

A.B. STRAUMAL^{*,**,#}, K.V. TSOY^{**}, I.A. MAZILKIN^{*,**}, A.N. NEKRASOV^{***}, K. BRYŁA^{****}

GRAIN BOUNDARY WETTING AND MATERIAL PERFORMANCE IN AN INDUSTRIAL EZ33A Mg CAST ALLOY

The grain boundary wetting phase transition in an industrial EZ33A cast alloy is studied. 12% of the grain boundaries are completely wetted at the temperature slightly higher than the eutectic transformation temperature (530°C). The fraction of wetted grain boundaries increases with temperature, reaches a maximum of 85% at 570°C, and does not change further until the alloy melts. In the as-cast state, the alloy has low ductile properties at the ambient temperature. The microstructure in the as-cast state corresponds to the wetting state at about 560°C, which indicates that the cooling rate in casting is almost equal to that in quenching. The volume and the surface fraction of the second phase and the hardness measured at the least wetted state of samples point to its good machinability. The wetting data are used to suggest a sequence of heat treatment and machining for processing EZ33A alloy parts.

Keywords: grain boundary, wetting, cast alloy, Mg, mechanical properties

1. Introduction

Mg-based cast alloys belong to the best-investigated cast alloys in modern materials science. They are widely used in the aerospace industry, the military industry, and the automotive industry due to their remarkable mechanical properties, good castability, and an extremely small specific weight. Numerous research groups are working on further improvement of the properties of Mg cast alloys. For example, the dependence of the structure and the properties of these alloys on their chemical composition [1-5] or the change in the structure after various types of mechanical treatment [6-8] were studied. Particularly, creep experiments [9] and the investigation of conventional [12] and laser [10,11] welded joints were performed.

The EZ33A alloy is an industrial Mg cast alloy with good creep resistance at temperatures up to 250°C, low microporosity, and good casting properties. It is used in permanent-mold and pressure-tight sand casting in the aerospace industry [13]. Although this alloy has been used for 60 years, it is still poorly understood. Only three papers were published in the last decade: one of them was dedicated to repairing the ZE41A alloy surface by laser welding with an EZ33A welding rod [10], and two others, to the structural stability of the welded joints of this alloy [12] and the structural evolution of the EZ33A alloy during high-pressure torsion (HPT) [6]. Neither of these papers

explained why the structure of the welded joint differs from the as-cast structure [12].

The main problem of this alloy is the hardness at the ambient temperature. Although it is an important property of the end product, it brings difficulties in the production of parts by machining (pressing, rolling). A higher ductility at the ambient temperature would be preferable. The high hardness and the low ductility of the material are explained by the existence of very hard intermetallic precipitates at Mg/Mg grain boundaries [6,14]. The intermetallic phase in the as-cast material covers almost all grain boundaries and, obviously, makes crack propagation easier during brittle fracture.

However, the properties of the alloy can be controlled. The as-cast structure is very similar to a structure with completely and incompletely wetted grain boundaries [12]; therefore, the solid/liquid wetting phase transition is assumed to exist in this system.

In 1977, Cahn theoretically predicted the existence of a special “wetting” surface phase transitions [15]. At first, external surface wetting was investigated [16-18]. The hysteresis and the temperature derivative jump of the surface energy that are peculiar to first order phase transformations were measured [19,20]. The wetting phase transition at the interfaces in solids was experimentally studied much later [21].

The external and internal surface wettings differ in the number of phases in contact at the vertex of the wetting angle. In

* NATIONAL UNIVERSITY FOR SCIENCE AND TECHNOLOGY “MISIS” (NITU MISIS), MOSCOW, RUSSIA

** INSTITUTE OF SOLID STATE PHYSICS, RUSSIAN ACADEMY OF SCIENCES, CHERNOGOLOVKA, RUSSIA

*** INSTITUTE OF EXPERIMENTAL MINERALOGY, CHERNOGOLOVKA, RUSSIA

**** PEDAGOGICAL UNIVERSITY OF CRACOW, FACULTY OF MATHEMATICS, PHYSICS AND TECHNICAL SCIENCE, INSTITUTE OF TECHNOLOGY, KRAKÓW, POLAND

Corresponding author: straumal@misiss.ru

the case of interface wetting, only two phases exist and, hence, the surface energy balance can be expressed as

$$\sigma_{GB} = 2 \sigma_{SL} \cos(\theta_{GB}/2),$$

where σ_{GB} is the grain boundary energy, σ_{SL} is the solid/liquid interface energy, and θ_{GB} is the wetting contact angle. The value of θ_{GB} reflects the energy balance between two solid/liquid interfaces and a grain boundary. The wetting phase transition of grain boundaries takes place if the energy balance shifts under changing system condition, such as an increase in temperature. Then, contact angle θ_{GB} becomes zero and the grain boundary is substituted by a complete second-phase layer and two solid/liquid interfaces. Technically, the grain boundary does not exist after the wetting transition. In polycrystals with many various grain boundaries with various energies, a spectrum of grain boundary wetting temperatures exists. It can be depicted on an equilibrium phase diagram by two tie-lines of the “wetting start” temperature, where the first grain boundary becomes completely wetted, and the “wetting finish” temperature, where the last grain boundary becomes completely wetted. Such tie-lines were experimentally obtained for Al-Sn, Zn-Sn, Cu-In, Al-Sn-Pb, W-Ni, Al-Ga and Al-Sn-Ga [22-28].

As for the EZ33A alloy, if a wetting phase transition occurs, it will be possible to control the number of grain boundaries covered by the brittle intermetallic phase by specific heat treatment, thus the mechanical properties, at various stages of production.

2. Experimental

2-mm-thick slices were spark-cut from an industrial EZ33A alloy ingot to minimize the material loss and the deformation of the sample surface in cutting. The ingot and the samples were chemically etched in a 75% HCl + 25% H₂O etching solution, since the oxide layer on the surface is electrically passive and prohibits spark cutting.

The samples were again etched and placed into quartz ampoules at a residual pressure $P = 4 \times 10^{-4}$ Pa to prevent oxidation during annealing. The samples were annealed in the temperature range from 340 to 590°C at a step of 50°C to determine the liquid/solid two-phase region for this composition preliminarily. Additional annealing at 525, 527, 528, 529, 530, 535, 545, 550, 555, 570 and 580°C was performed to find the solidus temperature exactly and to investigate the wetting phase transition. All annealings were carried out for 2 h to reach a stable structure state and then to be quenched in water. The time was chosen using earlier experiments on wetting with a liquid phase: after annealing for 30 min, the liquid phase wetting structures were stable and did not change at longer annealing. The liquidus temperature could not be determined, since the structure elements started to evaporate in the ampoule at higher temperatures prior to complete melting of the sample.

Metallographic preparation of all samples, including a sample in the initial state, was carried out. The samples were ground on grinding paper number 200, 400, 600, 800, 1200, 2000

and 4000 and then polished with polishing media with a grain size from 5 to 0.5 μm . The microstructure of the samples was investigated by scanning electron microscopy (SEM) (CamScan and Vega II microscopes, TESCAN). The chemical composition of phases was determined by energy dispersive X-ray (EDX) analysis on the same microscopes. A sample in the initial state and two samples annealed at 530°C and 550°C were also investigated by X-ray diffraction (XRD) analysis (Siemens D-500 diffractometer, Germany). Crystal structure information and the volume fractions of the phases were obtained by analyzing XRD data using the PowderCell software package (PowderCell for Windows. Version 2.4. 08.03.2000, Werner Kraus & Gert Nolze, BAM Berlin). The microhardness of the alloy was measured with a microhardness tester (PMT-3, Russia).

A microstructure was analyzed with the ImageExpert software package (NEXSYS ImageExpert Pro 2, Russia). The second phase on SEM images taken with a backscatter electrons (BSE) detector was visualized as bright gray areas against the background of dark gray α -Mg grains. No pores, which would be black, were found in the microstructures due to low microporosity, as was mentioned earlier. The wetting state of the grain boundaries, the mean wetting angle, the mean grain size, and the surface fractions of phases were determined. All measurements with the ImageExpert software package were manually performed. If the second phase connected two triple junctions with a continuous layer, such a grain boundary was taken as completely wetted and was added to “wetted” data. If gaps were visible in a second-phase layer, such a grain boundary was taken as incompletely wetted or not wetted and added to “not wetted” data.

3. Results and discussion

As was noted above, the as-cast structure is very similar to a structure with completely wetted grain boundaries. In Fig. 1, we can see that dark gray grains, apparently, an α -Mg type phase, are surrounded by a bright gray second phase, which is an intermetallic compound [6]. In some places, grain-boundary layers have gaps; however, about 75% of the grain boundaries are assumed to be completely wetted with the second phase. The mean grain size in the as-cast alloy is about 60 μm .

After the first annealing in the temperature range from 340°C to 590°C at a step of 50°C, we confirmed that the liquid/solid grain boundary wetting transition took place in this system. Our conclusion is based on several facts. From 340°C to 490°C, no significant changes in the sample structure have been found. That indicates that all phases at these temperatures are solid and the diffusion rate is too low to change anything in the structures within 2 h.

At 540°C, the sample structure changes radically. The mean grain size increases up to 100 μm , the fraction of completely wetted grain boundaries decreases from 75% to 34%, and second-phase layers change their shape significantly. In particular, the layers do not show any gaps any more: they are smooth and have

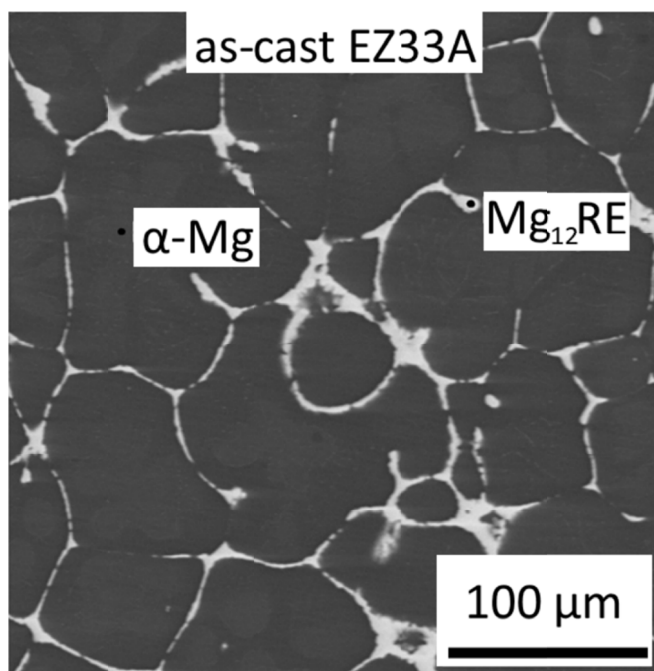


Fig. 1. As-cast microstructure of the EZ33A Mg-cast alloy

sharp acute wetting contact angles on incompletely wetted grain boundaries. These findings indicate that the diffusion rate during annealing was much higher than earlier, which can only be explained by the fact that the second phase at this temperature is liquid and grain growth occurs due to recrystallization through the liquid phase. 34% of the completely wetted grain boundaries confirm the existence of the liquid/solid grain boundary wetting phase transition in this alloy.

To investigate the liquid/solid grain boundary wetting phase transition in more detail, additional annealing was carried out. Additional annealing at 525, 527, 528, 529, 530, 535, 545, 550, 555, 570 and 580°C allowed us to find the solidus temperature and to investigate the wetting phase transition rate in this system. The solidus temperature was found to be $529^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. The microstructures of the samples annealed at these additional temperatures confirmed the conclusion about the existence of wetting transformation in the EZ33A alloy. In Fig. 2a, we can see the microstructure of the sample annealed at 530°C, slightly above the solidus temperature. It is clearly visible that the second phase changed its shape. Most grain boundaries are incompletely wetted or not wetted, the contact angles are far from zero, and the second phase concentrates in rather equiaxial particles rather than extended layers at grain boundaries. Only 12% of the grain boundaries are completely wetted, which indicates that the temperature of the onset of wetting is equal to the solidus temperature.

The sample shown Fig. 2b was annealed at 550°C; the wetting phase transition is seen to transform the initial microstructure. A much larger number of grain boundaries (about 60%) are completely wetted and the remaining nonzero contact angles are much lower and acute as well. Fig. 2c shows the structure of the sample annealed at the highest temperatures in the annealing temperature range. At 590°C, almost all grain boundaries are

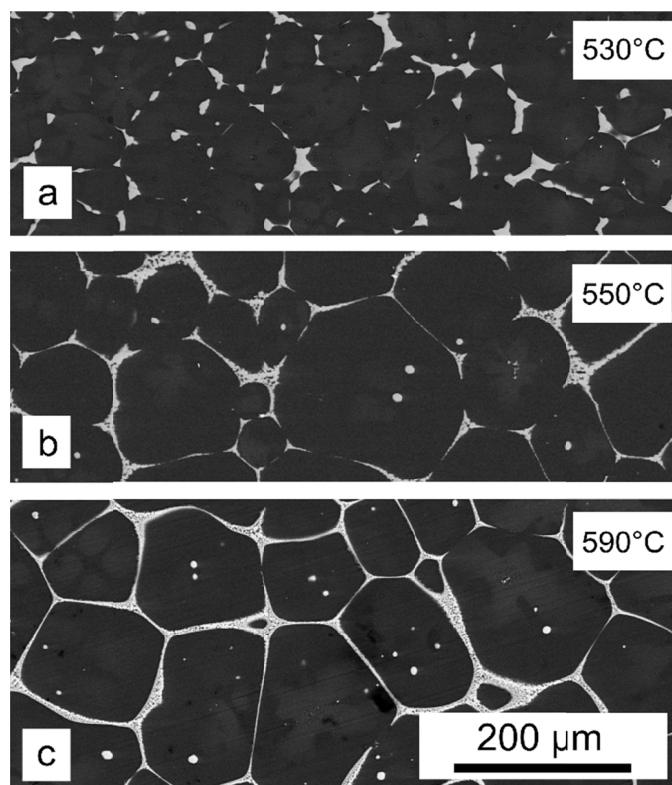


Fig. 2. Microstructures of EZ33A samples at various states of wetting grain boundaries after annealing at (a) – 530°C, (b) – 550°C and (c) – 590°C

completely wetted, only a small number of them have nonzero contact angles, and all of them are acute and tend to zero.

Three of the samples were also investigated by XRD. All the samples, i.e., as-cast and annealed at 530°C and 550°C, have the same phases. The matrix phase is the α -(Mg) solid solution with a hexagonal crystal structure (P63/mmc), and the second phase is the Mg_{12}RE phase (RE = rare-earth metal) with a tetragonal crystal structure (I4/mmm). Since the annealed structures have the same second phase after quenching, the as-cast structure is a metastable quenched state of the EZ33A alloy and it corresponds to the high-temperature wetting state after quenching at a lower cooling rate.

EDX of the samples shows that the EZ33A alloy consists mainly of Mg with (wt %) 2.5 Zn, 0.4 Zr, 0.6 La, 1.1 Ce, and 0.6 Nb. The α -(Mg) phase has (wt %) 94-97 Mg, 2.5-1 Zn, 2.5-1 Zr, and 0.5 La, Ce, and Nb. The second phase (Mg_{12}RE) has (wt %) 61-55 Mg, 9-15 Zn, 0 Zr, 8 La, 14 Ce, and 3.5 Nb. These concentrations depend on the annealing temperature. The Mg content increases with temperature in α -(Mg) and decreases in Mg_{12}RE . The Zn content decreases with increasing temperature in α -(Mg) and increases in Mg_{12}RE . Other element concentrations also change, but it is difficult to trace exact concentration trends due to the formation of a kind of eutectoid from the melt during quenching and, thus, due to the inhomogeneity of concentrations in this metastable state.

Fig. 3 shows the results of data analysis for the wetting phase transition and the volume and surface fractions of the second phase in the samples annealed at various temperatures.

Fig. 3a depicts the temperature dependence of the fraction of completely wetted grain boundaries. It is clear that this fraction increases with temperature up to a maximum of 85%. We assume that this fraction does not increase further, because the energy of the remaining grain boundaries is too low to allow the grain boundaries to be wetted [29]. At 21°C, we put the data point for the as-cast sample. If we draw a horizontal line from the as-cast point, we can see that the wetting state corresponds to wetting at 560°C or above.

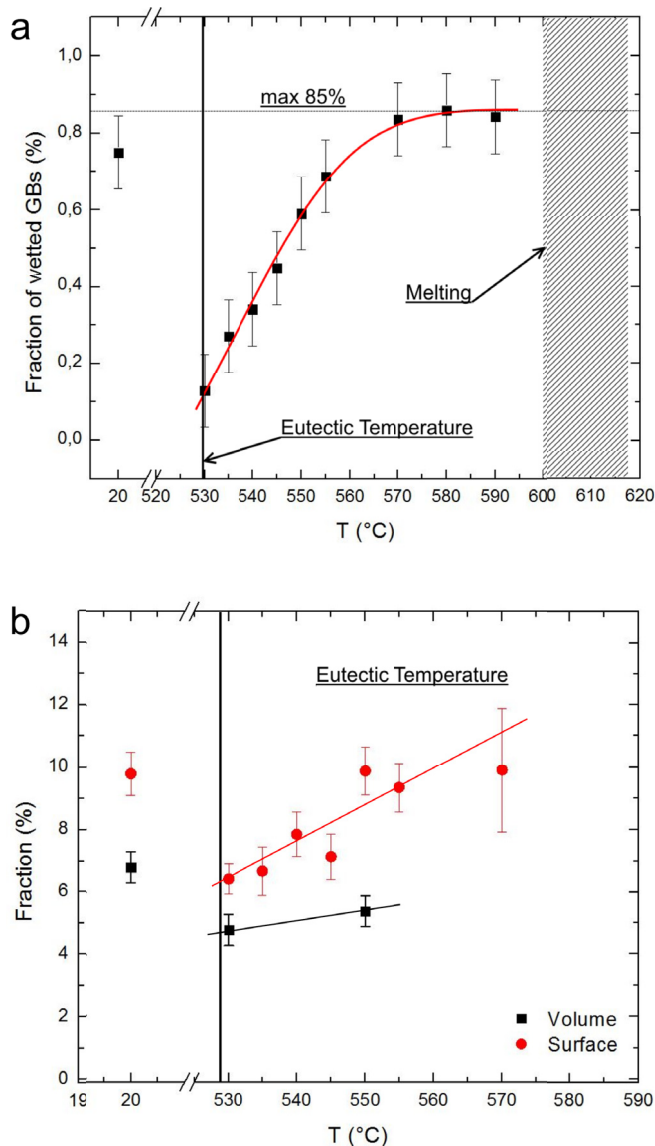


Fig. 3. Temperature dependences of (a) – fraction of completely wetted grain boundaries; (b) – volume fraction of a second phase (black squares), surface fraction of a second phase (red circles)

Fig. 3b displays the temperature dependence of the surface and the volume fractions of the second phase. The volume fraction was calculated from XRD data, and the surface fraction, from micrographs of structures. The dependence increases linearly with temperature. Similar to the fraction of wetted grain boundaries, the as-cast volume and the surface fractions of the second phase correspond to a temperature of about 560°C or above.

An obvious conclusion can be drawn from these results. To increase the overall ductility of the material, we have to decrease the fraction of the grain boundaries wetted with the (hard and brittle) intermetallic phase, because it is harder and cracks tend to propagate through this phase on the grain boundaries. By annealing the EZ33A alloy at 530°C, we can decrease the fraction of wetted grain boundaries from 75% to 12% and decrease the total amount of the intermetallic phase by 1.5 times. Therefore, when controlling wetting, we can increase the ductility.

The assumption that, after heat treatment at 530°C, the alloy should show higher ductility is based on the hardness measurements of the structural elements after annealing at various temperatures. The hardness of the intermetallic $Mg_{12}RE$ phase changes between 100HV and 350HV in every sample depending on the composition and the homogeneity. Fig. 4 shows the temperature dependence of the hardness of the α -(Mg) phase. The hardness grows with the annealing temperature. Obviously, it depends on the composition, which changes with the temperature. Nevertheless, it is always lower than the hardness of $Mg_{12}RE$ and is lowest after annealing at 530°C.

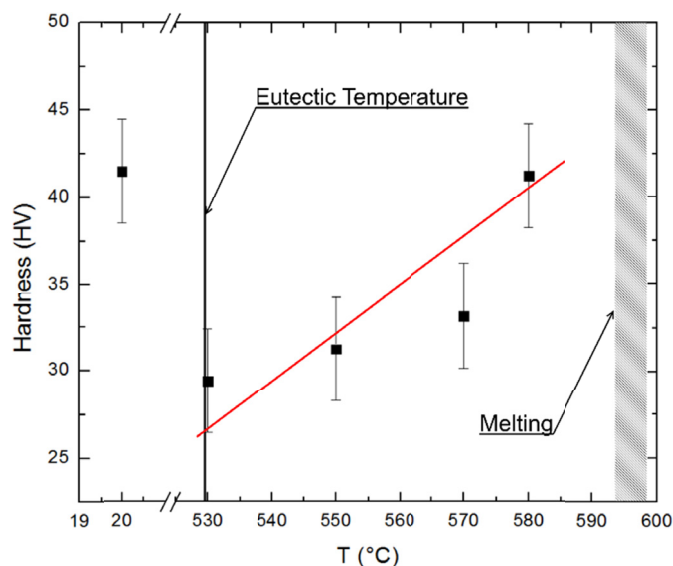


Fig. 4. Temperature dependence of the hardness of the α -Mg matrix phase for various annealing temperatures and the initial as-cast state

Based on all experimental data and the heat-treatment sequence, we can suggest how to increase the ductility in the process of production and to bring a high toughness and creep resistance back to the end product made of EZ33A. The first step would be annealing at 530°C or controlled cooling of the casting mold after holding at 530°C for about 2 h to form the least wetted state of the alloy structure. This would increase the ductility to the maximum value to be obtained in this material. The cooling rate after annealing is not important. It can be optimized to prevent cracking on cooling. The material can then be machined. After a half-finished product achieves the required shape, it can be annealed at 560-570°C for 2 h to form a wetting structure similar to the as-cast structure to be reached without

annealing at 530°C. Finally, the material would restore the initial high toughness and creep resistance.

To show and justify the potential of the suggested heat treatment to improve and control the mechanical properties of the EZ33A alloy, we are going to perform tensile and compressive tests and hardness measurements of the samples to be annealed at various temperatures.

4. Conclusions

Grain boundary wetting was observed in an industrial EZ33A Mg cast alloy. The wetting transition of grain boundaries starts from a eutectic phase transformation at 530°C. At this temperature, 12% of the grain boundaries are completely wetted by a second liquid phase. At about 570°C, the fraction of completely wetted grain boundaries reaches its maximum (85%). Then, the number of completely wetted grain boundaries was found to change weakly until melting.

In addition to wetting, the volume fraction of the second phase and the hardnesses of the phases are different at different annealing temperatures. After annealing at 530°C, the volume fraction of the second phase was shown to be only 4.8%, and the hardness of the matrix α -Mg phase was significantly lower than that in the as-cast state.

Based on the experimental data, we proposed a sequence of heat treatment and mechanical processing to use the advantages of the soft state of the least wetted structures and to restore the initial mechanical properties after machining.

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