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Investigation on the Duration of Action of Mg_3N_2 as a Grain Refiner for AZ80 Alloy

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Abstract: In magnesium alloys with aluminum as an alloying component, zirconium loses its grain refinement effect as a grain refiner. Instead of zirconium, Mg_3N_2 can be used, and promising results have already been obtained. However, the duration of action of Mg_3N_2 has not been elucidated yet. The aim of this work is therefore to determine the grain size of the AZ80 alloy as a function of the duration of action of Mg_3N_2 and thus the economically reasonable duration of use. It was found that the Mg_3N_2 reaches its full effect from 30 min after a complete remelting and does not lose this grain refinement effect even after 90 min. It thus proves to be a stable and reliable grain refiner. A grain size of $146.3 \pm 10.3 \mu\text{m}$ was achieved. Furthermore, a minimum tensile strength of 205 MPa with a break elongation of 5.99% was achieved.

Keywords: AZ80 alloy; grain refinement; Mg_3N_2 ; mechanical properties; thermal analysis; growth restriction factor



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1. Introduction

As lightweight construction is becoming an increasingly important consideration, magnesium alloys are becoming more and more important due to their low specific weight, good machinability and processability, and great recycling potential. Despite these positive aspects, the use of magnesium alloys still lags far behind other structural materials such as aluminum or plastics, which can be mainly attributed to a higher price and, in some cases, a lack of knowledge in processing. The main driving force behind the increased use of magnesium alloys is the automotive industry. Due to the increasingly important environmental aspect, the focus is increasingly on weight savings and the associated lower emissions. For example, as early as the 1930s, castings made of magnesium alloys were used in vehicles such as the VW Beetle, saving about 50 kg.

For engineering applications, magnesium is usually strengthened by alloying; it can be alloyed with other alloying elements such as aluminum, zinc, manganese, zirconium, and rare earth. According to the alloying elements, two types of Mg alloys (Al-containing and non-Al-containing) can be defined. One of the most widely used Mg alloy families is the AZ group (Mg–Al–Zn), which is mainly used in die casting (in particular, high-pressure die casting). On the basis of well-known Hall–Petch strengthening, effective grain refinement and thereby decreasing grain size is of great importance to improve the mechanical properties and the subsequent deformation properties [1–3]. To positively influence the mechanical properties, grain refinement is essential. Generally, grain refinement can be achieved through either inoculation treatment, which is a process of adding, or in situ forming, foreign particles to promote a heterogeneous nucleation rate, or restricting grain growth by controlling the constitutional supercooling, or both [3].

Various grain-refining methods have been developed for Mg-based alloys. For example, the addition of Zr [4] has been improved to be one of the most promising grain refinement methodologies. However, the grain refinement approach with zirconium [4], which is commonly used for non-Al-containing Mg alloys, does not work for this AZ

alloy family due to the formation of an AlZr intermetallic phase, which is ineffective for the grain refinement of Mg alloys [1]. Other grain refinement methodologies (i.e., rapid cooling, melt superheating, carbon inoculation [5–7], the addition of Al-Ti-C [8], B [9], Al-V-B master alloy [10], CaO [11], MgO [12,13], SiC [14], VN [15], Mg_3N_2 [16–18], AlN [19], TiB_2 [20], Ca [21], the application of ultrasonic treatment [22]) have therefore been widely investigated, with a focus on the effect of particles on the grain restriction factor [23–26] and dendritic grain growth [27] as well as phase growth [28,29]. However, rapid cooling may not be a viable option for particular castings, while superheating uses extra energy and increases the oxidation of the melt. Carbon inoculation creates a hazardous work environment. It is well-accepted that the addition of particles and alloying elements is effective for achieving grain refinement.

In particular, the grain refinement approach with Mg_3N_2 was investigated in more detail [16–18]. However, the duration of action of Mg_3N_2 has not been fully elucidated yet. The aim of this work is, therefore, to elucidate at which treatment time a sufficient grain refinement effect of Mg_3N_2 particles is achieved and how its effect behaves as a function of the holding time. In addition, the effect of the holding time on the mechanical properties was also investigated.

2. Materials and Methods

For the test series, the AZ80 alloy with eight percent aluminum and less than one percent zinc was investigated. The magnesium used has a purity of 99.83%, and the aluminum used has a purity of 99.99%. The alloy was designed to contain 11 kg of pure magnesium, and the amounts of the remaining alloying elements were calculated using the required contents, as listed in Table 1. All alloying elements were used as pure materials apart from manganese. Manganese was added in the form of an AlMn10 (wt.%) master alloy.

Table 1. Nominal composition of AZ80 alloy (wt.%).

Element	Si	Al	Mn	Zn	Cu	Mg
	0.1	8	0.12	0.73	0.05	Bal.

To prevent the AZ80 alloy from reacting with the oxygen contained in the air during the melting process, a reactive gas atmosphere was used above the melt. This was ensured by means of a crucible cover with gas protection. The reactive gas used was a mixture of 3% (vol. fraction) sulfur hexafluoride and argon. This protects the bath surface by reacting the magnesium with the fluorine to form MgF_2 . This compound is thermodynamically more stable than MgO and thus protects the melt from oxidation.

After the complete melting of the alloy, the grain refiner (Mg_3N_2 in the form of nanoparticles) was added. For this purpose, the crucible including the cover was lifted out of the furnace and placed on refractory bricks. In order to obtain reference values of the mechanical properties, two Diez samples were cast. It should be noted here that solidification also takes place under an argon atmosphere. The melt was then cooled, with the aim to add the Mg_3N_2 in a semi-solid state to avoid possible floating of the particles. To achieve this, the melt had to be repeatedly stirred mechanically during cooling using a drill with a spiral stirrer. Then, 50 g of Mg_3N_2 , as the grain refiner, was added while stirring continuously in a thixotropic state. Finally, the crucible was lifted back into the furnace and the melt was again superheated to 720 °C.

The influence of the Mg_3N_2 on the grain size and the mechanical properties was investigated. For the purpose of mechanical properties, in addition to the two reference die samples, which were cast before the addition of the Mg_3N_2 , three further samples were cast at intervals of 48, 76, and 94 min after a complete melting of the alloy. A 20 ppi filter was inserted, and the melt was poured in with the aid of a sprue funnel. Once again, an inert gas atmosphere was ensured over the free surface of the melt. After complete cooling,

the specimens were removed from the mold, and the sprue and the feeder volume were separated for mechanical testing. At least three samples were tested for each condition at room temperature by using a standard tensile testing instrument. For the purpose of grain size, standard TP-1 testing (with a cooling rate of about 4 °C/min) was performed. In order to subsequently determine the grain size of the TP-1 samples, all samples had to be cut at a height of 38 mm from the bottom of the TP-1 samples. For this purpose, a holder with the same cone as the specimens was used and the specimens were cut off using a band saw.

The cut specimens were subsequently ground with the aid of the ATM Saphir 350E grinding and polishing machine using grit sizes of 80, 320, and 800 and then polished. When polishing, it should be noted that only water-free polishing and lubricating agents are used. For fine polishing, a “Diamond suspension (oil-based) Mono 3 µm” from ATM was used, together with the corresponding lubricant, as well as “Etosil E”, also from ATM, in combination with ethanol as a lubricant. The polished samples were then etched with a Nital solution consisting of 100 mL ethanol and 3.3 mL 65% HNO₃ for 6 s. The etched samples were examined using the “Zeiss Axio Imager.A1m”. The average grain size was determined from the obtained optical microscopy images using the linear intercept method.

The samples for SEM were mechanically ground and polished in the same way as optical microscopy. Intermetallic phases along grain boundaries were measured using energy-dispersive X-ray spectroscopy (EDS, Oxford, UK) on an SEM JEOL 7200F instrument. In addition, the grain size and the presence of Mg₃N₂ were investigated using electron backscatter diffraction (EBSD) with an acceleration voltage of 20.0 kV and a step size of 1 µm. EBSD data were analyzed using AZtecCrystal 6.0 software.

In order to determine the effect of the addition of 50 g of Mg₃N₂ on the undercooling of primary Mg and eutectic phases, thermal analysis was also performed by using a Quick-cup at 90 min after the addition of Mg₃N₂.

3. Results and Discussions

3.1. Thermal Analysis

Figures 1 and 2 show the thermal analyses of the reference specimen (at the beginning of the test series) and the specimen at 90 min after the addition of Mg₃N₂ (at the end of the test series), respectively. Figure 1b,d is enlarged from Figure 1a,c to highlight the undercooling of primary α-Mg. Similarly, Figure 2b,d is enlarged from Figure 2a,c to highlight the undercooling of eutectic phases. The temperature and its first derivative are also plotted in the graphs. Four peaks (according to the first derivative curves) were observed. Table 2 shows the formation of the individual phases. The phases precipitated in each case are also listed in Table 2. In terms of primary α-Mg, it can be seen that the undercooling to initiate solidification is 47 °C (Figure 1b) without grain refiner. By adding the Mg₃N₂ nanoparticles, this can be reduced to 28 °C (Figure 1d) after only a short period of action (less than 5 s), strongly indicating an effective grain refinement of α-Mg grains. In terms of eutectic phases, it can be seen that the addition of the Mg₃N₂ nanoparticles results in an earlier nucleation of eutectic phases (Figure 2c). The formation of eutectic phases changes from 489 °C (Figure 2b, without Mg₃N₂ nanoparticles) to 548 °C (Figure 2d, with Mg₃N₂ nanoparticles). Furthermore, with the addition of Mg₃N₂ nanoparticles, no undercooling of eutectic phases was observed (decreasing from 1 °C (Figure 2b, without Mg₃N₂ nanoparticles) to 0 °C (Figure 2d, with Mg₃N₂ nanoparticles)), strongly indicating an enhanced nucleation of eutectic phases.

Table 2. The formation of intermetallic phases during solidification.

Nr.	Intermetallic Phases	T [°C]
1	Mg ₂ Si	496
2	Al ₁₂ Mg ₁₇	429
3	AlCuMg	406

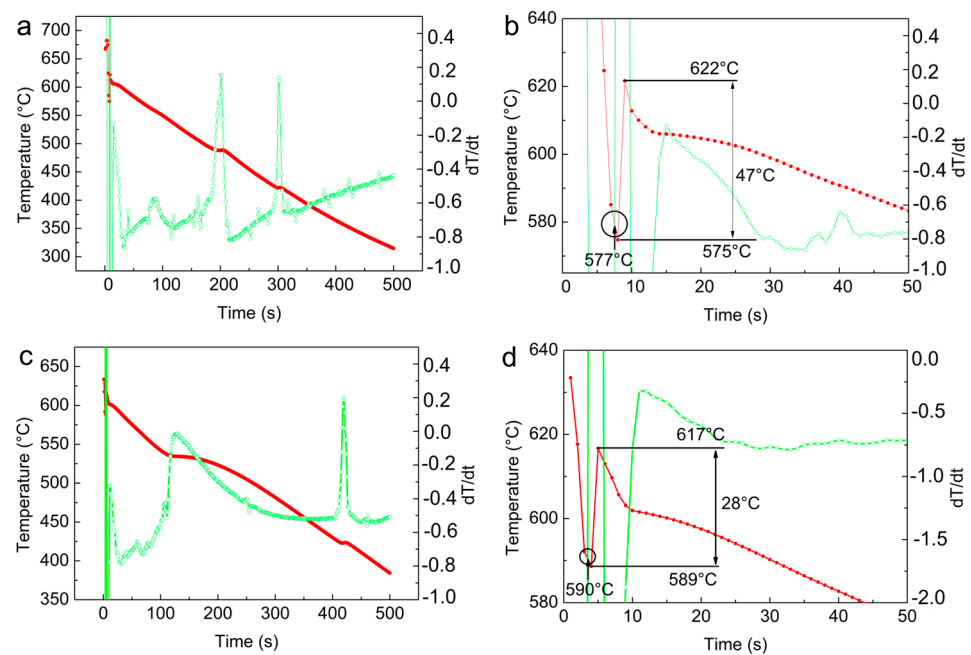


Figure 1. Thermal analysis of the reference specimen (at the beginning of the test series) (a,b) and the specimen at 90 min after the addition of Mg_3N_2 (at the end of the test series) (c,d), respectively. Figure 1b,d is enlarged from Figure 1a,c. The red line is taken from the temperature, while the green line is taken from the first derivative of the temperature.

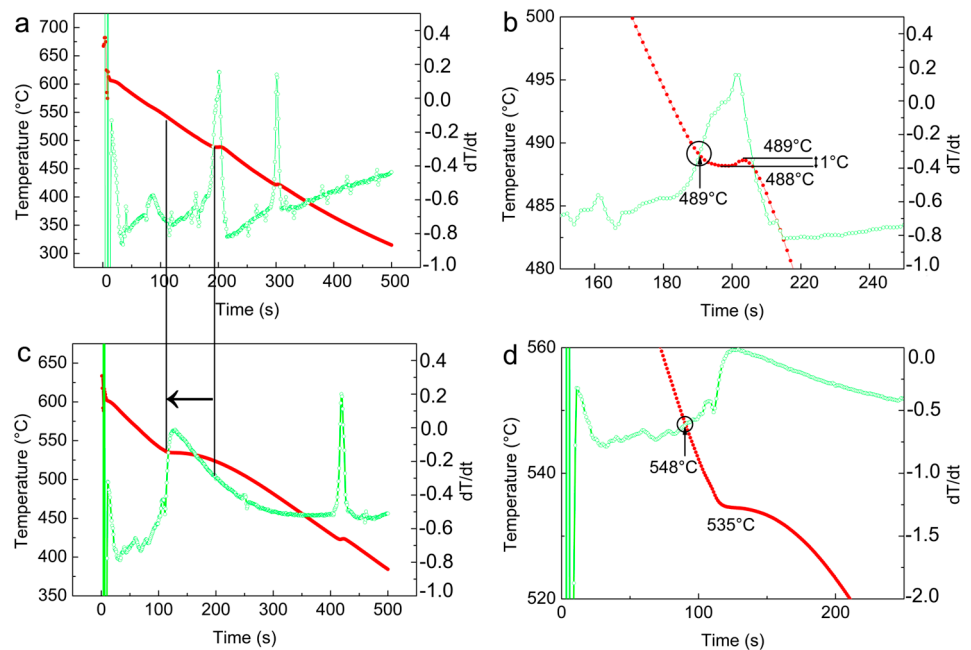


Figure 2. Thermal analysis of the reference specimen (at the beginning of the test series) (a,b) and the specimen at 90 min after the addition of Mg_3N_2 (at the end of the test series) (c,d), respectively. Figure 2b,d is enlarged from Figure 2a,c. The red line is taken from the temperature, while the green line is taken from the first derivative of the temperature.

3.2. Grain Size Measurement by Optical Microscopy

Figure 3 shows the micrographs of the etched TP1 samples with increasing duration of action of Mg_3N_2 . These images were taken at 10× magnification. Figure 4 shows the determined grain size curve as a function of duration of action of Mg_3N_2 . The minimum grain size ($146.3 \pm 10.3 \mu m$) was reached after 60 min, which is less than the measured grain

size (200 μm) with the addition of 1 wt.% Al-1Ti-1C master alloy into AZ31 [8], but higher than the measured grain size (200 μm) with the addition of 0.15 wt.% B into AM50 [9]. It should be noted here that AZ31 and AM50 have a lower Al content than the AZ80 alloy used here. The effect of a higher Al content in the AZ80 alloy on the grain size cannot be ruled out. When compared with the AZ91 alloy, the obtained grain size ($146.3 \pm 10.3 \mu\text{m}$) in the AZ80 alloy is larger than the measured grain size (53 μm) with the addition of 1.0 wt.% MgCO_3 into AZ91D [6], which can be also attributed to the different Al content (solute effect of Al) and different nucleants. It should also be noted here that the melt treated by MgCO_3 should be poured as soon as possible because the inoculation fading is quite quick. The microstructure sensitivity to the diameter of a cast rod is relatively high and the microstructures of the rods with large diameters are quite inhomogeneous [6]. In contrast, no significant fading was observed even up to 90 min in the present investigation. Compared with the measured grain size ($466 \pm 27 \mu\text{m}$) with the addition of 0.6 wt.% Al-3.4V-1B into AZ91 alloy [10], the obtained grain size ($146.3 \pm 10.3 \mu\text{m}$) is much smaller, although the addition level of Mg_3N_2 (0.45 wt.%, (50 g Mg_3N_2 into 11 kg AZ80)) is less than 0.6 wt.% Al-3.4V-1B.

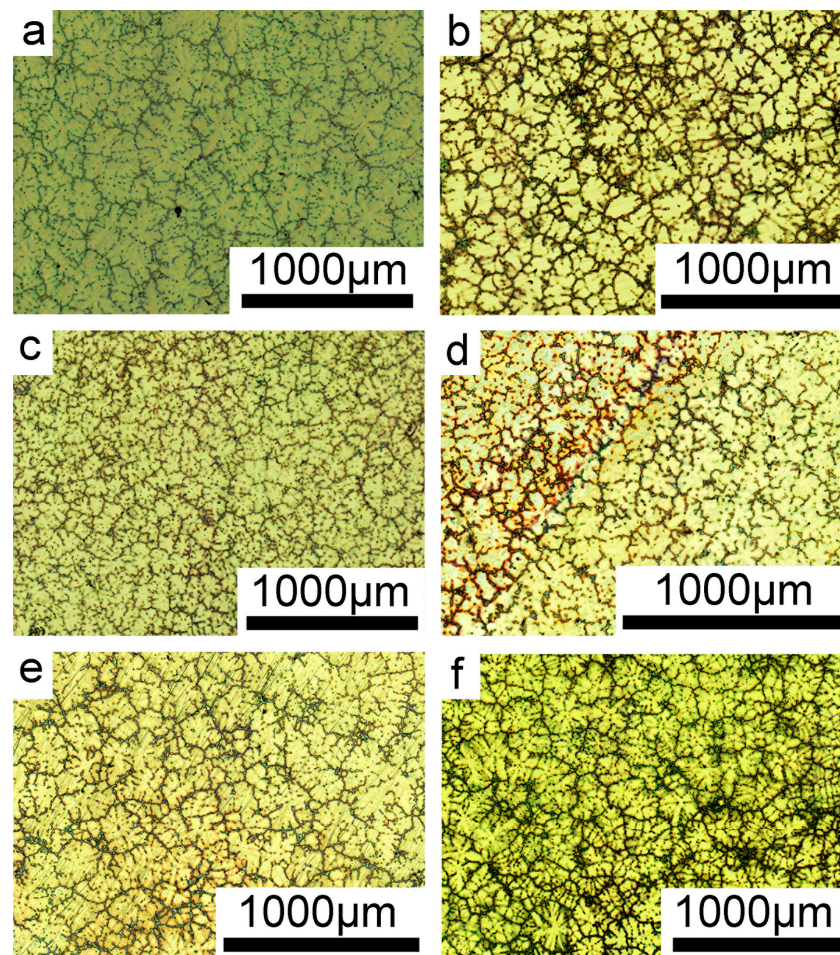


Figure 3. Cont.

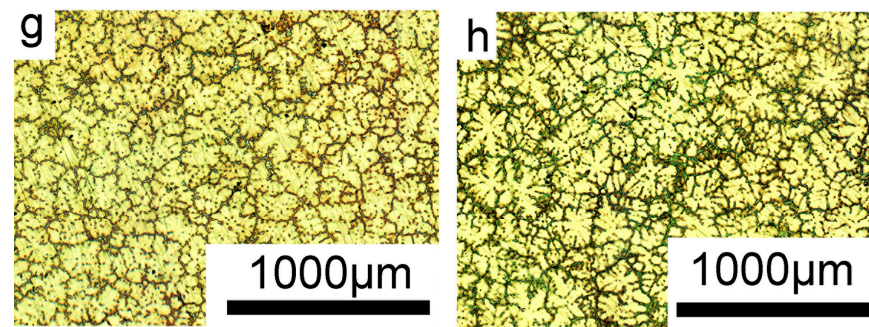


Figure 3. Microstructure evolution using the TP1 test after the addition of Mg_3N_2 as a function of the duration of action: (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, (g) 60 min, and (h) 90 min. All samples were etched and taken in the bright field image mode. The intermetallic phase along grain boundaries is indexed as $\text{Mg}_{17}\text{Al}_{12}$. Mg_3N_2 particles were not observed both within the Mg matrix and along grain boundaries due to the limited resolution of optical microscopy.

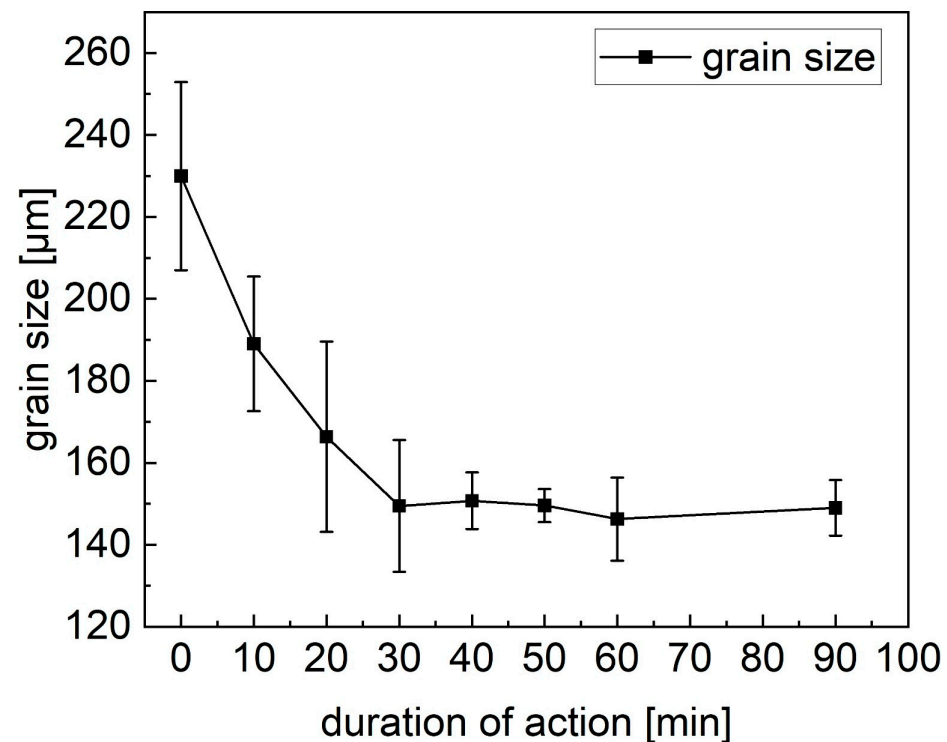


Figure 4. Grain size evolution as a function of duration of action.

3.3. Microstructure Characterization by SEM

Apart from the grain size measurement by using optical microscopy, SEM was also used to index the eutectic phase ($\text{Mg}_{17}\text{Al}_{12}$) and Al_6Mn phases, as shown in Figure 5a,b. More importantly, Mg_3N_2 was also observed together with the eutectic phase ($\text{Mg}_{17}\text{Al}_{12}$), as shown in Figure 5c,d.

The presence of Mg_3N_2 was also further confirmed by EBSD (Figure 6b). According to the EBSD analysis (Figure 6d), the size of Mg_3N_2 is measured to be $4.7 \pm 1.3 \mu\text{m}$, which is an eligible nucleation size according to the free growth mode [24,25]. It strongly indicates that the presence of Mg_3N_2 may have a significant effect on the nucleation of the eutectic phase, as described in Figure 2. It should be noted here that the grain size of primary $\alpha\text{-Mg}$ is only measured in the range from 100 μm to 200 μm . The smaller grains (less than 100 μm) are omitted in order to remove the effect of Mg_3N_2 particles. The measured grain size is about $117.8 \pm 16.1 \mu\text{m}$ (Figure 6c). In addition, it should also be noted here that

the presence of scratches (due to poor sample preparation for EBSD) on the sample has no influence on the grain size measurement.

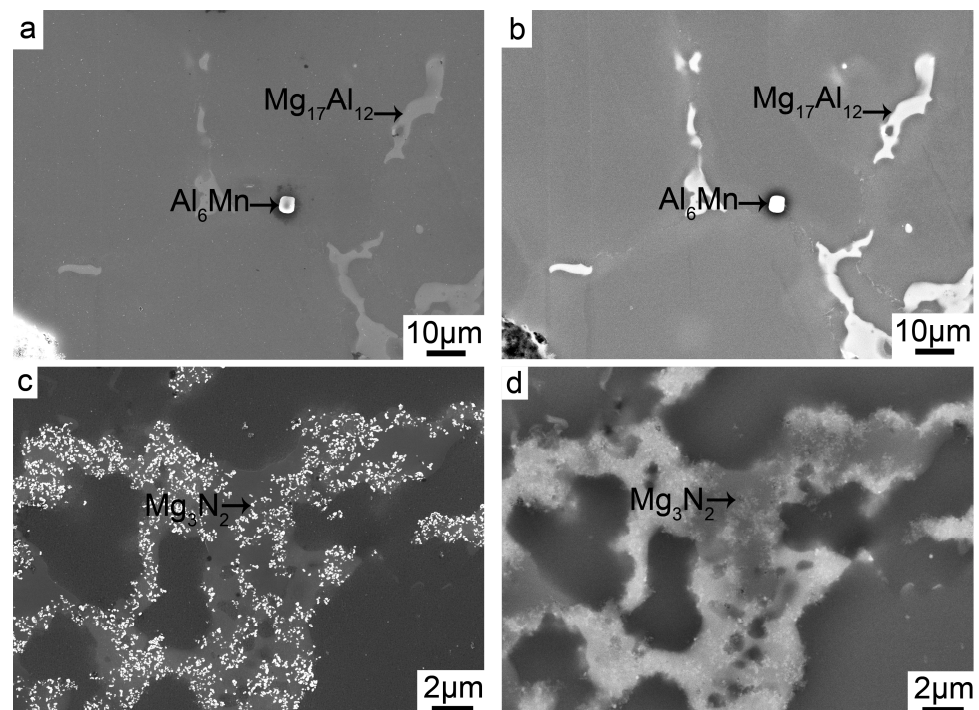


Figure 5. SEM secondary electron (SE) images (a,c) and backscattering (BS) images (b,d) of the sample at 30 min after the addition of the Mg_3N_2 nanoparticles. (a,b) Low magnification images. $Mg_{17}Al_{12}$ and Al_6Mn phases are indexed. (c,d) High magnification images. Mg_3N_2 was observed together with the eutectic phase ($Mg_{17}Al_{12}$).

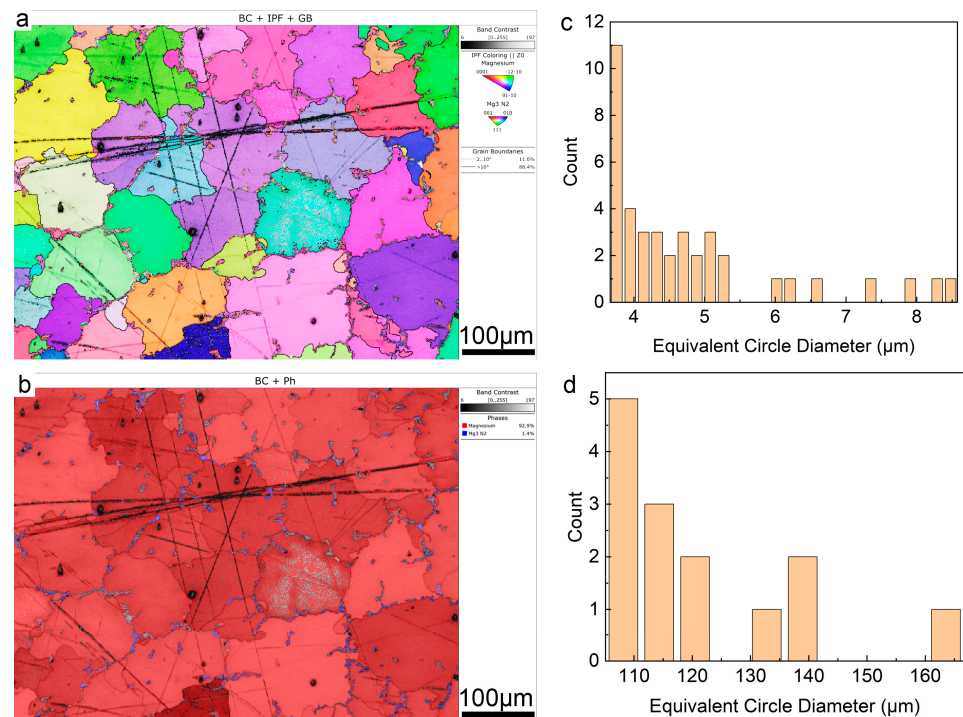


Figure 6. SEM EBSD results. (a) Inverse pole figure (IPF), (b) phase map, (c) size distribution of α -Mg grains, (d) size distribution of Mg_3N_2 particles. Mg_3N_2 was indexed by EBSD (blue in (b)).

3.4. Mechanical Properties

Figure 7 shows the mechanical properties of four samples (0 min, 48 min, 76 min, 94 min). The specimens were tested in terms of tensile strength, yield strength, and elongation at break, as marked in Figure 7. A tensile strength of 205 MPa and a maximum elongation at a break of 5.99% could be achieved after 76 min, which is fully consistent with the fact that the minimum grain size ($146.3 \pm 10.3 \mu\text{m}$) was reached after 60 min (Figures 3 and 4). After 76 min, the tensile strength, yield strength, and elongation at break decrease, as shown in Figure 7d, which can be related to the increased grain size (Figure 4).

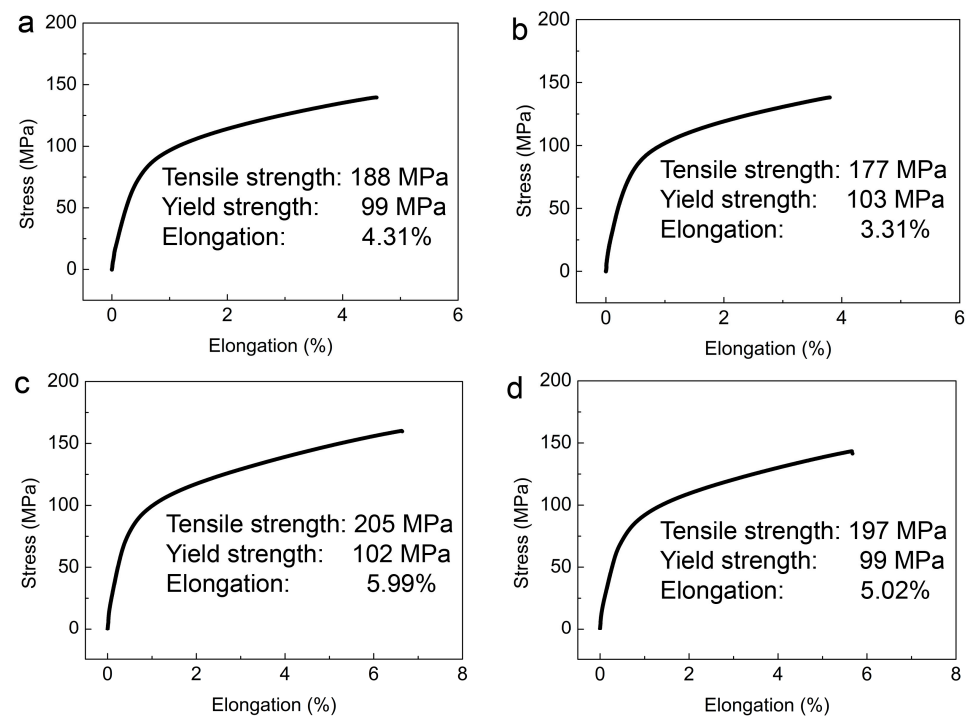


Figure 7. Mechanical properties of four samples (0 min (a), 48 min (b), 76 min (c), 94 min (d)). Tensile strength, yield strength, and elongation at break are marked. A tensile strength of 205 MPa and a maximum elongation at a break of 5.99% could be achieved after 76 min.

Figure 8 shows SEM SE images of the fracture surfaces of four samples (0 min (a,b), 48 min (c,d), 76 min (e,f), 94 min (g,h)). Figure 8b,d,f,h are enlarged from Figure 8a,c,e,g to show more details. Although all samples show ductile fracture surfaces, the addition of Mg_3N_2 is more likely to result in a change in fracture mode. More small dimples were observed in Figure 8c–h compared with Figure 8a,b. A more detailed investigation of the fracture mode is still needed.

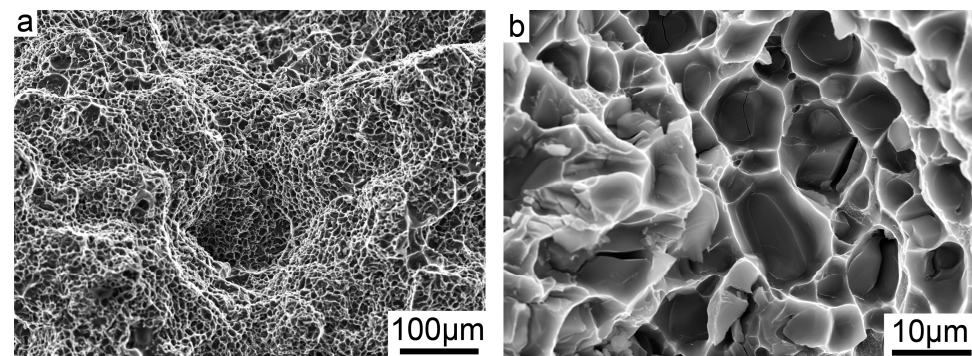


Figure 8. Cont.

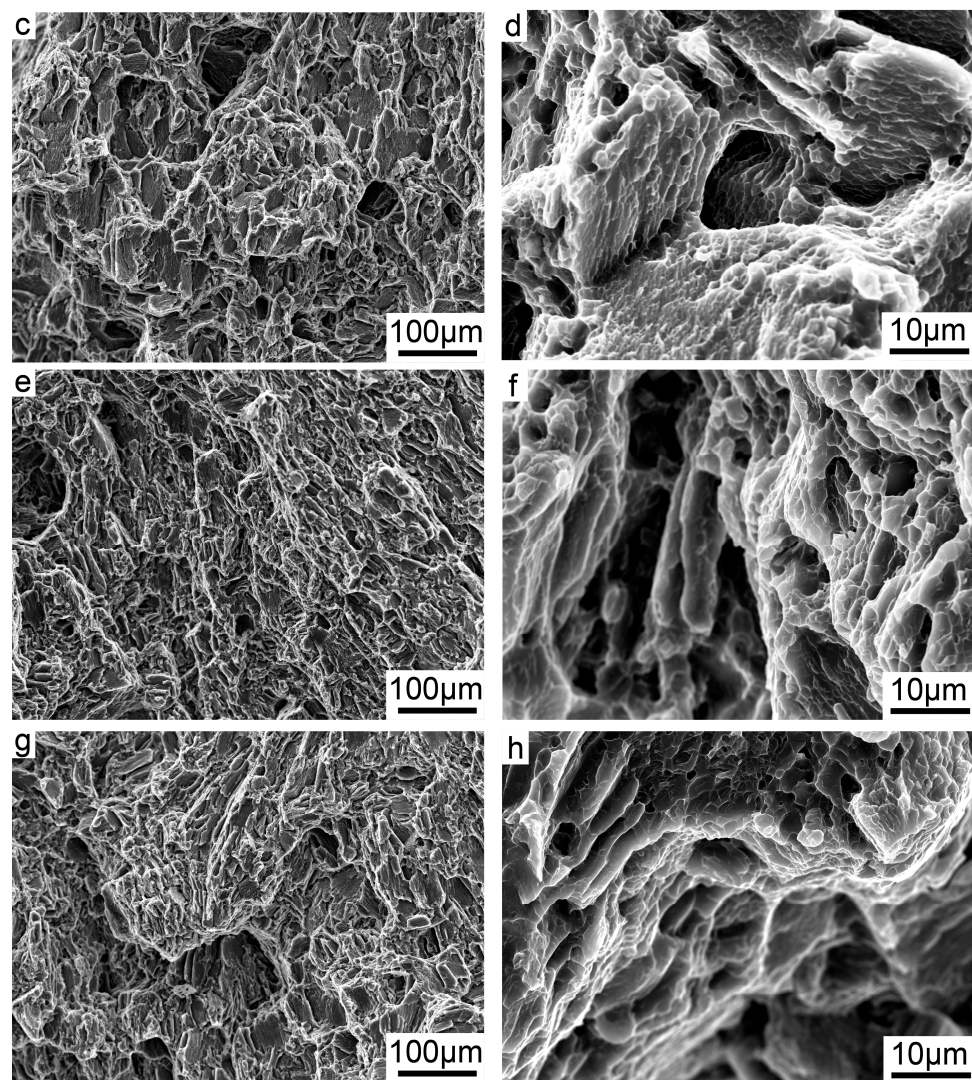


Figure 8. SEM SE images of the fracture surfaces of four samples (0 min (a,b), 48 min (c,d), 76 min (e,f), 94 min (g,h)). (b,d,f,h) are enlarged from (a,c,e,g) to show more details. All samples show a ductile fracture surface.

4. Conclusions

The grain size and mechanical properties of the AZ80 alloy as a function of the duration of action of Mg_3N_2 have been investigated. The main conclusions can be drawn as follows:

1. Mg_3N_2 nanoparticles can be mechanically stirred into the melt in a semi-solid state.
2. The grain size of $146.3 \pm 10.3 \mu m$ could be obtained. Furthermore, the best grain refining effect is achieved at the effective time of 60 min. Beyond this point, no significant change in grain size could be detected. This means that it has reached its full effect currently and no longer loses its effect, which provides sufficient process reliability.
3. The reduction in the grain size does not significantly increase the tensile strength, but the elongation at break could be significantly increased.
4. The undercooling to initiate solidification is $47^\circ C$ without grain refiner. By adding the Mg_3N_2 nanoparticles, this can be reduced to $28^\circ C$ after only a short period of action (less than 5 s). At the end of the test series, no more undercooling is observed, indicating that the grain refiner has worked adequately.

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tion, T.H.; writing—review and editing, J.L.; supervision, E.N. and J.L.; project administration, J.L.; funding acquisition, J.L. All authors have read and agreed to the published version of the manuscript.

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