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The Effect of Non-Equilibrium Solidification on the Structure and Mechanical Properties of AZ91 Alloy

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Abstract

AZ91 alloy was cast in a steel mould pre-exposed to three different temperatures: -196 ºC, 20 ºC and 650 ºC. The aim of the study was to determine the difference in the microstructure and mechanical properties between the castings formed in a cold mould and those solidifying under near-equilibrium conditions in a mould pre-heated to 650 ºC. Solidification at a low temperature led to dispersion of the structure elements as well as supersaturation of the solid solution of aluminium in magnesium. The heat treatment results indicate that the alloy solidified in the mould pre-exposed to 20 ºC can be successfully aged (heat treated to the T5 temper). It was found that the effect of the ageing process (T5 temper) was greater than the effect of the microstructure fragmentation, which was due to rapid solidification. The ageing results were assessed by comparing the microstructure and mechanical properties of AZ91 brought to the T5 condition with those obtained for the material in the T6 condition.

Keywords: AZ91 alloy, Microstructure, Mechanical properties, Heat treatment

1. Introduction

Magnesium alloys whose basic constituent is aluminium are the oldest and most common magnesium casting alloys. Generally, they contain by weight 6-10 % aluminium, up to 3 % zinc or up to 1.5 % silicon and 0.1-0.3 % manganese. Their mechanical properties are primarily dependent on the content of aluminium. Zinc and silicon increase the strength properties of the alloys, while manganese, forming an intermetallic phase with iron and magnesium, improves their corrosion resistance. Aluminium as an alloying element increases the critical shear stress in the (0001) plane, which is the basal plane of the slip in magnesium, and reduces the critical shear stress in the prismatic $(10\bar{1}0)$ plane [1]. These opposing trends are responsible for higher yield stress. Unlike unalloyed magnesium, supersaturated Mg-Al alloys can deform in the $\{10\bar{1}0\}<1210>$ system, and this improves their ductility [2]. Supersaturated AZ91 alloy accordingly has much higher strength and plastic properties than unalloyed magnesium [3].

AZ91 containing 9 wt.% Al, 0.5-1.0 wt.% Zn and 0.3 wt.% Mn is a popular magnesium alloy with a perfect combination of strength, ductility and castability, with castability being dependent on the aluminium content. The higher the content, the higher the castability. The microstructure of as-cast AZ91 alloy shows dendrites of a solid solution of aluminium in magnesium with a hexagonal close-packed lattice structure and a eutectic composed of an $Mg_{17}Al_{12}$ intermetallic compound and a solid solution of aluminium in magnesium. Depending on the rate at which the alloy solidifies, the eutectic morphology is either partially or fully divorced [4]. The Mg-Al phase diagram [5] shows that the maximum solid solubility of aluminium in magnesium is 11.8 at.% (about 12.6 wt%) when the eutectic temperature is 437 ºC; it decreases substantially with decreasing temperature. This indicates that AZ91 alloy can be strengthened through precipitation hardening.

Supercooling during crystallization results in fragmentation of the microstructure. When AZ91 alloy solidifies in a steel mould, it has a microstructure different from that formed in a sand mould; the difference lies mainly in the size of dendrites [6]. For example, the average grain size in a die casting alloy ranges between 15 and 20 µm [7]; in an AZ91 ingot, it is about 300 µm [8].

The study described in this article sought to determine how the initial temperature of a steel mould affected the microstructure and mechanical properties of AZ91 alloy. It was essential, firstly, to assess the influence of the cooling rate on the dispersion of the microstructure constituents and the mechanical properties of the alloy, and secondly, to determine whether the solidification was fast enough to reach supersaturation of the solid solution at which ageing would be effective.

2. Experimental procedure

Commercial AZ91 alloy (9.14 wt% Al, 0.64 wt% Zn and 0.23 wt% Mn) was used in the experiments. The material was melted at a temperature of 650 ºC and then poured into a steel mould with a weight of 1.2 kg. The cylindrical castings had a diameter of 18 mm and a height of 50 mm. The solidification of the alloy was carried out in a mould whose initial temperature was: -196 ºC (mould chilled in liquid nitrogen), 20 ºC (mould at room temperature) and 650 ºC (mould pre-heated in a furnace). The castings were removed from the mould at a temperature of about 100 ºC. A standard metallographic technique was used to prepare the specimens for optical and scanning electron microscopy (OM and SEM, respectively). The optical microscopic observations were conducted with a Nikon Eclipse MA200, while the scanning electron microscopic examinations were performed using a JEOL JSM-5400 equipped with an Oxford Instruments ISIS 300 energy dispersive X-ray analysis system. The first microscopic observations revealed that the surface zone of casings exhibited greater microstructural refinement. The thickness of this zone was about 1 mm. For this reason, castings were machined before further tests to reduce their diameter from 18 mm to 16 mm. The structural analysis and the Vickers hardness measurements were carried out in the specimen cross-section. The specimens for the compression tests were 16 mm in diameter and 16 mm in height. The compression test was performed using a Zwick/Roell screw-driven universal testing system at a strain rate of 5.2 x $10^{-4}s^{-1}$.

The heat treatment parameters used in this study were adopted from Avedesian and Baker [9]. AZ91 alloy was aged to the T5 temper by heating for 16 hours at a temperature of 175 ºC. Ageing to the T6 condition required holding the specimens for 24 hours at 425 ºC, quenching them in water and, finally, ageing them for 16 hours at a temperature of 175 ºC.

3. Results and discussion

Figure 1 shows optical images of the microstructure of as-cast AZ91 alloy at various magnifications. The casting was performed in a mould pre-exposed to a low, room or high temperature. The mould temperatures were -196 ºC (Fig 1a), 20 ºC (Fig. 1b) and 650 ºC (Fig. 1c), respectively. Solidification of the alloy began with the crystallization of the α-phase (a solid solution of aluminium in magnesium) in the form of dendrites. The rest of the liquid phase solidified as the eutectic, which consisted of an $Mg_{17}Al_{12}$ intermetallic compound and the α-phase. When the liquid alloy was poured into a hot mould (Fig. 1c), the casting microstructure was characterised by large dendrite arms and large eutectic particles. Solidification of the material in a cold mould resulted in a very fragmented microstructure. The microstructure of the AZ91 alloy cast in a mould pre-exposed to room temperature (Fig. 1b) was practically identical to that reported for the material solidified in a mould pre-cooled in liquid nitrogen to a temperature of -196 ºC (Fig. 1a).

The hardness of the alloy cast in a mould pre-cooled to -196 ºC (62.5 HV30) was similar to that measured for the alloy cast in a mould pre-exposed to 20 ºC (64 HV30). This result was rather unexpected. It seemed obvious that solidification of the alloy in a frozen mould would result in a greater supercooling effect compared with its solidification in a mould with room temperature. It should be noted, however, that after the mould was removed from liquid nitrogen, its surface, exposed to ambient humidity, was immediately covered with a thin layer of frost. Once in contact with hot liquid metal, the layer must have changed into water vapour, which acted as a 'barrier' isolating the mould from the solidifying alloy. Thus, freezing the mould in liquid nitrogen prior to casting was not effective. When the casting was performed in a mould pre-heated to 650 ºC, the hardness of the material was lower (51 HV30). Further tests were thus conducted for castings produced in a mould pre-exposed to 20 ºC or 650 ºC.

From the microscopic observations (Fig. 1 higher magnification) it is also evident that the one phase of the eutectic structure – $Mg_{17}Al_{12}$ is present in a massive form, whereas α phase (second phase of eutectic mixture) is distributed inside $Mg_{17}Al_{12}$ particles. These phases are separated by the interfacial boundary visible as a dark line. This morphology according to Dahle and others [4] indicates on partially divorced eutectic. The results of microstructure observations are consistent with the findings from previous studies [4, 6, 10]. The SEM images also reveal that the eutectic area was surrounded by a 'cloud' of very fine particles. Figure 2 shows the microstructure of a casting formed in a mould pre-heated to a temperature of 650 ºC; the results of the quantitative EDS analysis are also provided. The examination of the eutectic area (point 1) reveals a higher content of magnesium and a lower content of aluminium when compared with the stoichiometry of the $Mg_{17}Al_{12}$ phase. It is clear that the analysed area also contained the magnesium-rich α-phase, indicative of the partially divorced eutectic. The content of aluminium in the area of the 'cloud', formed by fine particles present in the immediate vicinity of the eutectic (Fig. 2 point 2), was higher than that in the more distant dendrite zone (Fig. 2 point 3). These results are in agreement with the linear analysis data (Fig. 3). Similar EDS line scan results were obtained for a casting formed in a mould pre-exposed to a temperature of 20 ºC (Fig. 4). These observations suggest that the 'clouds' were composed of the intermetallic phase particles, which were precipitated from the solid solution of aluminium in magnesium while the solidified castings were cooled. Although no further examination was carried out to identify the structure of these particles, their location in the vicinity of the eutectic suggests that the dendrites were chemically inhomogeneous. According to Dahle [4], the solid solution regions near the $Mg_{17}Al_{12}$ phase have higher aluminium contents (up to 10-13 wt.%. Al) than the dendrite cores, where aluminum concentrations are as low as 2 wt% Al. Because of the inhomogenity of the dendrites, a cellular structure could also form in the immediate vicinity of the eutectic. This phenomenon, however, was observed occasionally and only in the structure of castings formed in a mould pre-heated to a temperature of 650 ºC (Fig. 1c – high magnification).

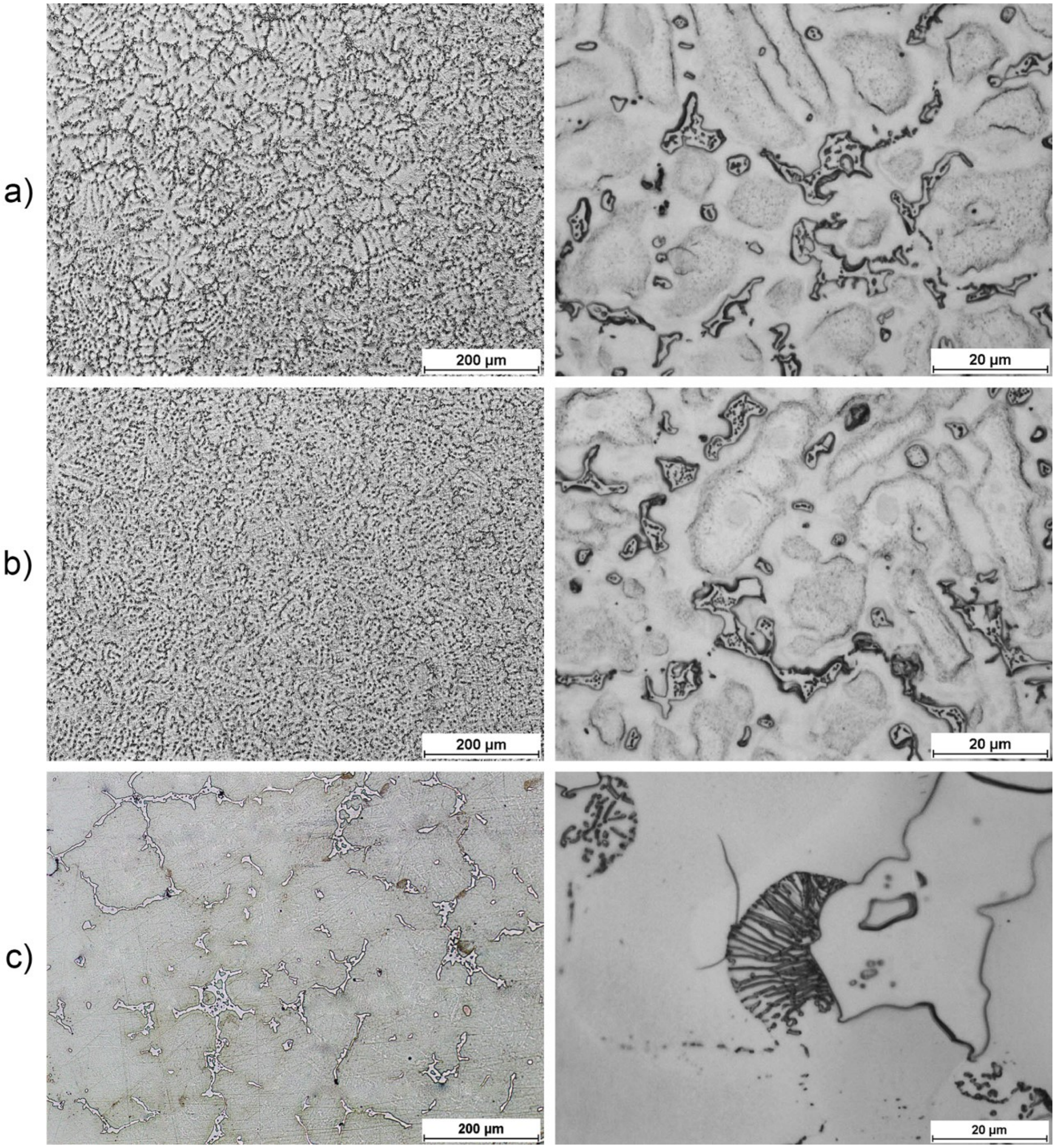
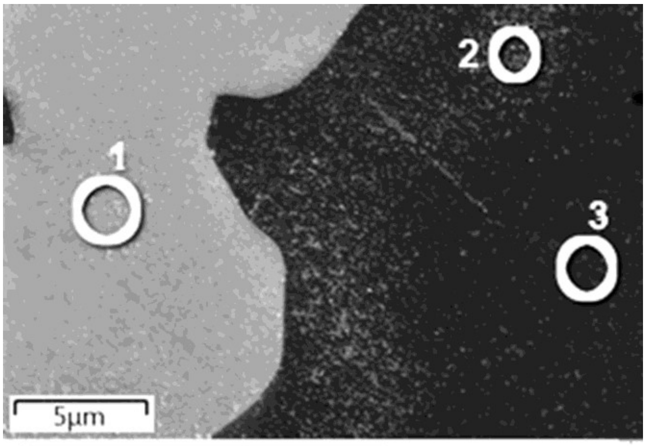


Fig. 1. OM images of the microstructure of AZ91 alloy after solidification in a mould with an initial temperature of: (a) -196 ºC, (b) 20 ºC, and (c) 650 ºC; low and high magnifications (left and right, respectively).



Result Type	Atomic %			
Spectrum Label	Mg	Al	Zn	Total
Spectrum 1	61.66	35.76	2.59	100.00
Spectrum 2	92.83	6.91	0.26	100.00
Spectrum 3	94.84	4.98	0.18	100.00

Fig. 2. SEM image of the microstructure with averaged results of the EDS analysis for the eutectic area (point 1) and the dendrite area (points 2 and 3); AZ91 alloy solidified in a mould pre-heated to 650 ºC

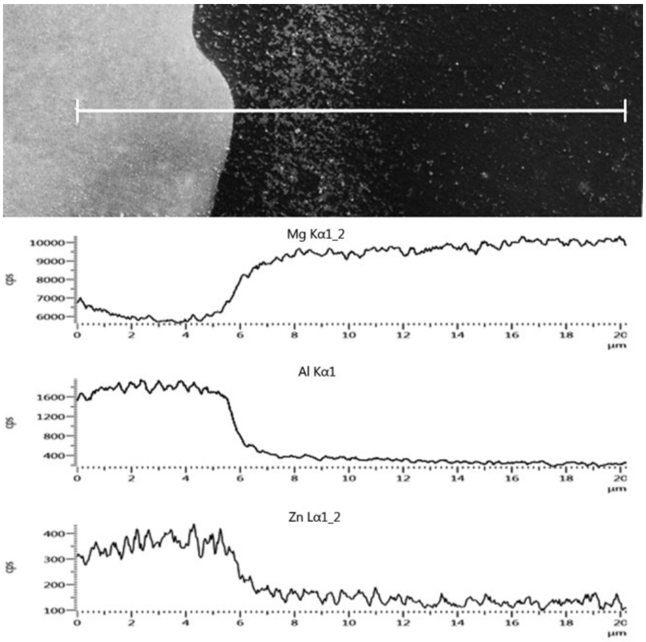


Fig.3. Linear distribution of Mg, Al and Zn in the dendrite-eutectic zone; alloy solidified in a mould pre-heated to 650 ºC

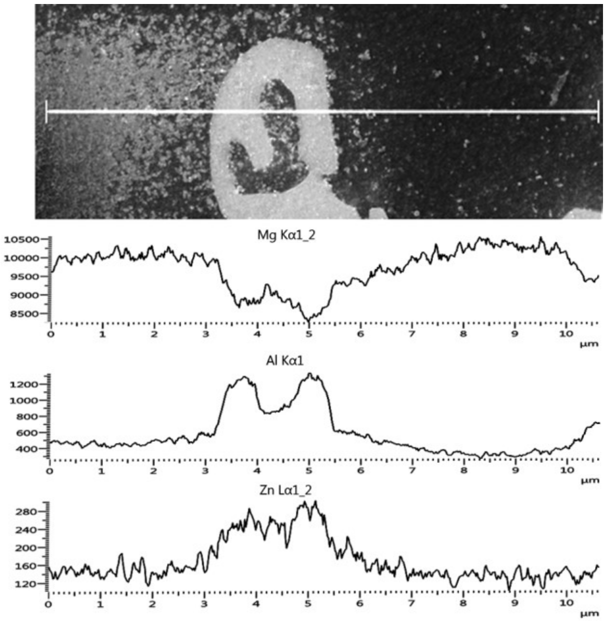


Fig. 4. Linear distribution of Mg, Al and Zn in the dendrite-eutectic zone; alloy solidified in a mould with an initial temperature of 20 ºC

The compressive strength tests were conducted on the AZ91 specimens machined from the castings formed in a mould pre-exposed to two temperatures: 20 ºC and 650 ºC. In both cases, the specimens failed in shear (Fig. 5). Table 1 shows the average values of the yield strength, compressive strength and plastic strain prior to fracture.

Fig. 5. AZ91 alloy sample after the compression test

It is obvious that the differences in the mechanical properties resulted primarily from the different degrees of dispersion of the $Mg_{17}Al_{12}$ intermetallic phase, which predominated in the eutectic. The microhardness of the $Mg_{17}Al_{12}$ phase was relatively high, ranging from 221 to 228 HV0.1 [11].

Further tests were carried out on the specimens cut from the castings made in a mould with an initial temperature of 20 ºC. They were aged (heat treated to the T5 temper condition) to determine whether or not and to what extent the alloy was supersaturated during casting. For comparative purposes, classical precipitation strengthening, i.e. solution heat treatment and ageing (T6 temper condition), was performed. The results of the compressive strength test are summarized in Table 2.

Table 1.
Mechanical properties of the castings formed in a mould with an initial temperature of 650 ºC or 20 ºC

Initial mould temperature ºC	Yield strength $R_{0.2}$ MPa	Compressive strength MPa	Plastic strain %
650	144	302	7.5
20	157	360	8

Table 2.
Mechanical properties of the castings heat treated to the T5 or T6 condition

Temper condition	Yield strength $R_{0.2}$ MPa	Compressive strength MPa	Plastic strain %
T5	181	368	6.5
T6	216	388	6.5

The data in Tables 1 and 2 concerning the castings formed in a mould with an initial temperature of 20 ºC indicate that the effect of the ageing process (T5 temper) was greater than the effect of the microstructure fragmentation, which was due to rapid solidification. However, the heat treatment to the T6 temper condition resulted in much higher strength properties of the alloy. It should be added that the effect of ageing reported for the cast made in a mould pre-heated to a temperature of 650 ºC was negligible.

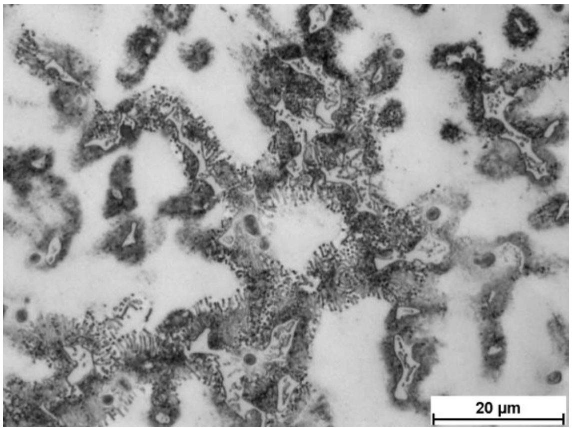


Fig. 6. Microstructure of AZ91 alloy in the T5 temper; alloy solidified in a mould with an initial temperature of 20 ºC

The major difference between the microstructure of the AZ91 alloy heat treated to the T5 temper and the microstructure reported in the T6 condition is the type and distribution of precipitates. Ageing to the T5 condition resulted in the formation of discontinuous precipitates around the eutectic (Fig. 6) and continuous precipitates in some regions of the dendrites (Fig. 7).

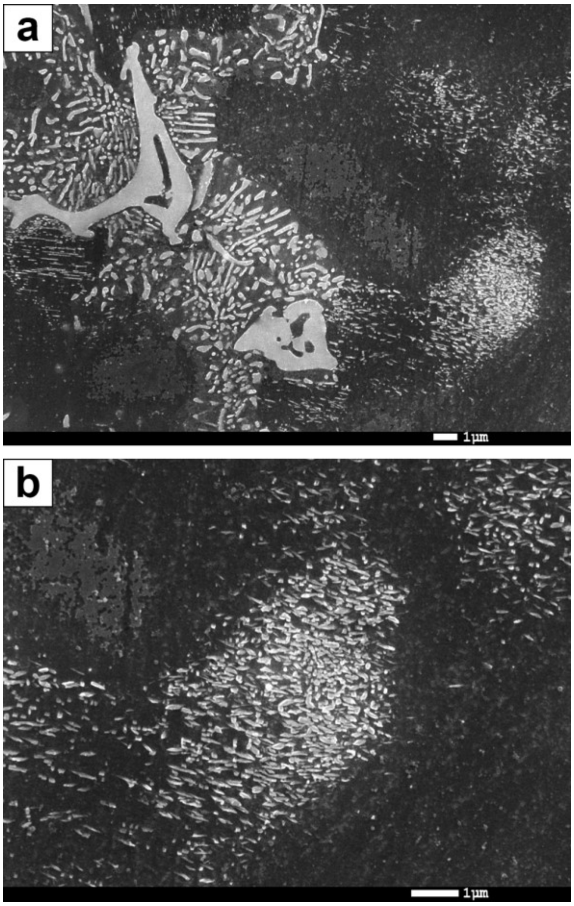


Fig. 7. SEM image of discontinuous and continuous precipitates near the eutectic region (a); high magnification (b) revealing locally observed continuous precipitates. Alloy solidified in a mould with an initial temperature of 20 ºC

In the T6 condition (Fig. 8), particles of continuous precipitates observed in the structure were more numerous, and they were distributed in a more regular manner together with discontinuous precipitates formed at the grain boundaries.

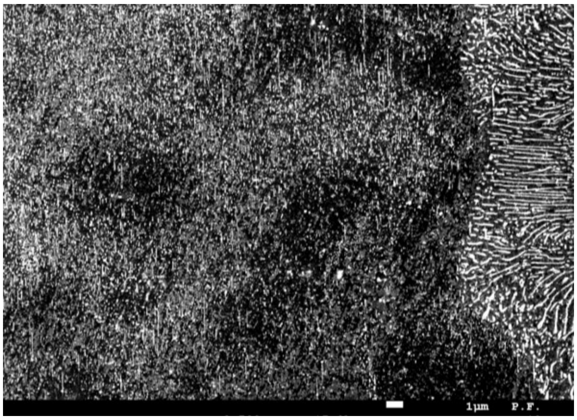


Fig. 8. Microstructure of AZ91 alloy in the T6 temper; alloy solidified in a mould with an initial temperature of 20 ºC

It should also be noted that continuous precipitation resulted in a structure with particles much finer than those formed during discontinuous precipitation (Fig. 9). This suggests their significant role in the strengthening of the alloy.

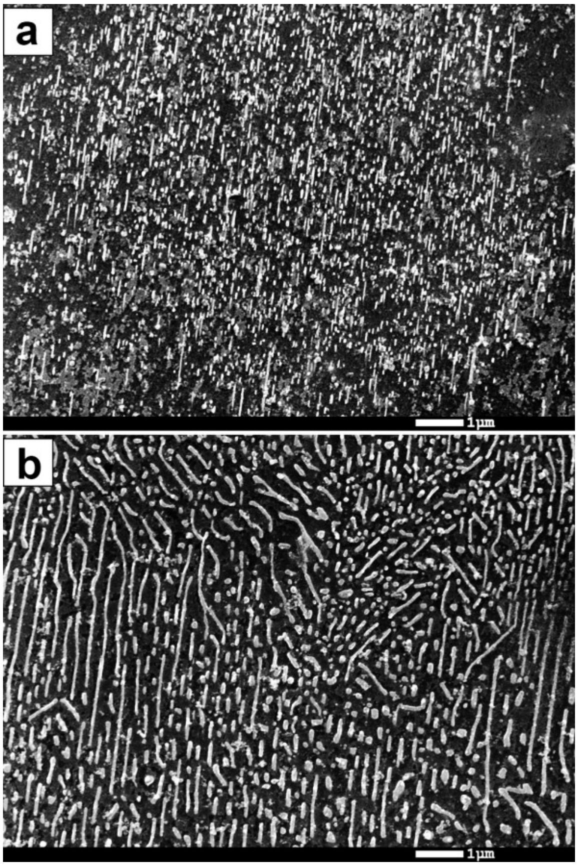


Fig. 9. Comparison of the sizes of continuous (a) and discontinuous (b) precipitates; alloy solidified in a mould with an initial temperature of 20 ºC and heat treated to the T6 temper condition

4. Conclusions

1. As-cast AZ91 alloy had a structure composed of a solid solution of aluminium in magnesium in the form of dendrites and a partially divorced eutectic. The high cooling rate caused significant fragmentation of the alloy structure and an increase in its strength properties.
2. The dendrites of the α-phase (a solid solution of aluminium in magnesium) were chemically inhomogeneous. Leaving a hot casting in the mould after solidification led to the formation of a 'cloud' of fine precipitates in the vicinity of the eutectic.
3. The ageing (heat treatment to the T5 temper) of AZ91 castings formed in a mould with an initial temperature of 20 ºC resulted in discontinuous precipitation mainly and a considerable increase in the yield strength. This increase was greater than that caused by the structure fragmentation. Obtaining higher strength properties requires heat treatment to the T6 temper condition.
4. Freezing the mould in liquid nitrogen before casting proved ineffective to achieve supercooling greater than that observed when AZ91 alloy was cast in a mould with an initial temperature of 20 ºC.

References

[1] Akhtar, A. & Teghtsoonian, E. (1969). Solid solution strengthening of magnesium single crystals – alloying behavior in basal slip. *Acta Metallurgica.* 17, 1339-1349.

[2] Akhtar, A. & Teghtsoonian, E. (1968). Solid solution hardening in magnesium alloys. *Transactions of the Japan Institute of Metals.* 9, 692-697.

[3] Cáceres, C.H. & Rovera, D.M. (2001). Solid solution strengthening in concentrated MgAl alloys. *Journal of Light Metals.* 1(3), 151-156.

[4] Dahle, A.K., Lee, Y.C., Nave, M.D., Schaffer, P.L. & St. John, D.H. (2001). Development of the as-cast microstructure in magnesium-aluminium alloys. *Journal of Light Metals.* 1(1), 61-72.

[5] Predel, B. (1998). *Landolt-Börnstein - Group IV Physical Chemistry (Numerical Data and Functional Relationships in Science and Technology).* Berlin: Springer-Verlag.

[6] Braszczyńska-Malik, K.N. (2011). Precipitates of γ-Mg17Al12 Phse in AZ91 Alloy. In Frank Czerwinski (Eds.) *Magnesium Alloys – Design, Processing and Properties.* 95-112. INTECH.

[7] Blum, W., Li, Y.J., Zeng, X.H., Zhang, P., Großmann, B. & Haberling, C. (2005). Creep deformation mechanisms in high-pressure die-cast magnesium-aluminium base alloys. *Metallurgical and Materials Transactions A.* 36(7), 1721-1728.

[8] Regev, M., Aghion, E. & Rosen, A. (1997). Creep studies of AZ91D pressure die casting. *Materials Science and Engineering: A.* 234-236, 123-126.

[9] Avedesian, M.M., Baker, H. (1999). *ASM Specialty Handbook: Magnesium and magnesium alloys.* USA: ASM International.

[10] Braszczyńska-Malik, K.N. (2009). Discontinuous and continuous precipitation in magnesium-aluminium type alloys. *Journal of Alloys and Compounds.* 477(1-2), 870-876.

[11] Mola, R., Bucki, T. & Dziadoń, A. (2016). Formation of Al-alloyed layer on magnesium with use of casting techniques. *Archives of Foundry Engineering.* 16(1), 112-116.