



Review

A review: Past, present and future of grain refining of magnesium castings

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Abstract

Magnesium is the lightest constructional metal, which makes it an important material for different applications like automotive, transportation, aviation and aerospace. There are several studies about developing properties of existing Mg alloys and introducing new alloy systems to industrial producers. An important way to improve properties of metallic materials is to decrease grain size that results almost in increasing all kind of properties of the material. This review paper aims to summarize the literature about grain refining of magnesium alloys. The text is consisting of three sections, which focused on the (1) grain refining methods used in the past, which are not used today, (2) grain refining methods currently being used in the industry and (3) novel and newly developed methods that may find usage in the industry in future. Before explaining grain refining methods of magnesium alloys a general summary about grain refinement of metals is also provided. © 2019 Published by Elsevier B.V. on behalf of Chongqing University.

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1. Introduction

World annual production of magnesium is increasing continuously year after year [1]. Because of its advantageous properties like low density, good castability and abundant deposits in the earth, magnesium is the third metal after steel and aluminum on the world annual production of metals [2–4]. Especially the usage of magnesium alloys in automotive industry is increasing because of weight reduction to obtain low fuel consumption and low CO₂ emission levels [5]. However limited mechanical properties (i.e. tensile, creep, wear), low ductility and poor corrosion resistance of magnesium alloys prevent these materials to be used in a wide range of applications [6–9]. The research work done in the last decades helped to overcome some of these challenges. For example, different surface treatments such as coatings, surface mechanical attrition treatment, cathodic plasma electrolysis, laser surface alloying/cladding and electrodeposition processes increased wear and corrosion resistance of Mg alloys [10–14]. Mechanical properties can be improved by addition of alloying elements like Ca, Sr, Rare Earths (RE), Sb or Si

[15–17]. Although addition of these alloying elements increases strength of magnesium alloys, the ductility of the material becomes even worse. The only way to improve strength and ductility at the same time in a given cast metal is to reduce grain size of the material. Reducing grain size causes higher hardness, tensile/compressive strength, wear resistance, and ductility [18–21]. Also finer grains cause a more homogeneous microstructure which reduces segregation and pore formation and also increases corrosion resistance [22–26].

Because of the advantages of finer microstructure, grain refinement of magnesium alloys is a subject of interest both for industrial engineers and for academic researchers. Although there are some patents about grain refinement of magnesium alloys going back to the early 1930s some of the grain refinement techniques are still not clearly understood [27]. Most of the early technologies for grain refinement are not being used for decades. Because these technologies are high in cost, often hazardous for environment or causing problems in other properties of the material. However, in this paper these old technologies will be summarized and new technologies that have been developed in the 21st century will be discussed.

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2. Grain refinement in metals and alloys during solidification

The grain refinement in metals and alloys during solidification can be achieved by different methods. The first method is increasing cooling rate during solidification. This procedure is not possible for most of the industrial castings especially ones with bigger wall thicknesses.

The other method is to add alloying elements to the melt. Because these elements usually have limited solubility in solidified grains enrichment of alloying elements occur in the liquid at solid/liquid interface. This enrichment of solute atoms in liquid restricts the growth of nucleated grains. Different alloying elements have different restriction ability [28].

Another method is to add solid particles into the molten alloy or particles form within the melt. These particles act as nucleants and help to increase the number of nucleated grains during solidification. The nucleant particles are also called “grain refiners” or “grain refining agents”, and there are different grain refiners for different metals. The last grain refinement method for metals can be called as agitation. In this method, molten metal is agitated before or during the solidification with mechanical stirring, ultrasonic cavitation or electromagnetic forces.

2.1. Increasing cooling rate

When a homogenous liquid solidifies without any nucleant particles, homogenous nucleation occurs inside the liquid to form solid phase. High driving force is needed for homogenous nucleation so nucleation reaction starts at a higher undercooling (at a lower temperature than the equilibrium melting temperature). On the other hand, if there are potent nucleant particles inside the melt these particles cause heterogeneous nucleation that needs smaller driving force and nucleation starts at a lower undercooling. Transformation from liquid to solid depends on extraction of heat from liquid phase. It is well known that increasing cooling rate during solidification causes a microstructure with finer grains [29]. Increasing heat flow from the molten metal causes a delay in the nucleation process so the nucleation starts at a lower temperature with a higher amount of undercooling. According to Eq. (1) increased undercooling causes a lower critical radius for nucleation. Also high undercooling increases the number of possible nucleants in the liquid metal. As a result, increasing cooling rate causes grain refinement. Although this effect is known for a long time it is not possible to use this phenomenon in most of the industrial castings. Die castings, permanent metal mold castings and castings with small wall thicknesses can be cooled rapidly during solidification. However, it is usually very hard or impossible to increase cooling rate for castings with bigger volumes and thick cross sections.

$$r^* = \frac{2\gamma_{SL}T_m}{\Delta H \Delta T} \quad (1)$$

where;

- r^* : critical nucleus radius
- γ_{SL} : surface free energy
- T_m : equilibrium melting point
- ΔH : latent heat of melting
- ΔT : undercooling [30]

It is interesting to note that a recent study reported that grain coarsening occurred when the cooling rate is increased above a limit value for Mg-1.4 wt.-% CaO, Mg-1.0 wt.-% Zr and Mg-2.8 wt.-% Al alloys. The reason for grain coarsening is explained with the delay of the establishment of the constitutional undercooling zone. When the cooling rate is high the solidification starts at lower temperatures and diffusivity of the solute atoms in solid is low. This situation results with a delay in the formation of undercooling zone which allows more time for the existing grains to grow larger. It was concluded that there is a critical value of cooling rate for every alloy that higher cooling rates than this value causes grain coarsening instead of grain refinement [31].

2.2. Addition of grain refiners

Grain refiners are solid particles added to the molten metal or formed *in situ* in the molten metal. The grain refiners are usually added to the molten metal as master alloys. There are some basic rules for a solid particle to act as a grain refiner and help nucleation of the alloy.

- The particle should be stable in the melt and should not dissolve or react with the elements in the melt [32,33]
- The particle and the nucleating phase should have a small crystallographic mismatch [32,34]
- The wetting angle between the particle and the growing solid should be small [32]
- The difference between densities of the molten metal and the particle is also important. If the particle is too heavy or too light compared to the molten metal this will cause settlement or floatation of particles which will cause an inhomogeneous distribution of grain refiner in the melt.

Also the physical surface properties of the particles are important, usually particles with rough or pitted surfaces are more potent nucleants [32].

These solid particles provide nucleation sites for the alloy during solidification and increase the number of nucleated grains in the material. There are different particles used as grain refiners in magnesium alloys.

2.3. Effect of solute elements

For most alloy systems solubility of solute atoms is lower in the solid state. As a result of this situation when a grain/dendrite grows the excess solute atoms diffuse from solid to the liquid. The concentration of solute atoms is higher in the solid/liquid interface and decreases gradually towards

liquid phase. Enrichment of solute atoms in the interface restricts the growth of the grain/dendrite. Also the liquid in the interface with high amount of dissolved solute atoms can cool to lower temperatures without solidifying because of the change of its chemical composition, this phenomenon is called constitutional undercooling. This undercooling may cause impurities to act as potent nucleants and formation of new grains in the interface.

2.4. Agitation

Relative movement of the liquid metal before (inside the crucible) or after (inside the mold) pouring can cause grain refinement. When molten metal is agitated and forced to move before or during solidification the impurities like oxides, intermetallics, nonmetallic compounds are distributed homogeneously and the solidified dendrite tips break and move into the liquid metal. The increase in the number of solid particles inside the melt causes an increase in the number of possible potential heterogeneous nucleation sites [35–37]. Some agitation methods can increase the wettability of the non-metallic particles in the melt [38]. The main reason for the grain refinement achieved by agitation is a result of increasing number of nucleants in the melt and providing homogenous distribution of these particles.

2.5. Interdependence theory

As explained in the previous sections both solute atoms and solid particles that act as nucleants, have an effect on the grain size of a cast material. Interdependence Theory combines effects of these two factors and also gives a model to predict grain size of the cast material depending on the alloying additions, nucleant particle number density and efficiency of the particles in the molten alloy. The concept of this theory is developed by Easton and StJohn during a study about effect of TiB₂ and solute Ti on the grain size of aluminum alloys [39]. The results of this study showed that solute atoms and nucleant particles have separate effects on the grain size but the effects of these factors can be combined together in an empiric formula;

$$d = a + b/Q \quad (2)$$

where;

$$Q = mC_0(k - 1) \quad (3)$$

In these two equations;

d : final grain size

a : constant

b : constant

Q : growth restriction factor

m : the gradient of the liquidus

C_0 : the alloy composition (wt.%)

k : the partition coefficient (C_s/C_l)

The constants a and b can be determined experimentally for different alloys and different particles. When grain size is

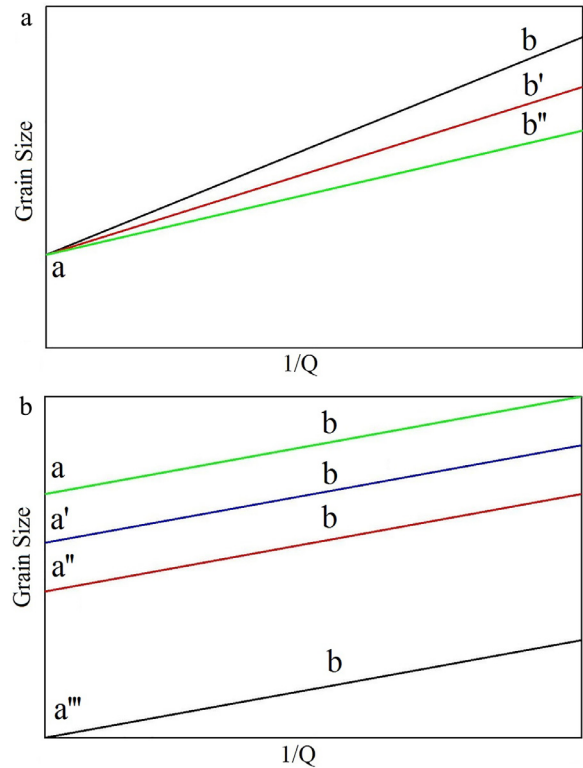


Fig. 1. Effect of nucleant potency (a) and nucleant particle density (b) on the grain size (adapted from [39]).

plotted against $1/Q$ it results with graphs like the schematic ones in Fig. 1. The term a is the intercept of the line of best fit with y -axis and the term b is the slope of the line. The term b is related to the potency of nucleant particles. As seen in the graph on Fig. 1(a) changes in nucleant potency changes the slope of the line but does not affect the intersect point (the value of a). On the other hand the term a changes with increasing number of nucleant particles. Although the slope of the lines are constant the intersections of the lines with y -axis change (Fig. 1(b)). The bottom line shows the achievable minimum grain size with addition of a certain type of nucleant particles [39].

More recently an extended version of Interdependence Theory is published by StJohn et al. [27,40]. With this publication a more detailed formula is developed to predict grain size of a cast material.

$$d_{gs} = \frac{D \cdot z \cdot \Delta T_n}{vQ} + \frac{4, 6 \cdot D}{v} \left(\frac{C_l^* - C_0}{C_l^* \cdot (1 - k)} \right) + x_{sd} \quad (4)$$

In this equation;

d_{gs} : grain size

D : diffusion rate in the liquid (m^2s^{-1})

$z\Delta T_n$: the incremental amount of undercooling required to re-establish ΔT_{n-min} ($^{\circ}C$)

v : the growth velocity (ms^{-1})

C_l^* : the composition of the liquid at the solid-liquid interface (wt.%)

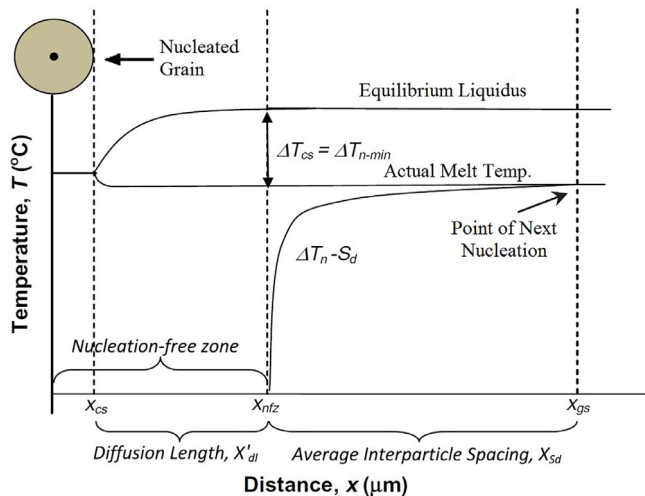


Fig. 2. The schematic representation of Interdependence Theory (adapted from [40]).

The first term of this equation is the amount of growth required to generate enough constitutional supercooling (CS) for nucleation. The second term is the length of diffusion field in front of the growing grain to the point where the critical amount of CS is achieved. x_{sd} is the distance from the point of maximum CS to the location of the most potent nucleant particle [41].

The concept of extended theory can be explained with Fig. 2. When a previously nucleated grain grows to a size of x_{cs} this causes a constitutional supercooling equal to the ΔT_{cs} . Around the growing grain a nucleation-free zone (x_{nfz}) is generated. In this zone the solute gradient suppresses nucleation of new grains. For a new grain to nucleate the CS zone needs to intersect with the nucleant particle spacing – nucleation undercooling curve ($\Delta T_n - S_d$ curve). This curve shows the change of required undercooling depending on the nucleant particle size. Which means when the undercooling around a nucleant particle is high enough the nucleation occurs. With each nucleated grain this sequence repeats. Every nucleated grain creates a nucleation-free zone until nucleation on the next suitable particle occurs [40,42]. The total distance from one nucleated particle to other nucleation event gives the predicted grain size of the material (x_{gs}). Recently the study of Prasad et al. showed a good relationship between numerical model to calculate nucleation free zone and interdependence theory [43].

3. Grain refinement of magnesium alloys

3.1. Past

In this section, some old grain refining methods which are not used for years will be explained. This is necessary for both to understand new techniques and the evolution of grain refinement in Mg alloys over the years.

3.1.1. Superheating

Heating magnesium alloy melts above usual pouring temperatures (150 to 300 °C above liquidus temperature) may cause grain refinement in the cast products [44]. This process is known as superheating, after holding the melt at a higher temperature for a certain time; the melt is rapidly cooled to pouring temperature and cast immediately. Grain refining with superheating is highly affected by the chemical composition of the alloy and the process parameters. Mg alloys containing less than 1% Al cannot be grain refined by this process. Also existence of Mn and Fe promotes the grain refining effect. However there is a critical limit for Mn, excess Mn (>1%) inhibits grain refining process. Ti, Zr and Be also reported as inhibiting elements for superheating process. Depending on the alloy composition, superheating temperature and time may show differences. For example, alloys containing higher percent of aluminum need less holding time at the super heating temperature. For all alloys after a certain time increasing holding time or repeating the superheating process does not have any effect on the grain size. Cooling the melt to the pouring temperature rapidly and pouring immediately have critical importance for obtaining grain refining effect. Slow cooling to pouring temperature or waiting at pouring temperature for a long time causes grain refinement effect to fade. Although superheating process is known for a long time the mechanism of grain refinement is still not clearly understood. There are some hypotheses to explain this effect:

- The grain refinement can be result of the magnesium oxide, aluminum oxide or other nonmetallic inclusions in the melt. Superheating can cause an increase in the amount of the oxide particles in the melt and can increase the number of nucleant particles. There are some limitations about oxide theory because the potential of the oxides as a nucleant is not known. Superheating process provides grain refinement under vacuum atmosphere, where no oxides can be produced. Addition of oxides of aluminum or magnesium does not provide grain refinement. Also the effect of the Mn and Fe in the alloy cannot be explained by oxide theory [3].
- The second hypothesis proposes nucleation on Al-Mn-Fe intermetallics which precipitate from the melt during cooling to pouring temperature [45,46]. This theory is supported by the data that increasing Al in the melt decreases solubility of Mn and Fe, which means increasing Al in the alloy will cause more Al-Mn-Fe precipitates in the melt [3]. However edge-to-edge matching model showed that Al-Mn-Fe compounds namely $Al_8(Mn,Fe)_5$ has a low potential as a nucleant in magnesium alloys [47].
- Another explanation for superheating process is nucleation on Al_4C_3 particles. Superheating causes C diffusion from the steel crucibles and Al_4C_3 particles form inside the melt [45,48]. There are a lot of studies showing Al_4C_3 as a grain refiner which will be discussed in the Carbon Inoculation section of the present paper. But there is no experimental data proving Al_4C_3 formation during superheating process.

- One other hypothesis about superheating process is called temperature-solubility theory. This theory proposes dissolution of the coarse particles in the melt at the superheating temperature and reprecipitating during cooling to pouring temperature. Reprecipitation causes a decrease in the size of precipitates and an increase in the number of precipitates that act as nucleants [48,49].
- Lately Cao et al. proposed a duplex nucleation theory with a negative effect. They assume Al_4C_3 particles exist in commercially and high purity Mg-Al alloys. Fe and Mn elements exist in all commercially pure Mg-Al alloys. According to the new theory Fe and/or Mn interfere with existing Al_4C_3 particles and form a layer on these particles and suppress their grain refining effect. The authors also explain native grain refining in Mg-Al alloys with this hypothesis. When the melt is superheated these layers are dissolved into the melt and when the melt is cooled to pouring temperature and poured immediately these layers cannot find time to form on the nucleant particles. Clean Al_4C_3 particles can act as nucleants and decrease the grain size of the material [50]. It is also shown by Tamura et al. that superheating does not change grain size significantly if the alloy is free of Fe and/or Mn impurities. If Fe and/or Mn impurities exist in the alloy superheating refines the grains because the grain size of the material without superheating is coarser than the high purity alloy [51].
- The efficiency of superheating also might be explained by the very prominent growth restriction factor of Fe itself. Even if the solubility of Fe in molten Mg is low, up to 150–170 ppm can be picked up at elevated temperatures used for superheating. This could be enough to form heterogeneous nucleation sites. With decreasing temperature rapidly, there are enough sites for newly formed grains. Also the fading effect could be explained because the level of Fe drops at slow cooling to casting temperature.

Because of increased power consumption, reduced crucible and furnace lives superheating method cannot find place in industrial applications.

3.1.2. Native grain refinement

It is known since Nelson reported that high purity Mg-Al alloys have finer grain size [52]. This effect is called native grain refinement and only occurs in binary Mg-Al alloys. The reason for native grain refinement is still unclear but it is attributed to the Al_4C_3 particles that exist in high purity and commercial purity Mg-Al alloys [53]. Fig. 3 shows effect of the purity of used magnesium source on the grain size of Mg-Al and Mg-Zn alloys. As can be seen from the graphs increasing purity of the used magnesium causes refinement in Mg-Al alloys but results with coarser grains in Mg-Zn alloys. Tamura et al. reported when small amounts of Fe, Mn, Be and Zr is added to high purity Mg-Al alloys grain size increases. It was believed that the impurity elements have a higher affinity to carbon and form some carbide particles with low grain refining potential in the melt [54]. Some Mg,

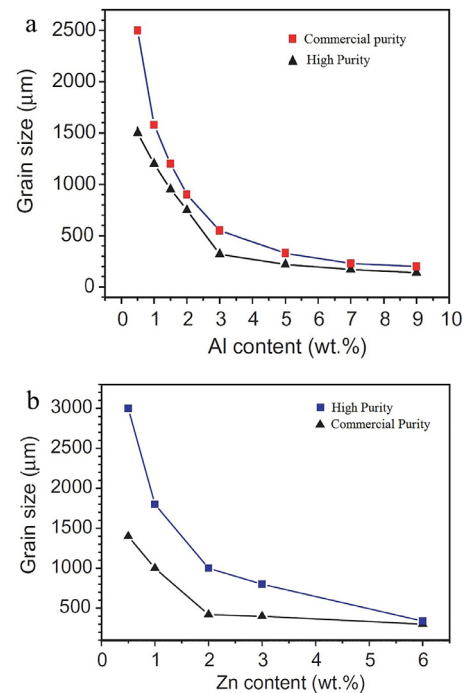


Fig. 3. Dependence of grain size on source magnesium purity of Mg-Al and Mg-Zn alloys (adapted from [53]).

Al, C and O containing particles was also reported by Tamura and coworkers in high purity Mg-Al alloys. Cao et al. also reported no native grain refining effect for both Mg-Ca and Mg-Zn alloys, and attributed native grain refinement of high purity Mg-Al alloys to heterogeneous nucleation on Al_4C_3 particles, however source and formation of the Al_4C_3 phase was not explained [53]. It is usually not possible to use high purity raw materials for castings because of their higher cost, so this grain refining method cannot be used commercially.

3.1.3. Elfinal process (FeCl_3 addition)

Addition of anhydrous FeCl_3 to molten magnesium was first realized in Germany at the end of World War II [55]. The addition was made based on the hypothesis that iron particles could act as nucleants for magnesium grains. Emley proposed addition of FeCl_3 to the melt causes formation of HCl fumes, which attack to steel crucibles and free some carbon into the melt [56]. Cao et al. used Al_2TiO_5 crucibles for melting Mg-3Al and Mg-9Al alloys with different FeCl_3 additions. Addition of FeCl_3 for both alloys melted in carbon free crucibles caused grain refinement, and the hypothesis of Emley was ruled out [57]. Iron removing elements such as Zr and Be inhibits Elfinal process [56]. Although FeCl_3 is an efficient grain refiner for some magnesium alloys, Fe has a detrimental effect on corrosion resistance of magnesium alloys [58–61] and release of Cl or HCl fumes during process causes environmental and health risks. Because of these disadvantages Elfinal process cannot find application in industrial castings.

3.2. Presence

There are some effective grain refinement methods which may have been discovered decades ago but are still useful. The methods currently being used in the magnesium casting industry will be summarized in this section.

3.2.1. Carbon inoculation

Introducing carbon to molten magnesium can reduce the grain size. Grain refinement of magnesium alloys with carbon addition provides lower process temperatures and grain refinement effect fades very slowly after elongated waiting times before pouring [62]. The grain refinement of Mg-Al based alloys were known for almost 75 years, but the mechanism of grain refinement with carbon addition is not clearly understood [56]. Carbon inoculation is only efficient in magnesium alloys with aluminum addition (usually > 2% Al) [54,63,64]. Existence of Be, Zr, Ti and Rare Earth (RE) elements has a negative effect on the grain refinement with carbon inoculation [56]. Carbon can be introduced into the melt in different forms such as graphite particles, master alloys containing C, paraffin wax, carbonaceous gases (CH₄, CO...etc.) or organic compounds [56,65–69]. It was believed that Al₄C₃ is the nucleant phase because carbon inoculation does not reduce the grain size of Al-free magnesium alloys [65]. But Yano and coworkers found that the nucleant is composed of Al, C and O and concluded that the particles have a chemical composition of Al₂CO [70]. Activity calculations showed that formation of Al₄C₃ is more favorable than formation of Al₂CO in magnesium alloys and formation of Al₂CO is impossible for alloys contain less than 10wt.-% Al [71]. Lu et al. suggested that the Al₂CO particles found on the microstructures were a result of the chemical reaction of Al₄C₃ with water during sample preparation [72]. While Zhang et al. showed that Al₂CO has a higher potential for grain refinement than the Al₄C₃ based on the edge to edge matching model [47], experimental work by Kim and friends showed that Al₈Mn₅ is the responsible compound for grain refining. They showed C inoculation has almost no grain refining effect on an AZ91 alloy without Mn. So they proposed a duplex nucleation theory and the nucleation sequence is explained as: Al₄C₃ forms directly after addition of C into the melt, Al₈Mn₅ layer forms on the surface of aluminum carbide, α-Mg grains nucleate on the Al₈Mn₅ phase [73]. On the other hand another duplex nucleation mechanism proposed by Han et al. suggested that nucleation sites were Al₄C₃ coated particles of Al_{0.89}Mn_{1.11} in C-treated AZ31 and Al₄C₃ coated Al₈Mn₅ particles in C-treated AZ63 alloys [74]. Co-clusters of Al₈Mn₅ and Al₄C₃ particles inside the α-Mg grains in an AZ91 alloy grain refined by Al-3C master alloy was also reported by another research [75]. Liu et al. also showed positive effect of Mn on grain refining with C inoculation [76]. It is also reported by Pan et al. and Du et al. that iron can increase the efficiency of carbon inoculation [77, 78]. On the other hand the research work of Wang and friends reports combined addition of Fe and Mn to Mg-3Al causes a poisoning effect on carbon inoculation. The poisoning effect

was proposed to be due to the formation of Al-C-O-Mn-Fe-rich intermetallic compounds. These compounds are not suitable nucleating substrates for α-Mg grains and cause grain coarsening [79].

The work of Jin et al. suggested that grain refinement with C addition is a result of growth restricting factor (GRF) and has nothing to do with heterogeneous nucleation on Al₄C₃ or Al₂CO particles [63,71]. Qian and coworker disagreed with this proposal. The solubility of C atoms in molten magnesium is around 20ppm. Most of the commercial Mg alloys contain this amount of C and no grain refinement effect has been reported [64]. There are also some other studies about grain refining of magnesium alloys with carbide additions. Guang et al. showed grain refinement effect on AZ31 alloy with addition of Al₄C₃ through a powder metallurgical Al-Al₄C₃ grain refiner [80]. Suresh and coworkers added charcoal as carbon source to AZ91 alloy and reported a reduction in the grain size from 100 μm to 30 μm in the as cast state [81]. It was reported by Nimityongskul et al. that addition of Al₄C₃ particles reduces grain size of AM60B and pure Mg whereas no grain refining effect is obtained in Mg-6% Al alloy. The mechanism of grain refining in AM60B alloy was duplex nucleation of α-Mg grains on polygonal Al₈Mn₅ phase nucleated on Al₄C₃ particles. For pure Mg it was reported that Al₄C₃ is the nucleant phase [82]. Wang et al. reported grain refinement of two Al-bearing Mg alloys with addition of magnesium carbonate (MgCO₃) and hafnium carbide (HfC). MgO and Al₄C₃ were the nucleants for MgCO₃ addition whereas Al₄C₃ was the only nucleating phase for HfC addition [83,84]. Recently it was reported by Chen et al. that the agglomeration of Al₄C₃ particles in the solidification front also restricts grain growth [85]. In another study Ding and Liu reported effective addition of carbon to Mg melt using Ni-C alloys. Unfortunately, there were no results about the effect of Ni on the corrosion behavior of the material [69]. A more recent study by Han and coworkers used Focused Ion Beam for machining samples for EBSD analysis. By using this method the samples were protected from pollution and hydrolysis. Existence of Al₄C₃ phase was confirmed inside the grains by EBSD phase mapping and patterns. It is also concluded that the nucleant Al₄C₃ phases usually consist of particle clusters rather than an individual particle [75].

3.2.2. SiC addition

Recently a lot of experimental studies have been conducted on the grain refinement of magnesium alloys with SiC addition. The refinement effect of SiC addition on Mg-3Al alloy can be seen on Fig. 4. Although SiC particles have a different crystal structure (cubic) than Mg (hexagonal close packed), they have a relatively low disregistry on close packed planes and directions [86]. Easton et al. reported addition of SiC to Mg-Al alloys with different Al contents reduced the grain size of the alloys [87], Günther et al. and Shen et al. showed a similar effect on AZ31 alloy [88,89]. There are different explanations to the grain refinement mechanism of SiC addition. The first explanation is formation of Al₄C₃

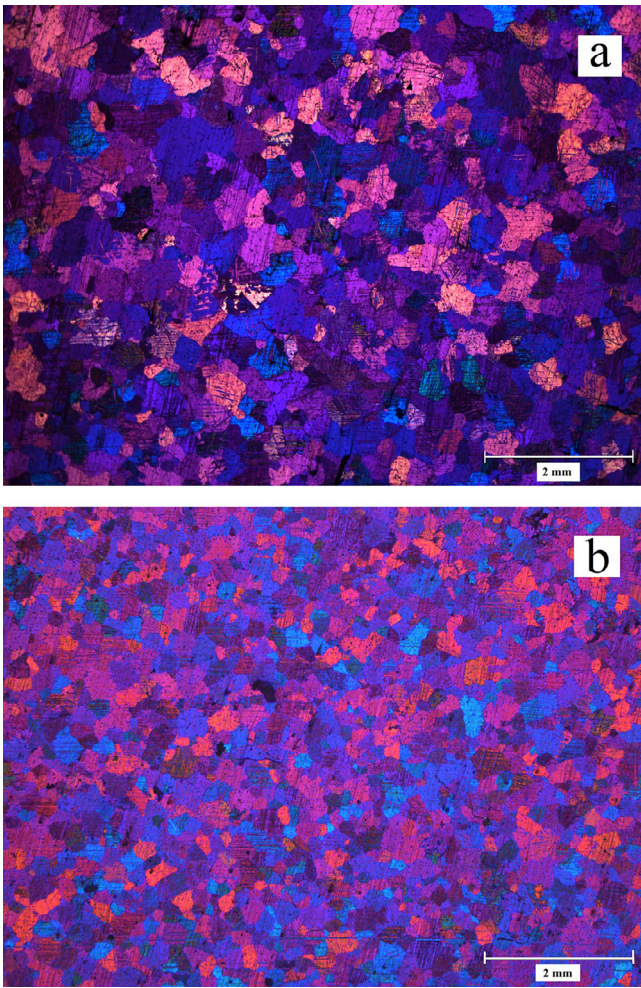
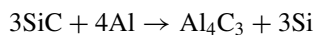
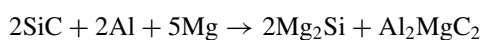


Fig. 4. Microstructure of Mg-3Al alloy (a) without SiC addition and (b) with 0.4 wt.-% SiC addition.

according to the



reaction [87,90,91]. If this hypothesis is true the grain refinement mechanisms of C inoculation and SiC addition are the same. The other theory is nucleation of primary magnesium phase on the SiC particles. Which means SiC particles can act as nucleants in magnesium alloys [92]. It was reported by Cai et al. that the discrepancy between magnesium phase and SiC particles is 2.3% while their crystallographic orientation relationship is $(10\bar{1}0)_{\text{Mg}} // (0001)_{\text{SiC}}$. However, SiC particles are generally polycrystalline. The crystallographic planes constituting their surfaces may not always be suitably oriented for nucleation of Mg phase [93]. Recently Yang et al. reported orientation relationship between α -SiC 6H and α -Mg using edge to edge model and EBSD analysis. It was concluded that α -SiC 6H particles are effective nucleants for α -Mg grains [94]. The last theory suggests that after addition of SiC to the melt ternary Al_2MgC_2 phase forms according to the



reaction and acts as heterogeneous nucleation sites [95–97]. More research is needed to clarify grain refining mechanism of SiC addition.

3.2.3. Zirconium addition

Zirconium is the most common grain refiner for Mg alloys that contain impurity level or no Al, Mn, Si, Fe, Sn, Ni, Co and Sb [2,48,98]. Zirconium forms stable compounds with these elements and cannot act as nucleant anymore. It has same crystal structure as Mg (hexagonal close packed) and the lattice parameters of Zr ($a=0.323$ nm and $c=0.514$ nm) are very close to those of Mg ($a=0.320$ nm and $c=0.520$ nm) [99]. The dramatic change in the grain size of commercially pure magnesium with Zr addition can be seen on Fig. 5. The Zr rich core structures in Mg-Zr alloys has been shown by Qian et al. as a proof of high grain refining potential of Zr [100]. The Zr particles with size between 1–5 μm act as active nucleants during solidification [41,101]. Zr rich corner of Mg-Zr phase diagram shows a peritectic reaction at 0.443 wt.-% Zr [101]. When the Zr content in the alloy is lower than this limit all the zirconium is dissolved. If the Zr content in the alloy is higher Zr rich particles exists in the alloy. Usually minimum added Zr is around 1% to ensure the existence of enough number density of the particles in the melt [102]. Size distribution of the Zr particles in the master alloy affects efficiency of the grain refiner. It is reported that active nucleant particles in Zr grain refined pure magnesium were smaller than 5 μm whereas particles greater than 5 μm were found to be inactive [103]. It was shown that grain refiners with higher number density of Zr particles between 1–5 μm are more effective grain refiners [104]. Except as a nucleant Zr has a high growth restricting factor (GRF), which means the solute Zr prevents growing of existing grains and creates some time for new grains to nucleate. This phenomenon will be discussed in another section of the present article.

There are some disadvantages of Zr, first of all producing Zr containing master alloys are expensive and cause an increase in the price of the final product. Also an excess of zirconium needs to be introduced in order to achieve the full zirconium content for optimum grain refinement which increases price more [105]. Steel vessels are usually used for melting magnesium alloys. The diffusion of iron from vessel to the melt causes a dramatic decrease in the grain refinement effect of Zr. Iron forms stable intermetallics with Zr and Zr cannot act as a nucleant anymore. Density of Zr is much higher than the density of Mg. If the molten metal is kept still for a long time before pouring this will cause settlement of the Zr particles in the bottom of the crucible and grain refinement effect will be faded [106,107]. If the melt is re-stirred before casting the homogeneous distribution of Zr particles can be obtained and grain refinement can occur. This situation was explained by Qian and coworkers as can be seen on Fig. 6 [108]. Another study by Qian et al. shows effects of soluble and insoluble Zr contents on the grain size of Mg alloys. According to this study the major effect of grain refinement comes from soluble Zr but insoluble Zr as undissolved Zr particles may contribute to

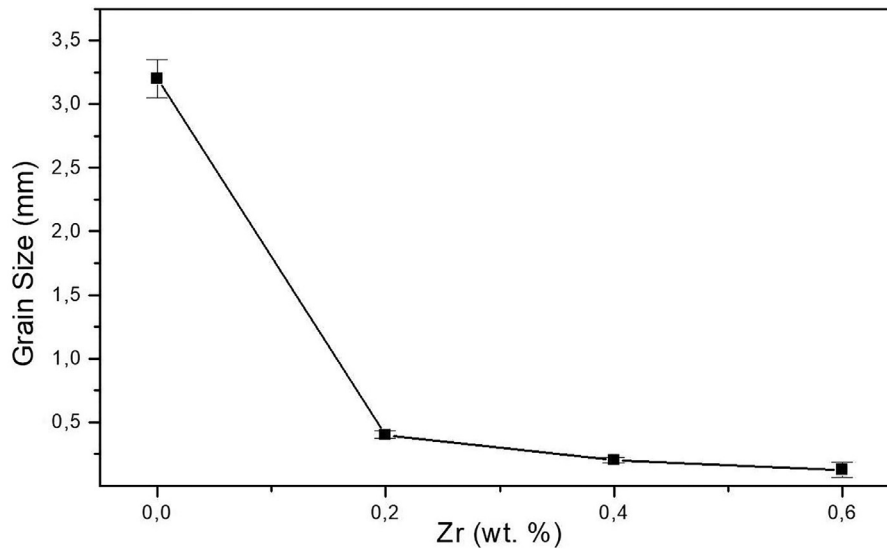


Fig. 5. Effect of Zr addition on the grain size of pure Mg.

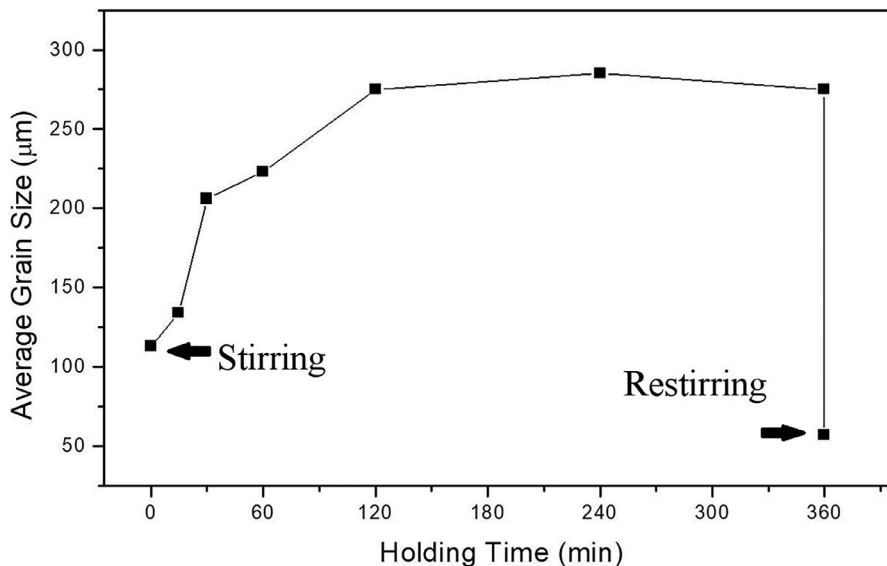


Fig. 6. Effect of restirring on grain size of 1% Zr added pure Mg at 780 °C (adapted from [108]).

approximately 30% of the grain refinement effect [109]. There are also some studies about addition of Zr to magnesium melts as salt mixtures [110]. Zr addition is still the most used grain refinement method for the Al-free Mg alloys. However, there are many studies to replace it with a low cost grain refining method.

3.2.4. Effect of solute atoms

It is well known that during solidification excess solute atoms that cannot be dissolved in the growing grains form a diffusion layer in the solid/liquid interface. The built up of solute atoms causes a change in the chemical composition of the liquid ahead of the solidification front. Enrichment of solute atoms gives opportunity to the liquid phase in the interface to be cooled to lower temperatures. This phenomenon is called as constitutional undercooling. Higher concentration

of solute atoms in the interface restricts the growth rate of the growing interface and gives time for further nucleation to occur. Also constitutional undercooling in the interface increases potential of the particles (impurities or grain refiners) in the melt to act as nucleants. Different alloying elements have different grain growth restriction abilities. This ability is called as Growth Restriction Factor (GRF) and defined as $mC_0(k-1)$, where m is the gradient of the liquidus, C_0 is the concentration of solute in the alloy and k is the partition coefficient between the equilibrium concentrations of the solid and liquid at the interface ($k = C_s/C_l$ at the interface temperature) [24]. Q values of some common alloying elements used in magnesium alloys are given in Table 1. It should be noted that the equation used to calculate GRF is only valid for binary alloys. If the alloy contains more than one solute element different equations should be used.

Table 1

Q values of some alloying elements in magnesium alloys taken from two different publications.

Element	Reported in Ref. [48]	Reported in Ref. [2]
Fe	52.56	52.68
Zr	38.29	30.24
Ca	11.94	8.786
Si	9.25	9.42
Ni	6.13	6.053
Zn	5.003	5.13
Cu	5.28	7.402
Ge	4.41	4.778
Al	4.32	4.26
Sr	5.51	3.474
Ce	2.749	2.74
Y	1.624	1.7
Sn	1.446	1.47
Sb	0.69	0.53
Mn	0.038	0.15

Al has a relatively small grain restriction effect because its Q value is relatively small. Since Al is present in the most of the industrial magnesium alloys it is important to understand effect of Al on the grain size of the Mg alloys. Fig. 7. shows the change of grain size of pure Mg with different Al additions. As the graph shows increased amount of Al causes grain refinement because of increased grain restriction effect. Q value for titanium in magnesium is calculated as 6591.21 and 59,500 by Lu et al. and Wang et al. respectively [111,112]. This value is dramatically higher than that of Zr which is used as ultimate grain refiner for Al-free Mg alloys. The Q value of titanium makes it as a great candidate for a grain refiner. However the results of studies about effect of Ti on the grain size of Mg alloys are conflicting. While the studies of Choi et al. and Lee et al. show no significant change in grain size; the study of Wang et al. reports a reduction from 1500 μm to 200 μm with addition of 0,01% Ti for same cool-

ing conditions [112–114]. The difference between the results of previous studies may be caused by low solid solubility of Ti in Mg or the formation of intermetallic phases with the Al (present as alloying element or impurity).

3.3. Future

Because of the scientific and industrial interest on Mg alloys, there is a lot of research work going on about grain refining of these alloys. In this section, new methods which can refine grain size of Mg alloys will be explained. These methods were gathered from the recent scientific publications and do not have any industrial applications yet.

3.3.1. Novel grain refiners for magnesium alloys

Because of the increased demand on magnesium alloys many researchers are trying to find an efficient grain refining method for magnesium alloys. Most of the attempts are focused on addition (or formation) of nonmetallic particles to the molten magnesium. Some of the recent studies and the results are summarized here.

It is reported by Qiu et al. that addition of 0.6 – 1.0% of Al to Mg-10Y alloy causes formation of Al_2Y in the melt. This compound acts as a grain refiner and reduces grain size of the cast material from 180 to 36 μm [115]. It was stated that 0.5% Al is not enough to form Al_2Y in the melt. When the Al content is below 0.5% Al atoms are dissolved in Mg grains during solidification. Addition of more than 1% Al to the alloy causes a slight decrease in the grain size [116]. In another study it was reported that only 1–2% of the formed Al_2Y particles act as nucleants and when the grain refinement is most effective optimum size of these active Al_2Y particles is 6–6.5 μm [117]. Another reported benefit of Al_2Y grain refinement is the high thermal stability of the grains. When Mg-10Y alloy with 1% Al addition was heat treated for 48 h at 550 $^\circ\text{C}$ the average grain size was 40 μm which is very

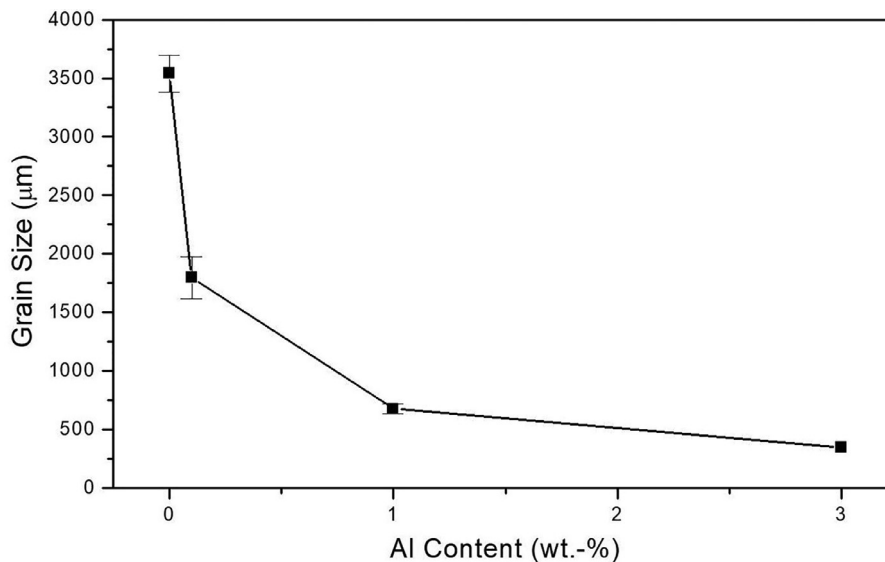


Fig. 7. Effect of Al addition on the grain size of commercially pure Mg.

close to the as cast grain size [115]. Similar grain refinement and thermal stability results were obtained for Mg-10Gd alloy with addition of Al [118]. A more recent publication with TEM study reported that $\{222\}_{\text{Al}_2\text{Y}}$ plane in the active Al_2Y nucleants serves as the heterogeneous nucleation substrate for Mg grains in Mg-10Y alloy. The interfacial energy calculations in the same publication indicate that Al_2Y together with other Al_2X ($X = \text{Gd}, \text{Sm}, \text{Y}, \text{Dy}, \text{Nd}$ and Ce) compounds whose interatomic spacing misfit f_r , is less than 2% with Mg matrix are located in fully wetting zone and hence they all have strong potential to act as effective grain refiners for cast Mg alloys [119].

Formation of Al_2Sm phase inside melt also resulted with similar grain refinement effect. It is shown that addition of Sm to Al containing Mg alloys first causes grain coarsening but when the amount of Sm is higher than 2.17 wt.-% grain refinement is achieved. The grain refinement is a result of formation of the nucleant phase of Al_2Sm [120]. Wang et al. studied effect of Al addition on grain size of different Mg-Sm alloys, and reported that grain size decreases with increasing Al content after 0.5 wt.-% for alloys Mg-6Sm and Mg-8Sm and 1 wt.-% for Mg-4Sm alloy [121]. Study of Hu and coworkers investigated the grain coarsening and grain refinement of Mg-3Al alloy with addition of Sm. It was reported that grain refining occurs when Al_2Sm is formed before solidification of α -Mg. If the Sm content of the alloy is not high enough for formation of Al_2Sm , combination of Sm with the Al-Fe-C-O phase forming an Al-Fe-Sm-C-O phase dramatically reduces the nucleation potency of this phase resulting with grain coarsening [122]. The effective grain refinement of RE containing alloys with Al additions is a result of formation of primary Al_2RE particles in the melt. Formation of these primary phases in the liquid metal is only possible for alloys with high RE content. Nevertheless, the obtained grain refinement and thermal stability is very important to improve these alloys especially when the possible high temperature applications are considered.

Another study shows the effect of Al-4Ti-5B master alloy on the grain size of AZ31. Al-Ti-B master alloys are well known grain refiners used in aluminum industry. The results of this study showed that this master alloy can cause grain refinement on AZ31 alloy. In other studies, grains of Mg-5Li-3Al and AZ91E alloys were refined with addition of Al-5Ti-1B master alloy [123,124]. It was concluded that TiB_2 particles act as heterogeneous nuclei in both studies [123,125].

Fu et al. reported addition of AlN particles with a particle diameter less than $5\mu\text{m}$ reduces grain size of both Mg-3Al and Mg-9Al alloys. Even though the mechanism of the grain refinement was not discussed in the article the similarity of the lattice parameters of AlN and α -Mg was mentioned [126].

Submicron sized ZnO particles also reported as a grain refiner for both pure Mg and Mg-Zn alloys. Addition of 3 wt.-% ZnO to pure Mg causes a decrease in the grain size from $1100\mu\text{m}$ to $410\mu\text{m}$. ZnO is unstable in Mg melt and reacts with Mg to form MgO and Zn. Although solute Zn affects grain size of the alloys, experiments showed that ZnO addition results with smaller grain size compared to the addition of

equivalent amount of solute Zn [127]. As reported by Liu et al. addition of ZnO with a particle size of $\sim 200\text{nm}$ to AZ31 causes grain refinement [128]. Although 200nm ZnO particles are too small to act as potent nuclei, reduction of ZnO to Zn solute causes grain growth restriction which results with finer grain size.

There are also other studies reporting different phases like CaO, NbB_2 , ZrB_2 , Mg_{24}Y_5 , TiB_2 and Al_2O_3 can be used as nucleant particles for different Mg alloys [129–135].

3.3.2. Solute additions

Addition of solute elements with high GRF can cause a higher undercooling in the solid/liquid interface. This higher undercooling can be effective to activate more particles to act as nucleants which results with finer grain size. Besides the elements used commonly as alloying elements Ca, Sr and Sb can refine grain size of Mg castings. It is reported that Ca addition can refine microstructure of pure Mg, AZ31, Mg-Al-Zn-Si alloys, AZ63 and AZ91 [136–139]. Sr has a lower GRF compared to Ca as can be seen on Table 1. But still can be effective for grain refinement of AZ31, AZ91 and AZ91D alloys [140–144]. The GRF of Sb is very small (0.53 according to [48] and 0.69 according to [2]) compared to the other alloying elements. However addition of small amounts of Sb can cause grain refinement in alloys like AZ91 (from 115 to $80\mu\text{m}$), Mg-5Al-1Zn-1Si (from 134 to $68\mu\text{m}$) and ZA84 (from 62 to $35\mu\text{m}$) [137,145,146]. There are two different theories about the mechanism of grain refinement with Sb addition. Both theories are about restriction of grains during solidification by intermetallic particles. In the first theory Mg_3Sb_2 particles restrict the grain growth, in the second theory Mg_2Si particles nucleate on the Mg_3Sb_2 particles and this finer Mg_2Si intermetallics restrict grain growth [137,146].

Other than alloying elements mentioned above there are numerous studies show grain refinement effect of Ce [147–149], Sc [150, 151], Si [152], Ti [112], B [153] and Bi [154] on magnesium alloys.

3.3.3. Agitation processes

It is well known that agitation of liquid metal (shaking, vibration, mechanical stirring, electromagnetic stirring or ultrasonication) before or during solidification can refine grain size of the material [155–160]. The main advantage of agitation processes is achievement of grain refinement without addition of any alloying element or grain refiner particles. In mechanical or electromagnetic agitation methods the grain refinement effect arises from breakage of dendrite tips or homogenous distribution of nonmetallic particles inside the liquid metal. However grain refinement caused by ultrasonic treatment has other reasons. When the intensity of ultrasonic power is high enough cavitation starts inside the liquid metal. Cavitation is formation of cavities filled with the dissolved gases in the molten metal [155]. These cavities have a very important effect on the microstructure of the solidifying metal. There are different theories about grain refinement of metals with ultrasonic treatment, which are as follows:

- The cavities formed inside the melt collapse in the pressure phase of the ultrasonic field. The shock waves generated from the collapse of cavities can cause breakage of dendrite tips and cause nucleation on these fragments. This phenomenon is called cavitation-induced dendrite fragmentation [161].
- The second theory is called cavitation-enhanced heterogeneous nucleation theory and is explained with three different mechanisms;
 - The first mechanism is called pressure-melting point mechanism. In this mechanism the pressure caused by the collapse of cavities changes the melting point of the metal according to Clapeyron equation (Eq. (5)). The increase in the pressure increases melting point of the metal which causes a higher undercooling and results with enhanced heterogeneous nucleation [162,163]. It was calculated by Qian and Ramirez that the increment in the melting point of the alloy is more than 6 K [164].

$$\Delta T_m = \frac{T \Delta P \Delta V}{\Delta H} \quad (5)$$

- The second mechanism is based on the wetting of the nonmetallic particles that exist in the liquid metal. The pressure caused by the collapse of cavities can cause wetting of these particles by liquid metal and increase heterogeneous nucleation rate [155].
- The last mechanism assumes rapid adiabatic expansion of gas inside the cavities that undercools the liquid at the cavity-liquid interfaces resulting in nucleation [165].

There are several studies in the literature showing grain refining effect of ultrasonic cavitation on different Mg alloys like AZ91, AS41, AJ62 or AZ80 [166–169]. Depending of the alloy composition and processing parameters ultrasonic cavitation can reduce grain size of Mg-Al alloys from $\sim 1000 \mu\text{m}$ to $\sim 130 \mu\text{m}$ and Mg-Zn alloys from $\sim 800 \mu\text{m}$ to $\sim 150 \mu\text{m}$ [170]. On the other hand the study of Bhingole and Chaudhari showed combined effect of inoculation and ultrasonic processing. This study shows that ultrasonic processing increases the grain refinement efficiency of nano-sized carbon black because of preventing agglomeration and enhanced wetting [171]. Another advantage of ultrasonic cavitation is degassing of the liquid metal during processing. This effect is caused by the diffusion of the dissolved gases into the cavities formed during ultrasonic processing of the melt [172].

Another agitation process for grain refining magnesium alloys was recently developed and patented by Fan et al. which is called Intensive Melt Shearing. In this method molten metal is processed with a device before casting. The device is consisting of a rotor/stator couple. When device is running the melt is forced to move inside the stator and then moved out from the small hole(s) on the stator by the rotation of rotor (Fig. 8) [173]. During melting and melt handling processes although protective gasses are used oxidation occurs. As a result of oxidation reactions MgO films with different structures are present in the melt. The movement of the molten magnesium provided by the melt shearing process ends with

fragmentation of the oxide film into individual oxide particles with a homogeneous size distribution [174–176]. Furthermore melt shearing can force the liquid metal to wet the dispersed oxide particles by overcoming the energy barrier for wetting [177]. It is reported that 45 s of intensive melt shearing can reduce grain size of AZ91D alloy from $690 \mu\text{m}$ to $175 \mu\text{m}$. Another finding was the dependence of the grain size on the pouring temperature was suppressed with melt shearing process [38]. In another study intensive melt shearing is applied to a twin roll cast AZ31 alloy for 60s just before casting, the grain size of the sheared samples were 10 times smaller than the conventionally cast ones [177].

The study reported by Peng et al. showed the effect of intensive melt shearing on Mg-0.5Ca-xZr alloys. Findings of this study showed that with intensive melt shearing it is possible to have almost same grain size with addition of% 0.1 Zr instead of% 1 Zr [178]. A more recent study reported that melt shearing can increase grain refining efficiency of Zr in Mg-0.1Zr alloy. It was concluded that intensive melt shearing exerts two effects: the first one is the dispersing of MgO film into MgO particles and increasing the number density of nuclei. The second is the enhanced adsorption of Zr on the surface of MgO. Zr adsorption decreased the misfit of MgO with α -Mg, resulting in the improvement of the nucleating potency of individual MgO particles [179]. In another study it was concluded that if only MgO particles distributed homogeneously by melt shearing process are present in the melt they will act as nucleants for heterogeneous nucleation at a larger undercooling [180].

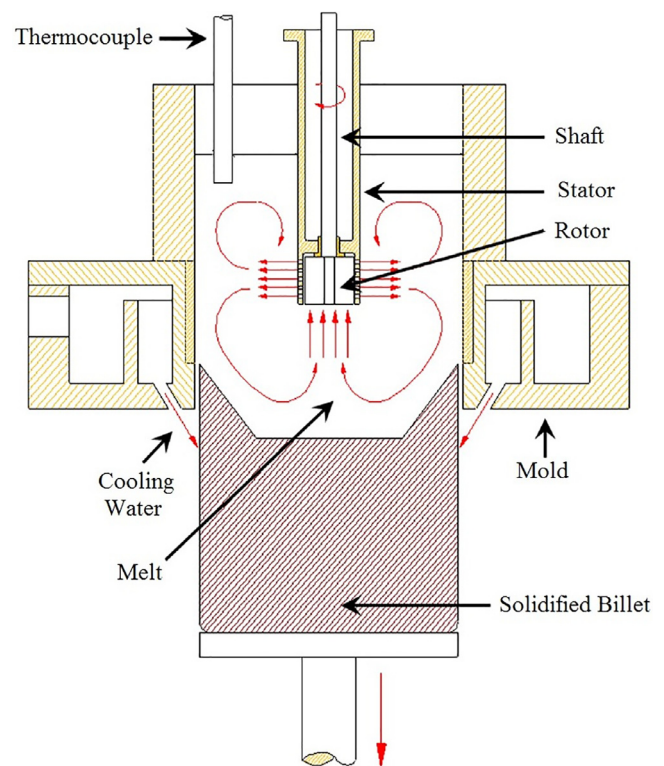


Fig. 8. Schematic drawing of the intensive melt shearing device in a vertical direct chill caster (adapted from [181]).

It is also reported by several researchers that mechanical or electromagnetic vibrations can refine grain size of different magnesium alloys like AZ91D, Mg-3Zn-0.8Ca, AZ31 and ZK60 [182–187].

4. Conclusion

A review of published literature about grain refinement of magnesium and its alloys is summarized in this paper under three sections depending of the industrialization of the methods. A brief summary of theoretical aspects of grain refinement of cast metals also provided to support the understanding of the methods used for Mg alloys. It is interesting that the mechanism of grain refinement in some methods that have been used for decades like carbon inoculation or ultrasonic cavitation is still not clear. Different theories were reported by different researchers to clarify these situations.

The amount of research work done to understand existing grain refining mechanisms or to develop new grain refining methods for Mg alloys increased continuously in the last two decades. Which is mainly a result of the demand for materials with higher specific strength to obtain lightweight design in different applications. When the superheating and native grain refinement methods are considered it can be concluded that small amount of impurities (mainly Fe and Mn) in the alloys can affect the grain size of the material. The significant effect of impurities on the grain size of the Mg alloys is possibly the main reason of the contradictory results reported in the literature. Super heating and native grain refinement methods are only effective in the alloys that contain certain amount of Al and when the results in the literature are compared, the mechanisms of these two grain refinement methods are most likely the same. The mechanism is related to the formation of intermetallic phases as a coating on the nucleant particles which reduces effectiveness of these particles. On the other hand addition of FeCl_3 also reduces grain size of some Mg alloys but it is not possible to use this method because of the detrimental effect of Fe on corrosion resistance of magnesium.

Carbon addition to Mg-Al alloys known to be an effective grain refining method and has been used in the industrial applications. It is known that at least 2% Al is needed for carbon inoculation to work which indicates the nucleant phase contains both Al and C atoms. In the past the first suggested nucleant was Al_4C_3 later other researchers conclude Al_2CO as the nucleant particle. Also duplex nucleation theories were proposed by other researchers including Al_8Mn_5 phase. The main problem in identifying the nucleant particles in carbon inoculation is chemical reaction of Al_4C_3 with water during sample preparation which produces a particle that consist of Al, C and O atoms. Finally, recently Han et al. confirmed Al_4C_3 particles in the center of Mg grains with EBSD analysis [75]. Another similar method is addition of SiC to the Mg-Al alloys. It is known that SiC reduces grain size but the mechanism is still not established clearly. Some of the research in literature suggest that Al_4C_3 forms and nucleates Mg grains when SiC is added to the melt, others suggest

Al_2MgC_2 forms and acts as nucleants. The third theory is nucleation of Mg grains on the SiC particles which have a small crystallographic mismatch.

When it comes to the Al-free alloys Zr addition is the ultimate grain refining method and results with finer and homogenous grain structure. It is also easy to find commercial Zr containing grain refiners for industrial production. However production of Mg-Zr grain refiners are costly and also an excess amount of Zr is usually added to the melt to ensure effective grain refining of the cast material which increases cost of the process more. The difference of densities of Mg and Zr causes settlement of Zr particles to the bottom of the crucible, stirring of the melt is required to achieve effective grain refinement. Another concern about Zr grain refiners is that the effectivity of the grain refiner is changed depending on the Zr particle size distribution in the grain refiner.

The summary above shows that a more effective grain refiner is needed for the main group of Mg alloy castings namely Mg-Al alloys. Although Zr is used for Al-free Mg alloys grain refinement process of these alloys can also be improved.

Because reducing iron content of primary Mg under a certain level is highly costly, all commercially pure Mg ingots have some iron and to overcome the detrimental effects of Fe some Mn addition is usually made to these ingots. So it is crucial to understand the individual and combined effects of impurities like Fe and Mn on grain refining of Mg-Al alloys. More research is needed to establish the relationship between grain refining efficiency of different methods and alloy purity. Although particles like NbB_2 , ZrB_2 , Mg_{24}Y_5 or TiB_2 have been tried, grain refiners with higher efficiency for Mg-Al alloys is also needed. To achieve this edge-to-edge matching model suggests useful information.

The efficiency of Zr grain refiners can be improved by controlling particle size distribution of the grain refiner during production process. Obtaining grain refiners with a narrow particle size distribution where most of the particles are between 1–5 μm should increase the efficiency of these grain refiners and reduce the cost and excess addition of Zr.

Although addition of grain refiners is the major way of grain refining the results of the research also shows that agitation processes can be very effective. Ultrasonic cavitation is a method known for decades now and proven to be very effective. The change of grain size depending on the distance from the ultrasonic radiator can be considered as a drawback of the method and more work is needed to obtain a more homogeneous grain size distribution [188]. Another agitation process called intensive melt shearing shows promising results for both Mg-Al and Al-free alloys. It is reported that the relative movement of the melt caused by high shearing enables MgO particles to act as nucleants. Optimal industrialization of this process can help to obtain castings with refined microstructure without need of any grain refiner addition. On the other hand, it is also shown that intensive melt shearing increases efficiency of Zr grain refining, which is possibly a result of decreasing the average particle size of Zr particles in the melt. This method might overcome the problems

caused by the difference in the particle size distributions of the Mg-Zr grain refiners.

Despite research work is going on for decades now, still there is no economical and reliable grain refining method that can be used in the industry. Although Interdependence Theory shed some light on the combined effects of solute additions and nucleant particles on the grain size of cast materials, development of more effective grain refining technology for different Mg alloys is still an important problem. Therefore, more research work is necessary to understand the mechanisms of existing methods and to find some new methods for refining microstructure of magnesium alloys. Reliable and reproducible results of these research works will raise the opportunity to magnesium and its alloys to be used in wide range applications.

Conflict of interest

No conflict of interest is stated by the author.

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