipped with an EDS detector (VOYAGER of NORAN INSTRUMENTS). EDS analysis was performed with an accelerating voltage of 15 keV. The phase identification of these alloys was conducted by X-ray diffraction (JDX-75) using Cu Kα radiation. A program for image analysis "Met-ilo" [10] was used for determination of the volume fraction of intermetallic phases.

3. Results and discussion

3.1. Microstructure of sand cast ZRE1 magnesium alloys

Optical micrograph taken from as-cast alloy is shown in Fig. 1a, from which it can be seen that as-cast microstructure of this alloy consist of α-Mg matrix and second phase crystallize along the grain boundaries. SEM observations of analyzed alloy reveal that the grain boundary second-phase shows a kind of massive morphology with bright contrast (Fig. 1b). The results of microanalysis by EDS showed that second phase was composed of magnesium, zinc and rare earth elements (point 1), however, precisely determined of magnesium content in the second phase is difficult, due to interaction between electron beam and magnesium matrix. The solid solution contains small amount of zinc. The content of rare earth elements in magnesium is below of quantity sensitivity of X-ray energy dispersive spectroscopy analysis (point 2).



Point	Chemical composition, %at.				
	Mg	Zn	La	Ce	Nd
1	84.0	10.5	1.5	3.1	0.9
2	99.4	0.6	-	-	-

Fig. 1. Optical micrograph (a) and SEM micrograph (b) of as-cast ZRE1 alloy with marked points of chemical analysis

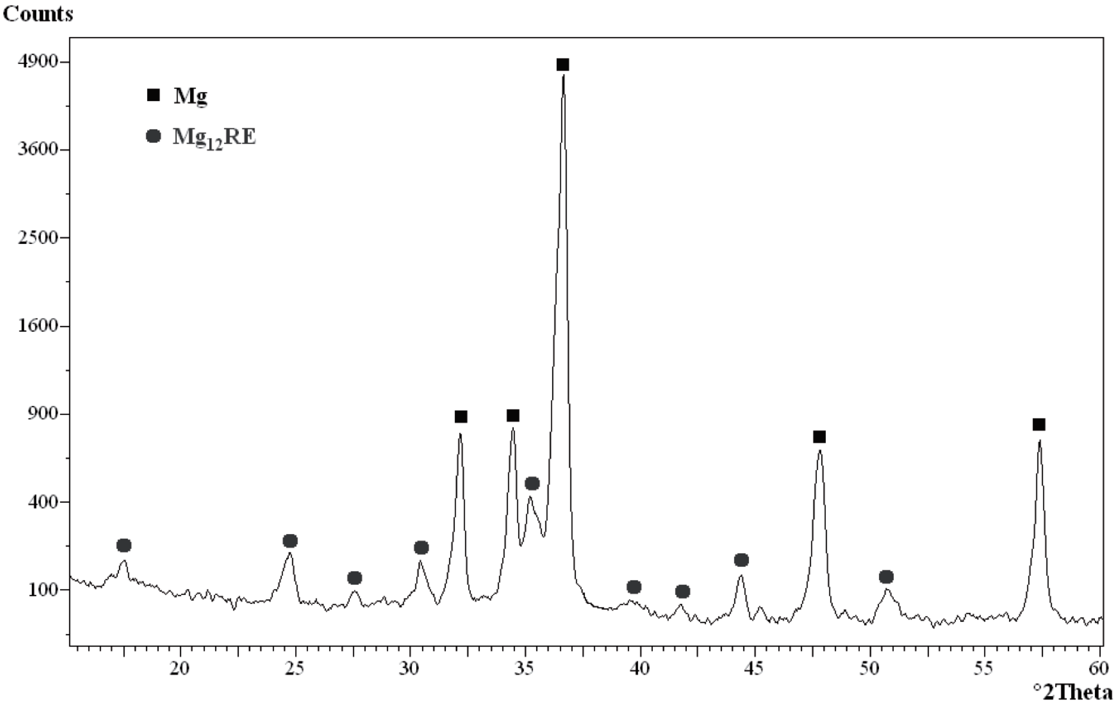


Fig. 2. XRD pattern of sand cast ZRE1 alloy

XRD analyses were performed on selected specimens to identify the phases existing in the alloys studied and the results are shown in Fig. 2. It can be seen that the alloy consisted of two phases, the α-Mg matrix and $Mg_{12}Ce$ intermetallic compound. Based results of chemical microanalysis this second phase can be identified as $Mg_{12}Ce$ with some lanthanum and neodymium substituting cerium. Moreover, this intermetallic compound contains zinc, which substitutes part of magnesium due to small differences between atomic radiuses of these elements. Therefore, molecular formula of this phase can be written as $(Mg,Zn)_{12}RE$.

3.2. The castability of cast ZRE1 magnesium alloy

The pouring temperature of metallic alloys into the mold is one of the critical factors in founding, since the fluidity of the liquid and its subsequent solidification and cooling determine whether the cast shape will be properly formed, internally sound and free from defects [11]. Fig. 3 shows the influence of pouring temperature on the fluidity of ZRE1 alloy. Fluidity can be expressed by the distance that molten metal has flew during filling and solidification. For ZRE1 magnesium alloy, its filling length increases slowly when the pouring temperature increases from 730 to 780°C, but increases rapidly when the pouring temperature increases from 780 to 830°C.

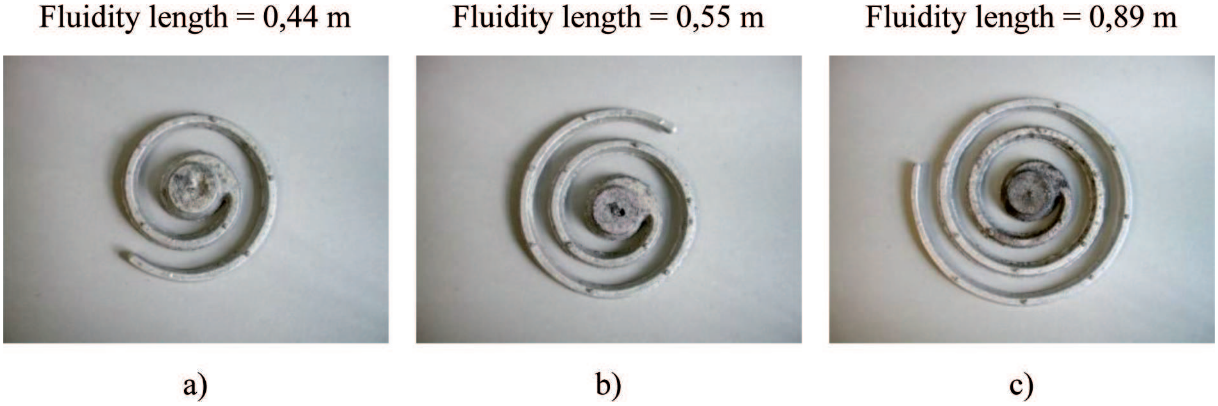
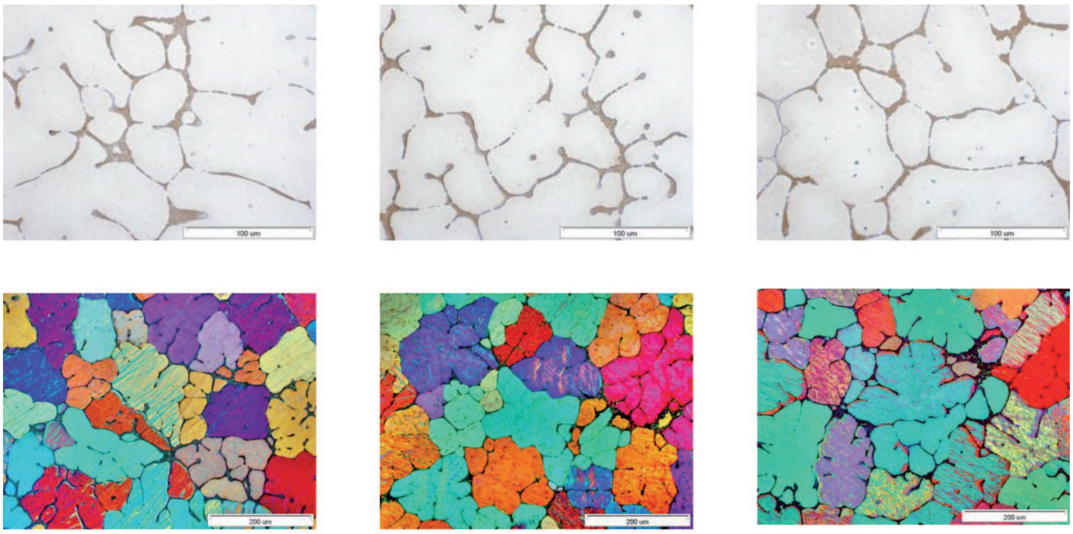


Fig. 3. Spiral cast of ZRE1 alloy poured at the temperature of 730°C (a), 780 (b) and 830°C (c)

Generally, a better fluidity in higher temperature is connected with the decreasing viscosity and surface tension of molten metal with the increase of pouring temperature, which leads to the increasing filling speed. At the same time, the heat capacity of molten magnesium alloy rises with increasing temperature of the pouring, what results in the increase of filling time. On the other hand, the oxidation liability of magnesium alloy increases with the increasing of casting temperature, which will increase the viscosity and decrease the filling length. This effect is insignificant within the investigated range of pouring temperature.

3.3. The influence of pouring temperature on the microstructure of cast ZRE1 alloy

Microstructures of ZRE1 alloy after casting at different temperatures are shown in Fig. 4. In each case the microstructure of the alloy consists of solid solution α-Mg surrounded with a discontinuous network of $(Mg,Zn)_{12}RE$ compound. The pouring temperature also does not influence on the phase composition of ZRE1 alloy (Fig. 5). Tab. 1 shows the results of quantitative metallography as a function of pouring temperature and associated coefficients of variation. One can see in the Table 1, that the area fraction of $(Mg,Zn)_{12}RE$ phase does not change fundamentally with the increase of the casting temperature within the range studied here.



730ºC 780ºC 830ºC

Fig. 4. Microstructure of ZRE1 after casting at different pouring temperatures

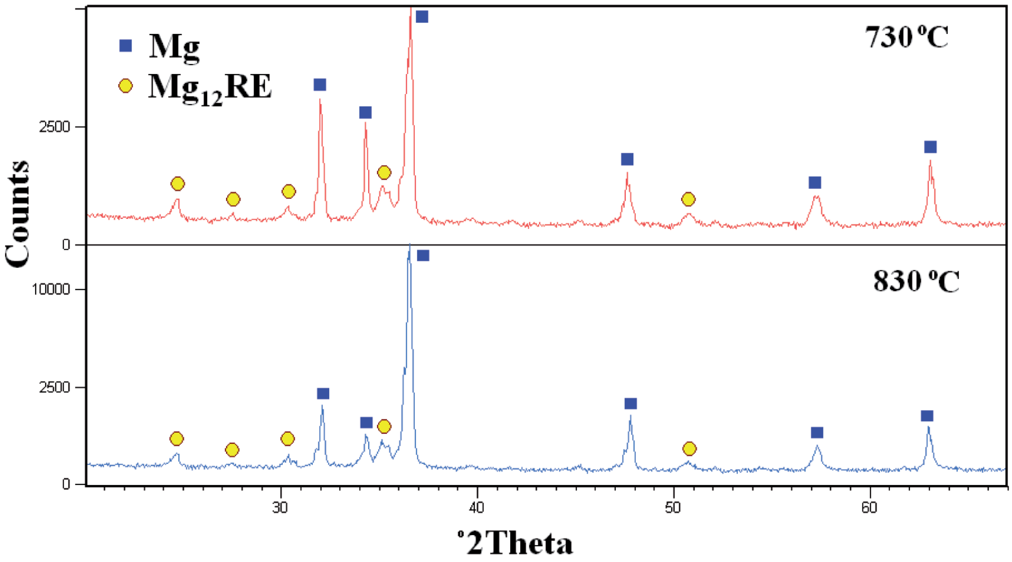


Fig. 5. X-ray diffraction patterns of ZRE1 alloy after casting at 730°C and 830°C

TABLE 1
The influence of pouring temperature on the area fraction of $(Mg,Zn)_{12}RE$ phase and the grain size of ZRE1 alloy. The values of coefficient of variation are inserted in brackets

Temperature	730°C	780°C	830°C
Area fraction [%]	7.2 (21)	7.6 (28)	7.4 (26)
Number of analyzed grains	444	723	719
Mean area of grain plane section [µ m^2]	973 (102)	1211 (95)	1368 (86)
Elongation factor [-]	1.5 (20)	1.51 (21)	1.50 (21)
Shape factor [-]	0.75 (22)	0.72 (24)	0.75 (19)

These results are related to very low solubility of rare earth elements in solid solution. The presence of rare earth elements in magnesium decreases also the solubility of zinc in magnesium. Therefore, during solidification the rare earth elements form $(Mg,Zn)_{12}RE$ phase until the available RE were used without any formation of other compounds.

In samples taken from spiral cast the grain size (mean area of plane section) rises with the increasing of the casting temperature. The elongation factor and shape factor do not depend on casting temperature (Tab. 1). Statistical comparison (non-parametric Kruskall-Wallis test) between grain size in samples poured at different temperatures showed significance difference [12]. Thus, the pouring temperature influences on the grain size of ZRE1 alloy. The grain size (mean area of plane section) rises with the increase of the casting temperature due to longer time of self-cooling of casting mould (lower cooling rate). Moreover, coefficient of variation has a lower values at higher pouring temperature (Tab. 5), that is grain structure is more homogeneity.

3.4. The influence of pouring temperature on the mechanical properties of cast ZRE1 alloy

The influence of pouring temperature on the hardness and tensile properties is reported in Table 2. It can be seen that the Vickers hardness and ultimate tensile strength decrease slightly with the increase of casting temperature. The mechanical properties of ZRE1 alloy are comparable in samples which were poured at 730°C and 780°C. The clear reduction of hardness and tensile strength is observed in alloy poured from 830°C. It is known that the mechanical properties of metallic materials are affected by their grain size. The alloy poured from 730°C shows the highest UTS and hardness, which can be ascribed to finest grain size. Tensile yield strength and elongation does not depend on the pouring temperature.

TABLE 2
The influence of pouring temperature on the mechanical properties of ZRE1 alloy

Pouring temperature	Hardness HV3	UTS [MPa]	YTS [MPa]	Elongation [%]
730°C	50.5±2.9	119.2±1.0	80.3±1.2	2.9±0.3
780°C	50,0±1.5	118.8±1.8	78.9±2.3	2.4±0.1
830°C	47,6±1.4	106.5±0.1	82.0±0.1	2.8±0.1

3.5. The microstructural stability of ZRE1 magnesium alloy

Good creep strength of ZRE1 magnesium alloy enables its application up to 200°C, therefore, the thermal stability is important factor deciding its mechanical properties at elevated temperature. Fig. 6 shows the microstructure of the ZRE1 magnesium alloy after annealing at 150°C in air atmosphere for 1000 h. It can be seen that microstructure of the alloy is similar to that in as-condition. The annealing at 150°C does not cause fundamentally changes in morphology and chemical composition of the $(Mg,Zn)_{12}RE$ compound, even after 1000 h (point 3, Fig. 6). The clusters containing zirconium were observed in the inside the grains (point 2, Fig. 6). These clusters probably contain the small precipitates of Zn_2Zr_3 or ZrH_2 as reported in refs [13], however it requires further examinations. The content of zinc in solid solution α-Mg does not change after heat treatment at 150°C (point 1, Fig. 6).

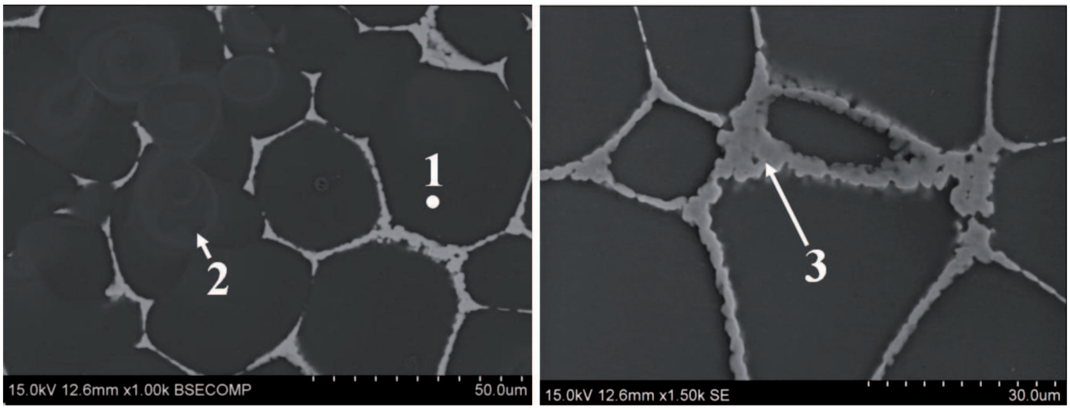


Fig. 6. Microstructure of the ZRE1 magnesium alloy after annealing at 150°C in air atmosphere for 1000 h. The points marked by arrows indicate where the microanalyses were taken. The chemical composition is as follow (%at.): Point 1 – 99.5Mg-0.5Zn, point 2 – 98.7Mg-1.3Zr, point 3 – 87.0Mg-9.3Zn-1.1La-2.0Ce-0.6Nd

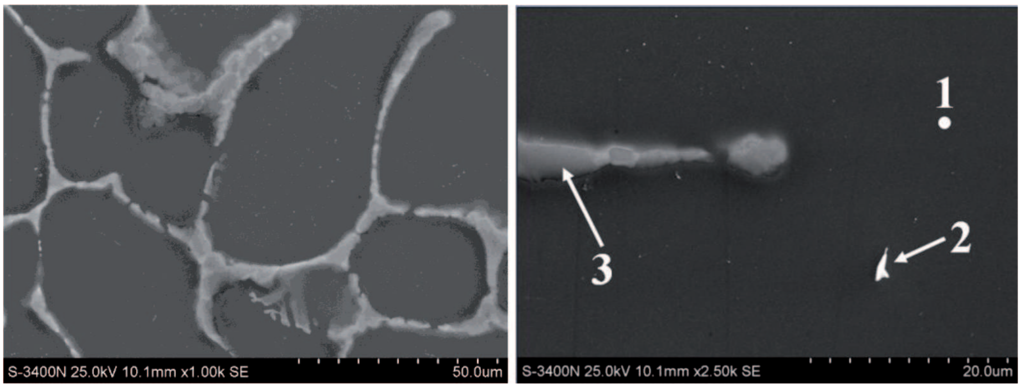


Fig. 7. Microstructure of the ZRE1 magnesium alloy after annealing at 200°C in air atmosphere for 1000 h. The points marked by arrows indicate where the microanalyses were taken. The chemical composition is as follow (%at.): Point 1 – 99.6Mg-0.4Zn, point 2 – 90.9Mg-1.1Zn-8.0Zr, point 3 – 86.4Mg-9.3Zn-0.9La-2.8Ce-0.7Nd

The microstructure of the ZRE1 alloy after annealing at 200°C is shown in Fig. 7. The $(Mg,Zn)_{12}RE$ phase appears to be stable, however the first stages of spheroidizing can be observed. The chemical composition of this compound is close to that in as-cast state (point 3, Fig. 7). The small precipitates containing zirconium and zinc were found in the inside the grains (point 2, Fig. 7). The chemical composition of the solid solution α-Mg is stable during annealing at 200°C. The volume fraction of $(Mg,Zn)_{12}RE$ phase does not change after annealing at temperatures of 150°C (V_v = 7.2%) and 200°C (V_v = 7.6%).

Fig. 8 shows the microstructure of the ZRE1 magnesium alloy after heat treatment at 400°C in air atmosphere for 3000h. It can be seen that microstructure of the ZRE1 alloy after 3000 hours of annealing is different to that in as-cast condition (Fig. 1). The reduction of volume fraction of the $(Mg,Zn)_{12}RE$ (V_v = 4.6%) is observed and new compound with bright contrast is formed. The microanalysis performed on these particles with EDS system indicated that irregular precipitates contain magnesium, rare earth elements and oxygen (Fig. 8). Analysis of the X-ray diffraction pattern of ZRE1 alloy after annealing at 400°C for 3000h (Fig. 9) reveals the presence solid solution α-Mg, $(Mg,Zn)_{12}RE$ and oxide $(RE)O_{1.75}$ ($(Nd_{0.5}Ce_{0.5})O_{1.75}$). The occurrence of a rare earth oxide in the microstructure is related to low oxidation resistance of the ZRE1 magnesium alloy at elevated temperature. After annealing at 400°C the porous MgO layer was observed on the surface of the specimen. Therefore this layer is not a protective film against further oxidation.

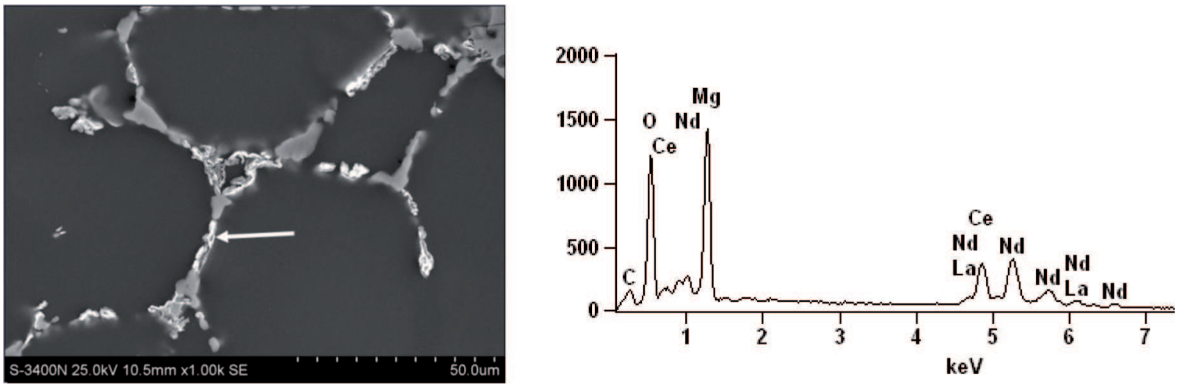


Fig. 8. Microstructure of the ZRE1 magnesium alloy after annealing at 400°C for 3000 h and EDS spectrum taken from irregular compound (marked by arrow)

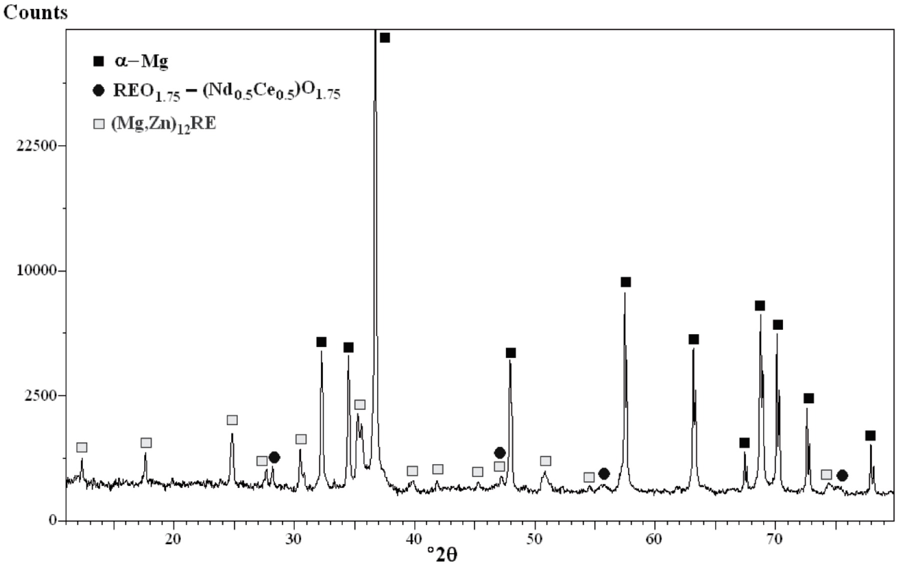


Fig. 9. XRD pattern of sand cast ZRE1 alloy after annealing at 400°C for 3000h

The results of the Vickers hardness measurements are summarized in Table 3. The hardness of the ZRE1 magnesium alloy after annealing at temperature of 150°C and 200°C is higher than that of the as-cast alloy. It is related to the precipitation of small zirconium-rich particles in the inside the grains. After annealing at 400°C the hardness is comparable to that of the as-cast alloy due to oxidation of $(Mg,Zn)_{12}RE$ phase.

TABLE 3
The Vickers hardness (HV2) of ZRE1 magnesium alloy in as-cast state and after annealing at different temperatures

Temperature	Annealing time			
	As-cast	1000h	2000h	3000h
150°C	51	63	–	–
200°C	51	56	60	57
400°C	51	49	49	48

4. Summary

The microstructure of the ZRE1 magnesium alloy is comprised of solid solution zinc in magnesium and $(Mg,Zn)_{12}RE$ phase at the grain boundaries. The increase of pouring temperature results in the increase of the fluidity as well as grain size and the decrease of the mechanical properties. Good mechanical properties and good castability are obtained for alloy, which is poured from 780°C. Therefore this temperature is recommended in sand cast technology of ZRE1 magnesium alloy.

The $(Mg,Zn)_{12}RE$ compound exhibited high stability of the chemical composition and morphology at temperature 150°C for 1000 h. At this temperature the precipitation process of zirconium-rich particles (probably ZrH_2 or Zn_2Zr_3) from solid solution of magnesium takes place. The emerging of the precipitates containing zirconium leads to the increase of the hardness. After annealing at 200°C the first stages of spheroidizing of the

$(Mg,Zn)_{12}RE$ are observed, therefore the hardness of the ZRE1 alloy is slightly lower than that in the alloy annealed at 150°C. The degradation of the microstructure of the ZRE1 alloy at 400°C is induced by the low oxidation resistance at this temperature. This effect causes the formation of the porous MgO layer and the oxidation of the $(Mg,Zn)_{12}RE$ compound. Thus the ZRE1 magnesium alloy cannot be heat treated above this temperature.

Acknowledgements

The present work was supported by the Polish Ministry of Science and Higher Education under the research project POIG.01.01.02-00-015/09 (FSB-71/RM3/2010).

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Received: 10 January 2011.