Research Article

Modification of Magnesium Alloys by Ceramic Particles in Gravity Die Casting

Urs Haßlinger,[1] Christian Hartig,[1] Norbert Hort,[2] and Robert Günther[1]

[1] *Institute of Materials Physics and Technology, Hamburg University of Technology, Eißendorfer Straße 42, 21073 Hamburg, Germany*
[2] *Helmholtz-Zentrum Geesthacht, Magnesium Innovation Centre (MagIC), Max-Planck-Straße 1, 21502 Geesthacht, Germany*

Correspondence should be addressed to Urs Haßlinger; hasslinger@tuhh.de

A critical drawback for the application of magnesium wrought alloys is the limited formability of semifinished products that arises from a strong texture formation during thermomechanical treatment. The ability of second phase particles embedded into the metal matrix to alter this texture evolution is of great interest. Therefore, the fabrication of particle modified magnesium alloys (particle content 0.5–1 wt.-%) by gravity die casting has been studied. Five different types of micron sized ceramic powders (AlN, MgB_2, MgO, SiC, and ZrB_2) have been investigated to identify applicable particles for the modification. Agglomeration of the particles is revealed to be the central problem for the fabrication process. The main factors that influence the agglomerate size are the particle size and the intensity of melt stirring. Concerning handling, chemical stability in the Mg-Al-Zn alloy system, settling and wetting in the melt, and formation of the microstructure in most cases, the investigated powders show satisfying properties. However, SiC is chemically unstable in aluminum containing alloys. The high density of ZrB_2 causes large particles to settle subsequent to stirring resulting in an inhomogeneous distribution of the particles over the cast billet.

1. Introduction

Due to their low density and their high specific strength magnesium wrought alloys reveal great potential for light weight applications in the transportation industry. Nevertheless, magnesium wrought alloys still exhibit a few drawbacks which make their application difficult. One is the limited formability of semifinished products like sheets that arises from a strong texture formation during the thermomechanical treatment. To overcome this drawback a significant part of current research on magnesium wrought alloys aims at designing alloys that show an altered recrystallization behavior. For this purpose those recrystallization mechanisms in magnesium wrought alloys have to be identified and fully understood that can change the texture evolution. A possible recrystallization mechanism that is mainly known from other metals is the so called particle stimulated nucleation (PSN) [1]. Although PSN in magnesium wrought alloys is not fully understood, Laser [2] has shown that basically it works. Typically, the starting material for the thermomechanical treatment is produced by casting and particles are created

by adding alloying elements to the melt that form precipitates. However, precipitates exhibit several disadvantages that complicate the systematic investigation of the influence of particles on texture formation. Precipitates usually change the solid solution content of an alloy and thereby its properties. Depending on the amount of deformation particles should at least have a size of a few microns to act as nucleation sites [1]. However, the size distribution of precipitates is bound to precipitation kinetics and they tend to fragment during deformation. This can be overcome if, instead of precipitate forming elements, chemical stable ceramic particles are added to the melt in a comparable content. Normally, magnesium alloys can be easily cast by gravity die casting. Only a tilting furnace with a standard agitator to homogenize the alloying elements and a protective gas system that prevents the melt from oxidation is required. Therefore, this technique is comparatively inexpensive and highly available which makes it favored also for the fabrication of alloys modified by ceramic particles. The content of ceramic particles in wrought alloys that try to benefit from the influence of the particles on the

texture formation will in general be different than for other applications of ceramic particles like grain refinement or the fabrication of metal matrix composites. Therefore, findings to the latter applications can only be applied to a limited extent. This makes further investigations on the fabrication of magnesium wrought alloys modified by ceramic particles in gravity die casting necessary. One important aspect of these investigations is to deal with processing issues like the addition of the particles to the melt or the homogenization of the particles in the melt by stirring. Another aspect is to identify applicable ceramic particles that reveal sufficient chemical stability and wetting in the melt as well as a good connection to the matrix in the cast material.

1.1. Selection of Ceramic Particles. For the mechanical properties of the particle modified alloys a good connection, that is, a mechanical stable interface, between the particles and the magnesium matrix is important. The mechanical stability of the interface is expected to increase with decreasing interface energy between particle and matrix. Low interface energy between the particle and the matrix is also desirable for grain refinement by heterogeneous nucleation during solidification of the melt. Therefore, an obvious way to determine suitable ceramic particles for the modification of magnesium alloys is to use the knowledge developed to identify appropriate inoculation particles for heterogeneous nucleation. Turnbull and Vonnegut [3] have shown that the misfit of the lattice parameter in close packed planes between nucleus and substrate is a suitable parameter to identify such appropriate particles. They observed grain refinement for a misfit up to ~15 %. This approach has successfully been applied to find potent grain refiners for magnesium alloys [6]. On this basis 5 ceramic phases with a low misfit (see Table 1) have been selected for this study. The interfaces that form between the selected particles and the matrix will in general at most be partial coherent.

2. Experimental Procedure

2.1. Fabrication of the Alloys. For the investigation of the as cast microstructure of the particle modified alloys, in particular for the analysis of the particle distribution, billets of a diameter of about 10 cm and a weight of 4–6 kg (minimal height 30 cm) have been cast using a tilting furnace from Nabertherm (Lilienthal, Germany) with a steel melting crucible. The melt has been protected against oxidation by a protective atmosphere consisting of SF_6 and argon. First the matrix material was molten and heated up to the casting temperature (typically T_L = 988 +/− 15 K (715 +/− 15°C)). As matrix material four different compositions from the well-known Mg-Al-Zn alloy system have been chosen: pure magnesium (Mg), Mg with 1 wt.-% zinc (Z1), Mg with 3 wt.-% aluminum (A3), and Mg with 3 wt.-% aluminum and 1 wt.-% zinc (AZ31). The former three are model alloys which in particular allow for the investigation of the chemical stability of the ceramic particles in different alloy systems. Subsequently, up to two stirrers were inserted into the melt. The agitators (Eurostar power control-visc from IKA, Staufen, Germany) exhibit a maximum power output of about 100 W.

Three different types of impellers shown in Figure 1 have been used in this study (flat blade disc turbine, propeller, and dissolver) to investigate the influence of stirring on the particle distribution in the cast billet. The rotational speed of the stirrers has been adapted depending on the type of impeller in the range of about 150–500 rpm, which for all impellers was in the region of turbulent flow. After the start of stirring the ceramic particles have been added. Due to the protective layer on top of the melt it is not possible to add the particles directly. Therefore, two different methods of adding particles to the melt have been tested as follows.

(i) One is the addition of loose powder wrapped in aluminum foil in the shape of a ball. The balls have been produced manually under argon atmosphere and were stored in argon until the transfer into the melt.

(ii) The other way of adding particles to the melt is the application of a master alloy. The production of master alloy tablets via milling as used for grain refinement has already been described in a previous publication [6]. The particle content in the master alloy usually was 10 vol.-%. The size of the ceramic particles is reduced by the milling process. For example, the size of the AlN particles used in this study (cf. Table 1) is reduced to about $d_{p,50} \approx 5\,\mu m$.

The desired particle content in the cast material was in the range of 0.5–1.0 wt.-% (equals ~0.3 vol.-%). After addition of the preheated aluminum foil balls or master alloy tablets ($T \approx$ 373 K (100°C)) the melt is stirred for typically about 10 min. In order to prevent leftovers from the melt from burning, the stirrers have to be removed before the melt is cast into the preheated steel die ($T \approx$ 473 K (200°C)). Therefore, the time between switching off the stirrers and beginning to cast was at least 30 s. The billets have been air cooled to room temperature with a typical cooling rate of about 1 K/s [7].

2.2. Metallography. The specimens for optical and electron microscopy were sectioned from the cast billets, grinded, and polished. In order to investigate the grain structure via optical microscopy using polarized light (see Figure 6) some homogenized (20 h at T = 673 K (400°C)) specimens were etched by a solution of picric acid similar to that used by Kree et al. [8]. Grain sizes have been determined using the line intercept method on the basis of ASTM E 112-96. The grain sizes given here are the mean value of all completed line segments. To investigate the agglomerate distribution macroscopic images have been made by a stereo microscope (Leica M205 C) with a ring light, which makes the particles appear bright and the matrix appears dark (see Figure 4). Particle and agglomerate sizes have been determined from microscopic images using the particle detection function of the Scandium Software from Olympus. The software is able to identify the particle or agglomerate area by the grey scale contrast to the matrix.

3. Results and Discussion

3.1. Addition of Particles to the Melt. Adding the loose particles to the melt in form of aluminum foil balls proved

TABLE 1: Properties of the selected ceramic particles: misfit of the lattice parameter in closed packed planes calculated according to Turnbull and Vonnegut [3] using the crystallographic data of Villars and Calvert [4], density, and particle size according to manufacturer's specifications.

Material	Misfit [%]	Density [g/cm^3]	Powder		
			Manufacturer	Denotation	Size [μm]
AlN	2.8	3.26	H.C. Starck[1]	Grade A	$d_{p,50} = 7$–11
MgB$_2$	3.9	2.57	H.C. Starck[1]	Grade A	$\bar{d}_p = 2$–5
MgO	7.3	3.58	H.C. Starck[1]	−325 mesh; 98%	$d_p < 44$
α-SiC(6H)	4.0	3.23	ESK[2]	Gruen Mikro F600-D	$d_{p,50} = 9.3$
				Gruen Mikro F1200-D	$d_{p,50} = 3.0$
ZrB$_2$	1.3	6.10	ESK[2]	−400 mesh	$d_p < 37$

[1]H.C. Starck GmbH, Goslar, Germany.
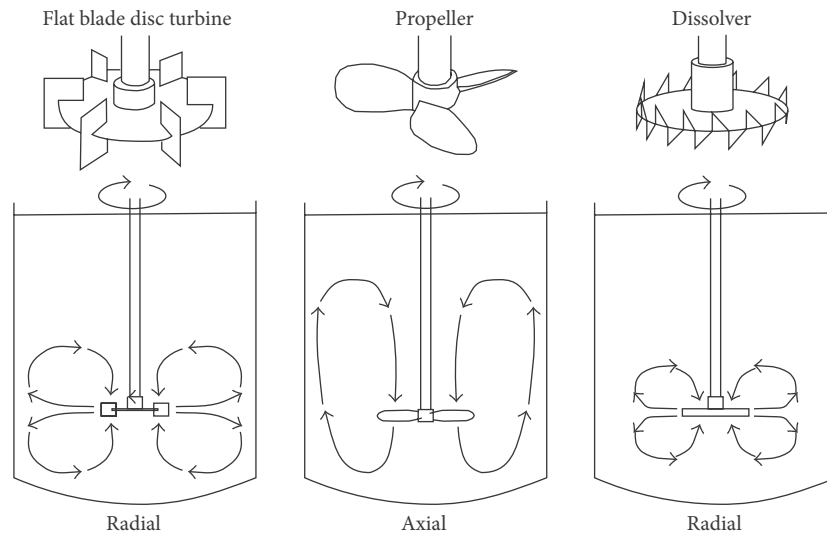[2]ESK CERAMICS GMBH & CO. KG, Kempten, Germany.

FIGURE 1: Shape, flow pattern, and primary direction of flow for the impeller systems used in this study according to [5].

to be difficult to handle. In order to introduce the particles to the melt the ball has to sink. Therefore, it has to have a higher density than the melt. The density of the ball depends on the amount of enclosed gas which depends on the ball's packing density and the porosity of the particles. While the former is difficult to adjust in the manual fabrication process of the balls the latter varies from one ceramic powder to another. For instance, balls of the MgO powder used in this study never sank due the high porosity of the magnesium oxide. Thus it is generally difficult to produce balls manually, which reproducibly sink into the melt. In addition, the balls are exposed to air when transferred into the furnace and thereby can introduce undesired oxygen to the melt.

Due to the low porosity and high density of the tablets a master alloy proved to be a better way of adding the particles to the melt. Nevertheless, in both cases, either addition of the powder in a ball or application of a master alloy, most of the particles form agglomerates when introduced to the melt, as Figure 2 shows. Therefore, the spacing between the particles within the master alloy is not large enough to avoid agglomeration. Longer milling can increase the distance between the particles in the master alloy by distributing the particles more homogeneously. However, it also leads to a stronger size reduction of the particles. The spacing between the particles in the master alloy can also be enlarged by lowering the volume content of the particles. Yet, this rapidly increases the amount of master alloy in the cast alloy making it not insignificant anymore.

3.2. Homogenization of Particles in the Melt. The ceramic powders exhibit a higher density than the magnesium melt. Therefore, they tend to settle within the melt causing a macroscopic inhomogeneous distribution of the particles over the cast billet. This could be avoided for the ceramics with moderate density (AlN, MgB$_2$, MgO, and SiC, cf. Table 1). In contrast a macroscopic homogeneous distribution of the ZrB$_2$ particles could not be achieved, as Figure 3 shows. The inverted X-ray image of an AZ31 cast billet which contains 1 wt.-% ZrB$_2$ particles reveals a region of higher density at the bottom, which can be ascribed to the settling of the ZrB$_2$ particles.

In gravity die casting the particles can settle in the melt during stirring if the stirring is not sufficient. Qian et al. [9] described the settling of particles in an unstirred melt using
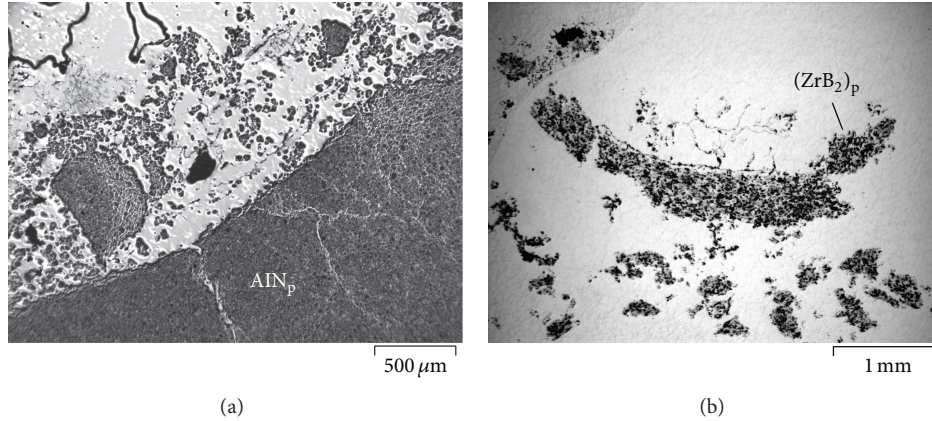
(a)

(b)

FIGURE 2: (a) Agglomerates detach from a ball of AlN particles; (b) agglomerates of ZrB_2 particles originating from a master alloy tablet below the image.

FIGURE 3: Inverted X-ray image of an AZ31 cast billet containing 1 wt.-% ZrB_2 particles revealing a region of higher density at the bottom.

a constant settling velocity that results from equilibrium of gravity, buoyancy, and Stokes drag force for a sphere in laminar flow. This description is also applicable to the particles used in this study. The equilibrium velocity for particles of a few microns is reached in much less than a second. The assumption of laminar flow is sufficiently fulfilled even for 50 μm sized ZrB_2 particles (Reynolds number Re~ 0.4). The Brownian movement of particles in the micrometer regime is negligible. It has to be taken into account for much smaller particles (d_p < 0.1 μm). Stirring is supposed to counteract the settling of the particles. An important parameter for the layout of the stirrer is the settling power of the particles which is the time derivative of the potential energy of the particles and can be calculated using the equilibrium settling velocity. According to [5] the agitator power is supposed to be a multiple of the settling power to counteract settling. This condition is easily fulfilled for the alloy billet shown in Figure 3 since the settling power is only about a few mW. However, the influence of agglomeration on the settling of the particles is difficult to predict exactly. The application of Stokes drag force for a sphere in laminar flow implies that the particles do not interact (infinite dilution). According to Richardson and Zaki [10] the interaction of the laminar flow fields of the particles can lead to a decrease in settling velocity. If the agglomerates act like single particles of larger size, the settling velocity increases. In practice an increase of the settling velocity of about 50% can be observed that can be ascribed to the clustering of particles [11]. But even

if the agglomerates in the alloy that is shown in Figure 3 are assumed to act as 100 μm sized single particles, the settling power is only about 25 mW. Therefore, the stirring system used in this study is even sufficient to counteract the settling of agglomerated particles and the settling visible in Figure 3 is caused by particles which do not settle during but subsequent to stirring.

In order to cast the melt into the die the stirring has to be stopped. As soon as the flow caused by the stirrer ceases, the particles start to settle. Therefore, the time between stopping the stirrer and casting of the melt into the die (typically about 30 s) is critical for the settling of the particles. Within that time, according to the equilibrium settling velocity, 40 μm sized ZrB_2 particles have already settled about 10 cm. Due to their lower density the other investigated ceramics (AlN, MgB_2, MgO, and SiC) settle more than two times slower. In order to achieve a homogeneous distribution of coarse particles with a high density like the ZrB_2 powder used in this study, faster casting techniques, for example, using a melt pump, have to be used.

Figure 4 exemplary shows the agglomerates in three different alloys that have been produced using master alloy tablets. Using a flat blade disc turbine as impeller and fine powder (SiC F1200-D, see Table 1) leads to a relatively large mean agglomerate size of $\overline{d}_{a,ECD}$ = 56 μm (Figure 4(a)). Smaller agglomerate sizes ($\overline{d}_{a,ECD}$ = 31 μm, Figures 4(b) and 4(c)) can be achieved using a propeller together with a dissolver as impellers and coarser powder (AlN, see Table 1). Some of the agglomerates that detach from the master alloy tablet during dissolution (see Figure 2) are much bigger than those in the cast alloy. Therefore, the size of the agglomerates is reduced by the stirring process. In the melt the size of the agglomerates is determined by two factors: the strength of the agglomerates and the forces the stirred melt exerts on the agglomerates. As described by Pietsch [12] the strength of the agglomerates can be associated with the coordination points between neighboring particles, where adhesive forces occur. Assuming that the forces at the coordination points between the different particles are of similar magnitude in the examined systems (Mg, Z1, A3, and AZ31) the agglomerate's

Z1 + 0.5 wt.-% SiC$_p$ (F1200-D)
T_L = 720°C

(a)

AZ31 + 0.5 wt.-% AlN$_p$
T_L = 700°C

(b)

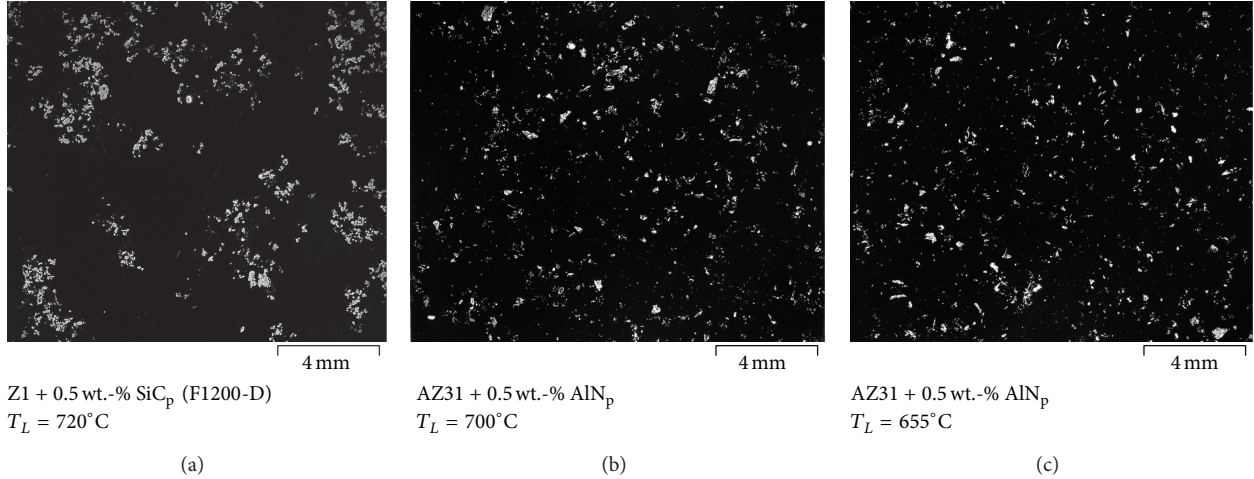AZ31 + 0.5 wt.-% AlN$_p$
T_L = 655°C

(c)

FIGURE 4: Macroscopic images (matrix dark, particles bright) of three-particle-modified-alloy cast at different temperatures T_L using different stirrers ((a) flat blade disc turbine and ((b) and (c)) propeller and dissolver stirrer).

AZ31 + 0.5 wt.-% SiC$_p$ (F600-D)

(a)

Z1 + 1 wt.-% SiC$_p$ (F1200-D)
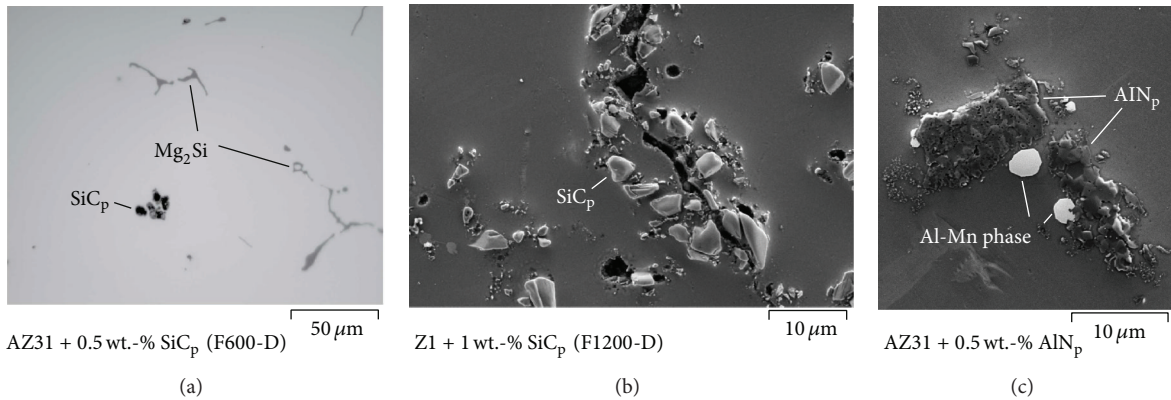
(b)

AZ31 + 0.5 wt.-% AlN$_p$

(c)

FIGURE 5: Images of ceramic particles and precipitates in different alloys.

strength mainly depends on the number of coordination points per volume. The smaller the particles and the wider the size distribution of the particles the higher the number of coordination points per volume and thereby the strength of the agglomerate. The small particles play an important role for the strength of the agglomerate since they fill up the space between larger particles and create a large amount of coordination points [12]. Small particles could be removed from the powder by sieving making the agglomerates mechanically less stable. However, during fabrication of the master alloy new small particles are created by milling. The higher the strength of the agglomerates is the more intense the stirring has to be in order to reduce the size of the agglomerates. The stirring causes a turbulent flow with microvortices. Since the agglomerates are not sheared inside the microvortices they cannot be smaller than the size of the vortices λ. The size of the vortices is decreased with increasing stirring power and with decreasing melt viscosity η_{Mg} ($\lambda \sim \eta_{Mg}^{3/4}$ [5]). The change of the viscosity with temperature according to Qian et al. [9] is too small to cause a significant change in the size of the agglomerates. Therefore, the reduction of the melt temperature from 973 K to 928 K (700°C to 655°C) does not influence the agglomerate size (cf. Figures 4(b) and 4(c)).

In addition to the particle size the smaller agglomerate size in Figures 4(b) and 4(c) compared with Figure 4(a) can be ascribed to the use of two independent agitators, one that primarily counteracts settling and one that reduces the size of the agglomerates. The flat blade disc turbine or the propeller creates a large amount of flow that counteracts the settling of the particles. Due to the low viscosity of the magnesium melt they also cause the melt to rotate. The rotation of the melt can create a funnel at the melt surface that perils the integrity of the protection layer. In addition, the melt's rotation pushes the particles towards the wall of the crucible and reduces the relative velocity between impeller and melt. The latter reduces the power that is introduced into the melt by the agitator. Therefore, the ability of the flat blade disc turbine and the propeller to reduce the agglomerate size turns out to be limited. This can be overcome by using an additional independent stirrer that causes only little flow but creates a large local shear gradient in the melt that breaks the agglomerates apart like the dissolver used in this study. The

AZ31
Average grain size: $\overline{d}_g \approx 380\,\mu$m

(a)

AZ31 + 0.5 wt.-% AlN$_p$
$\overline{d}_g \approx 120\,\mu$m

(b)

AZ31 + 1 wt.-% (ZrB$_2$)$_p$
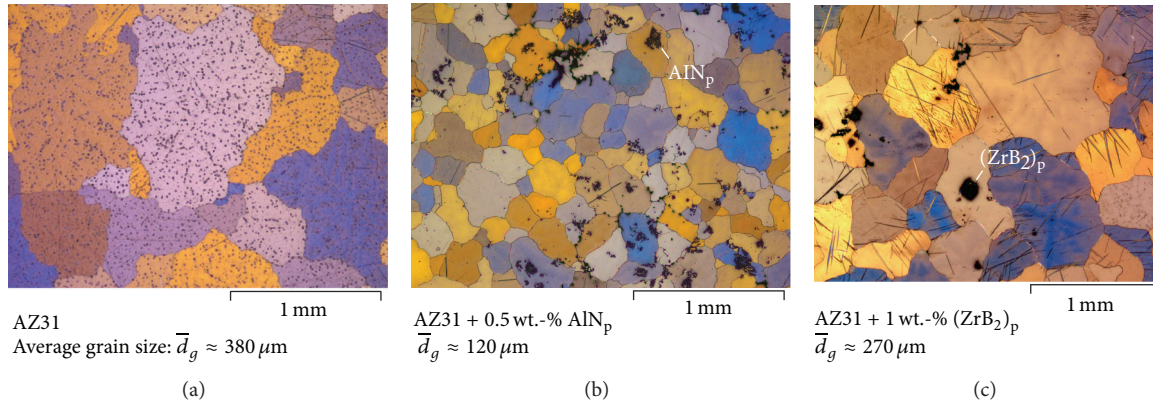$\overline{d}_g \approx 270\,\mu$m

(c)

FIGURE 6: Images (polarized light) of the etched microstructures of different homogenized alloys.

rotational speed of this additional stirrer will in general be much higher than that of the stirrer that counteracts settling. In order to further reduce the agglomerate size more complex setups have to be used. For example, baffles can be installed into the crucible that disturb the rotation of the melt or more elaborate stirring devices like being used for intensive melt shearing by Fan et al. [13] can be applied.

3.3. Chemical Stability of the Particles in the Melt. The only ceramic which proved to be chemical unstable in this study was SiC in the alloy systems containing aluminum (A3 and AZ31). As Figure 5(a) shows, only a small number of SiC particles can be found in the microstructure of these alloys. Instead, a large amount of Mg$_2$Si precipitates occur. Most of the SiC reacts forming Mg$_2$Si and aluminum containing carbides. Due to the metallographic preparation the water soluble carbides are difficult to detect in the microstructure. In contrast, SiC is stable in aluminum free Z1 (see Figure 5(b)). Thermodynamical calculations by Schmid-Fetzer et al. [14] show that SiC will begin to stabilize in AZ31 for an initial SiC content of more than about 4 wt.-% due to the aluminum depletion of the melt. The chemical instability of SiC in the MgAl alloy system is not disadvantageous for the application as grain refiner for cast material, since the aluminum containing carbides that form from the dissolution of SiC can also be suitable for heterogeneous nucleation during solidification [15]. However, our experiments show that the kinetics of the SiC dissolution is too fast to use as a stable particle for the investigation of the particle stimulated nucleation during thermomechanical treatment in the aluminum containing alloys of this study.

Figure 5(c) shows that Al-Mn-phases (likely Al$_8$Mn$_5$) form on the AlN particles in AZ31. Clear evidence for a decomposition of AlN resulting in Al-Mn phases and magnesium nitride was not found. Due to the highly positive reaction enthalpy such a reaction is not likely.

3.4. Formation of the As Cast Microstructure. Most of the particles form agglomerates that are randomly distributed over the microstructure. The agglomerates exhibit a compact outer shape with a low aspect ratio. The particles inside the agglomerates are loosely packed and the space in between

the particles is completely filled by the magnesium matrix. A small number of particles are found as single particles in between the agglomerates. In general, the particles exhibit a good connection to the matrix. In the casting experiments an increased deposition of the selected ceramics in pores or at the melt surface due to poor wetting was not observed. In the simple model alloys (Mg, Z1, and A3) often cracks occur along the agglomerates (see Figure 5(b)) which can be associated with the thermal shrinkage of the billet in solid state during cooling. The thermal contraction of the ceramic particles is negligible compared to that of the matrix. Therefore, the missing contraction of the particles has to be compensated by the matrix. This leads to complex stress states within the agglomerates. In contrast to AZ31 the model alloys do not exhibit the required toughness to compensate those stress states by plastic deformation without the initiation of cracks.

The particle modified alloys often reveal a refined grain structure (see Figures 6(b) and 6(c)) in comparison with an unmodified reference alloy (see Figure 6(a)). This can qualitatively be understood by heterogeneous nucleation during solidification of the melt caused by the ceramic inoculants. The effect of a grain refiner is depending not only on the interfacial energies between the inoculant and the melt or nucleus but also on the size distribution of nucleation sites in the melt, as Gosslar et al. [16] have shown, for example. Therefore, despite agglomeration the AlN powder used in this study shows a grain refinement that is comparable to known potent magnesium grain refiners like SiC and more pronounced than that reported before by Lee [17] for AlN in A1. The inhomogeneous distribution of the ZrB$_2$ particles caused by the settling can lead to a local variation of the grain size, as already has been shown [18].

4. Conclusions

The investigation of the modification of magnesium alloys by ceramic particles in gravity die casting revealed the following results.

(i) All ceramic powders used in this study tend to agglomerate. Most of the particles already pass in

form of agglomerates from the powder or master alloy into the melt. The agglomerate size is reduced by stirring of the melt. The main factors determining the agglomerate size in the cast material are the particle size and the stirring intensity. However, a standard stirring system is normally not able to dissolve the agglomerates completely. For that purpose more elaborate casting techniques have to be used.

(ii) The standard stirring system used in this study is sufficient to counteract the settling of the particles in the melt. Settling of the particles only takes place subsequent to stirring. While this is not critical for the ceramics of this study with moderate density (AlN, MgB_2, MgO, and SiC) the settling of the large ZrB_2 particles leads to an inhomogeneous distribution of the particles over the cast billet.

(iii) All ceramics used in this study except SiC reveal sufficient chemical stability for the content range of about 0.5–1 wt.-% in the investigated alloy systems (Mg, Z1, A3, and AZ31). SiC proved to be unstable in the aluminum containing alloys (A3 and AZ31).

In general the investigated particles exhibit adequate wetting in the melt and a good connection to the matrix in the solid state.

The basic casting techniques used in this study are sufficient to produce magnesium wrought alloys modified by ceramic particles that at least enable the systematic investigation of particle stimulated nucleation (PSN) during thermomechanical treatment as [19] shows. This is an important requirement for using particles in a targeted manner to design magnesium wrought alloys that reveal a weakened texture formation and, thereby, an improved formability.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

References

[1] F. J. Humphreys and M. Hatherly, *Recrystallization and Related Annealing Phenomena*, Elsevier, Amsterdam, The Netherlands, 2nd edition, 2004.

[2] T. Laser, *Einfluss von intermetallischen Phasen in der Magnesiumknetlegierung AZ31 auf Rekristallisation, Texturausbildung und mechanische Eigenschaften [Ph.D. thesis]*, Hamburg University of Technology, Hamburg, Germany, 2008.

[3] D. Turnbull and B. Vonnegut, "Nucleation Catalysis," *Industrial & Engineering Chemistry*, vol. 44, no. 6, pp. 1292–1298, 1952.

[4] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM International, Metals Park, Ohio, USA, 2nd edition, 1991.

[5] P. Hentrich, *Handbook of Mixing Technology*, EKATO GmbH, Schopfheim, Germany, 2000.

[6] R. Günther, T. Ebeling, U. Haßlinger, N. Hort, C. Hartig, and R. Bormann, "All purpose grain refinement of Mg alloys by inoculation based on ceramic particles: simulation and experiments," in *Magnesium: Proceedings of the 8th International Conference on Magnesium Alloys and Their Applications*, K. U. Kainer, Ed., pp. 1268–1275, Wiley-VCH, New York, NY, USA, 2009.

[7] R. Günther, C. Hartig, and R. Bormann, "Grain refinement of AZ31 by $(SiC)_P$: theoretical calculation and experiment," *Acta Materialia*, vol. 54, no. 20, pp. 5591–5597, 2006.

[8] V. Kree, J. Bohlen, D. Letzig, and K. U. Kainer, "The metallographical examination of magnesium alloys," *Practical Metallography*, vol. 41, no. 5, pp. 233–246, 2004.

[9] M. Qian, L. Zheng, D. Graham, M. T. Frost, and D. H. StJohn, "Settling of undissolved zirconium particles in pure magnesium melts," *Journal of Light Metals*, vol. 1, no. 3, pp. 157–165, 2001.

[10] J. F. Richardson and W. N. Zaki, "The sedimentation of a suspension of uniform spheres under conditions of viscous flow," *Chemical Engineering Science*, vol. 3, no. 2, pp. 65–73, 1954.

[11] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics*, Martinus Nijhoff Publishers, The Hague, The Netherlands, 1983.

[12] W. Pietsch, *Agglomeration in Industry*, Wiley-VCH, Weinheim, Germany, 2005.

[13] Z. Fan, Y. B. Zuo, and B. Jiang, in *Proceedings of the 5th International Light Metals Technology Conference*, H. Dieringa, N. Hort, and K. U. Kainer, Eds., vol. 690, pp. 141–144, Materials Science Forum, 2011.

[14] R. Schmid-Fetzer, J. Gröbner, and H. Chen, *TU Clausthal*, Personal Communication, Institute of Metallurgy, Thermochemistry & Microkinetics, 2010.

[15] Y. Huang, K. U. Kainer, and N. Hort, "Mechanism of grain refinement of Mg-Al alloys by SiC inoculation," *Scripta Materialia*, vol. 64, no. 8, pp. 793–796, 2011.

[16] D. Gosslar, R. Günther, U. Hecht, C. Hartig, and R. Bormann, "Grain refinement of TiAl-based alloys: the role of TiB_2 crystallography and growth," *Acta Materialia*, vol. 58, no. 20, pp. 6744–6751, 2010.

[17] Y. C. Lee, *Grain refinement of magnesium [Ph.D. thesis]*, University of Queensland, Brisbane, Australia, 2002.

[18] R. Günther, C. Hartig, N. Hort, and R. Bormann, "On the influence of settling of $(ZrB_2)_P$ inoculants on grain refinement of Mg-alloys: experiment and theoretical calculation," in *Magnesium Technology 2009*, E. A. Nyberg, S. R. Agnew, N. R. Neelameggham, and M. O. Pekguleryuz, Eds., pp. 309–313, TMS, Warrendale, Pa, USA, 2009.

[19] U. Haßlinger, *Einfluss von keramischen Partikeln auf die Texturausbildung von Magnesiumknetlegierungen [Ph.D. thesis]*, Hamburg University of Technology, Hamburg, Germany, 2013.