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Grain Refinement of AZ91 Magnesium Alloy: A Review

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Abstract

Grain refinement is an established technique that reduces the grain size of material with the direct intention of improving its finished properties or characteristic. The main objective of grain refinement is to produce a fine, uniform, and equiaxed grain structure. On the other hand, grain refinement of cast magnesium can be achieved by two methods represented by increasing the cooling rate and adding a chemical grain refiner. AZ91 is a cast magnesium alloy used to produce die-cast components. In contrast, the basic microstructure of this alloy consists of a primary α- phase in which the aluminum-rich β- phase ($Mg_{17}Al_{12}$) is precipitated along grain boundaries in cast magnesium alloy. Cast AZ91 alloy generally exhibits low strength and ductility due to the network-like eutectic β- $Mg_{17}Al_{12}$ distributed at the grain boundaries. In this review article, the research methods of grain refinement and its effect on the characterization of microstructure and mechanical properties of AZ91 magnesium cast alloy.

Keywords: Grain refinement; AZ91 magnesium alloys; ß-phase (M g17 Al 12).

1. Mg and Mg-Alloys

Magnesium The Greek word Magnesia, an ancient Greek city now a prefecture in Thessaly, central Greece, gave rise to the name Mg. Sir Humphry Davy performed the first extraction in England in 1808; however, it wasn't until the early 19th century and the development of lightweight aircraft that magnesium began to garner attention [1]. According to the American Society for Testing and Materials ASTM, magnesium alloys are classified [2]. Magnesium alloy is called "green engineering materials"[3].

These alloys have a 1.624 c/a ratio with a hexagonal close-packed (hcp) lattice structure [4]. Due to their low density of 1.74 g/cm^3, which is 35% lighter than aluminum's 2.7 g/cm^3 and almost five times lighter than steel's 7.9 g/cm^3, as well as their good castability, thermal conductivity, high electromagnetic shielding characteristics, good die casting, weldability, good mechanical properties, and excellent recyclability they have always been appealing to designers [5-6-7-8-9].

Magnesium alloys have some limitations despite having many positive traits. Low melting point is the main drawback, and insufficient ductility at room temperature and associated poor cold working capabilities are additional drawbacks [10]. In general, die-cast magnesium alloys fall under one of four commercially prevalent categories:

- Mg- Al- Zn-Mn (AZ series),
- Mg- Al-Mn (AM series),
- Mg-Al- Si (AS series), and
- Mg- Al- RE (AE series) [11-12].

The most popular alloys are those in the AZ series [13]. Of all the magnesium-based alloys, the magnesium AZ91 alloy, which contains aluminum and zinc as major alloying elements, has one of the best combinations of castability, mechanical strength, and ductility 14]. This alloy's chemical composition is (Mg -9 Al- 0.7 Zn- 0.2Mn) [15]. There are several variations of the magnesium alloy AZ91, including AZ91A, AZ91B, AZ91C, AZ91D, and AZ91E [16]. The primary phase is a solid solution of Mg and Al; the - phase (Mg_{17} Al_{12}), which is a compound made of Mg and Al and Mg and Al and precipitated along the grain boundaries and eutectic α-Mg + β- phase (Mg $_{17}$ Al_{12}). Figure 1 represents the Mg-Al phase diagram, and Fig. 2 shows the corresponding microstructure [17-18].

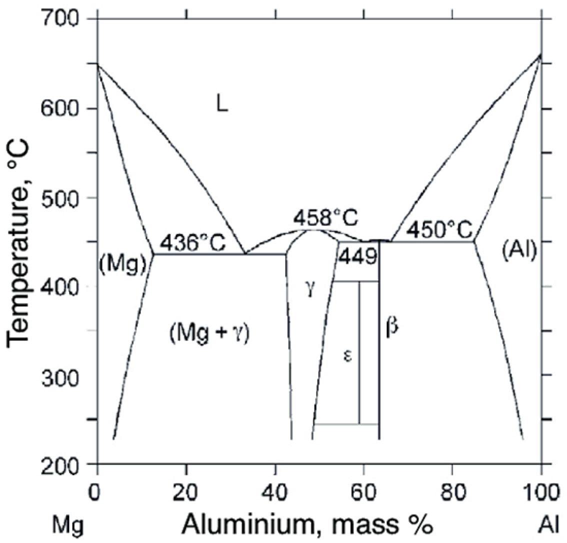

Fig.1 The Mg-Al phase Diagram [17].

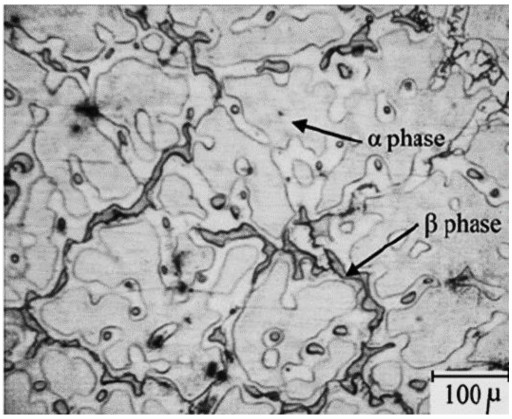

Fig. 2 Microstructure as cast of AZ91Mg alloy [19].

Due to its ideal blend of castability, mechanical strength, low production cost, ductility, and excellent corrosion resistance, AZ 91 is the most sought-after alloy. Its characteristics are listed in table 1 [20–21]. Sand and die castings use a general-purpose alloy [22]. Table 1: Properties of Commercially available die-cast AZ91 Mg alloy:

Property	**Value**
Density	1.81gm/cc
Melting Point	$470-595C^0$
Yield Strength	150Mpa
Tensile Strength	230Mpa
% Elongation	3%
Elastic Modulus	44.8Gpa
Shear Strength	140Mpa
Hardness	75BHN
Thermal Conductivity	72W/mk
Coefficient of Thermal Expansion	25µm/m^{0}k
Electric resistivity	14.1µΩcm
Fatigue Strength	70Mpa

2- Grain Refinement of AZ 91Mg alloys

Since the late 1930s, Mg alloy grain refinement has been crucial to the broader adoption of alloys in various industrial applications [23]. The best way to increase the strength and plasticity of magnesium alloys is through grain refinement. The main objective of grain refinement is to produce a fine, uniform, and equiaxed grain structure, leading to a significantly improved, stable, and predictable set of mechanical properties. The cast surface and the surface that will be machined later have improved surface finish thanks to small interconnected holes with homogenous porosity distribution [24–25]. They also improve machinability, uniform mechanical properties, increasing castability, and more homogenous distribution of second phases. Two main techniques are widely used:

2.1 Rapid cooling

Rapid cooling of liquid metal during solidification: Rapid cooling prevents the diffusion of atoms from the liquid phase to the solid phase, which promotes the establishment of constitutional undercooling. For instance, superheating, Mechanical shearing, " ultrasonic wave and electromagnetic fields".

2.2 Chemical grain refinement method

This method involves adding elements or compounds to the melt to promote heterogeneous nucleation. For instance, C inoculation and the addition of other solutes such as Silicon Si, Strontium Sr, and Calcium Ca. And Elfinal process [3-26-27].

2.1.1 By superheating

According to a 1931 patent, one of the earliest techniques developed to regulate the grain size of Mg-Al-based alloys was superheating. Superheating is the usual term used to describe high-temperature treatment. And the procedure entails quickly cooling to the pouring temperature and a brief holding period at that temperature before casting the melt at a temperature significantly higher than the alloy's liquids, typically in the range of 453k to 573k.

Although many variables can affect how effectively superheating refines grains, there are some fundamental characteristics of this process. To begin with, only Mg-Al alloys with a minimum addition of Mn/Fe content can produce a noticeable grain refinement response. The grain refining effect must then be maximized at a specific temperature above the pouring temperature. The final requirements for producing fine grains include quick cooling from the overheating temperature to the pouring temperature and a short holding time [28–29]. In the previous studies, by Mehmet Unal [30], the hardness of alloys has been increased with cooling rates increase and silicon addition to this alloy. Also, with silicon addition in the 2 wt % to AZ91 that have occurred Mg_2Si phases. Depending on the change in the cooling rate, the phase of $Mg_{17}AL_{12}$ has been changed, and thinner grains have been obtained. The distance between the α- Mg particles is narrowed.

In another work for fast cooling by Haonan Li [31], results reveal that grain coarsening occurs in cast AZ91 alloys when the cooling rate exceeds 90 k/s while it can be effectively inhibited upon adding NPs. The marked inhibition effect may originate from the formation of TiCNor ɤ- Al_2 o_3 Np- can also promote further nucleation events and lead to significant grain refinement. An analytical model has been established to quantitatively account for the restriction effect of NPs on grain growth. It work may shed new light on the grain coarsening of cast alloys during fast cooling and provide an effective approach to circumvent it.

2.1.2 By vibrations

The vibration processes of mechanical, ultrasonic, and electromagnetic waves have all been documented [32]. Solid pieces of the solidified alloy make up the best grain refiner for an alloy. Growing dendrites are broken up by vibration, which promotes heterogeneous nucleation. Low-frequency vibrations cause the entire melt to oscillate in phase, with no mixing occurring in most liquid. However, surface waves are produced, and shearing occurs at the melt's free surface. Surface waves may be to blame for the observed grain refinement in these circumstances, with nuclei forming at or near the free surface and mixing by convection during filling. If the nuclei are not remelted in the flowing metal, this mechanism works as intended [33].

Many ways to produce vibrations in molten metals and alloys, including low-frequency vibration of the mold and direct generation of vibrations within the melt using electromagnetic fields and ultrasonic probes [34]. The influence of varying amplitudes at a constant frequency on the grain size and mechanical properties of AZ91Mg ally was investigated by Katja Pranke [35], As a result, there achieved a reduction in grain size as well as an increase in tensile strength, hardness, and elongation.

2.2.1 By carbon inoculation

Nearly 75 years have passed since the discovery of the grain refinement of Mg-Al-based alloys, but the grain refinement mechanism with carbon addition is still not fully understood [27–36]. The introduction of carbon into the molten magnesium at 700–800 C^0 is the crucial step in this process [1-31]. Hexachlorobenzene (C_6Cl_6), hexachloroethane (C_2Cl_6), silicon carbides SiC, aluminum carbides Al_4C_3, calcium carbides CaC_2, and master alloys such as Al4C3 - SiC / Al and Al- 1.5 C 26-31] are just a few examples of the many carbon-containing materials that can be added to molten magnesium. This process investigated by M. Suresh [37], the addition of charcoal particles effectively refines the grains in AZ91 Mg alloy. Maximum grain refinement is achieved with 0.4 wt% charcoal addition, which is found to be optimum. Both the Al_4C_3 and Al_2MgC_2 particles act as effective nucleates for magnesium grains. As a result of the fine-grained structure and the presence of hard particles, charcoal-treated alloys show better hardness and tensile properties. Also, investigated by HuiHan [38], Al_4C_3 particles have been fabricated successfully by powder in situ synthesis process under argon atmosphere, In-situ Al_4C_3 shows perfect grain refining effect for AZ

91D alloy. With the addition of 0.6%Al_4C_3, the sharp decrease of grain size and finer dendrite are readily obtained. And the grain refinement mechanism is attributed to Al_4C_3 can act as the efficiently heterogeneous nuclei of primary α-Mg and decrease the degree of undercooling the primary α-Mg phase. And another study by TiJun Chen [39], indicates that $MgCo_3$ can decrease its grain size from 311 to 53 µm. Correspondingly, the tensile properties are improved.

2.2.2 Elfinal process or $FeCl_3$ process

At the end of World War I, in Germany, the process was first discovered [36]. Fe- Mn- Al compound nucleation. The process involves adding 0.4–1% of a hydrous ferric chloride $FeCl_3$ powder to a molten magnesium alloy at temperatures between 740 and 780 C^0 [28]. The Prives Study by Xiaoying,[40]. The effect of $MnCO_3$ addition on the grain refinement efficiency of AZ91Mg alloy has excellent grain refining efficiency for AZ91balloy, which is mainly attributed to the AL_4C_3 Particles formed in the melt, Mn is indispensable to grain refinement in Al-bearing magnesium alloys. There is an optimal addition amount of 0.6% at 740 C^0 and the grain size is reduced from 245 to 91µm. At the same time, the corrosion resistance performance $MnCO_3$-added AZ91 alloy is improved.

2.5 Solute additions

An increase in undercooling at the solid/liquid interface can result from adding solute elements. With more particles acting as nucleants due to the higher undercooling, the grain size will be finer. Reported that Ca,Sr and Si [36]. This finding agreed with the work done by Hai Hao, [41]. Indicated that the addition of 1.5 wt% Sm with or without 0.8Si/Ca led to a decrease in the volume fraction of the β-$Mg_{17}Al_{12}$ Phase and the formation of the intermetallic compounds of Al-Sm, Mg_2Si, MgAlCa and AL_2Ca. The microstructure of AZ91 alloy was significantly refined, and distribution became discrete with the addition of Sm and Ca; the average grain size of the α-Mg matrix was reduced from 239.7± 16.9µm to 66.43± 5.10µm. The AZ91- Sm-Ca alloy exhibited a good combination of yield strength at 135 Mpa, ultimate tensile strength at 199 Mpa, and elongation at 4.32%, ascribed to grain refinement strengthening. Furthermore, the T6-treated AZ91-Sm-Ca alloy possessed yield strength of 154Mpa and elongation of 7.1%, which was due to grain refinement strengthening and reduction in discontinuous precipitates.

3. Advantages and Disadvantages of Grain refinement methods

Regarding the capable, technical, economic, environmental, and safety aspects, a new and superior grain refinement process is required [26]. Superheating and C inoculation, for instance, can significantly refine grains while the Elfinal process only slightly refines them. In contrast, solute addition can significantly reduce grain size even without the addition of a nucleant. While it was that some grain refinement has been achieved, added Sic works fairly well. However, when Fe and Mn are both present, poisoning happens. Despite the fact that these methods have some issues from the perspectives of technical, economic, and environmental issues, Superheating is challenging to control, and C inoculation is the only commercially available method at this time.

4. Future Considerations

Considerations for specific grain refinement techniques can be summed up as follows:

- C inoculation and Sic; A successful commercial strategy has not yet been developed, and grain refinement's effectiveness is only marginally better than average.
- The Elfinal procedure: While there is circumstantial evidence that this occurred, it is challenging to find concrete proof. Additionally, it is challenging to use this method to account for all observations due to the wide variety of effects. However, it is worthwhile to make further efforts to find a powerful grain refiner for these alloys given the commercial significance of Mg-Al-based alloys.
- Solvent additions; a lack of physical data that would allow the developed predictive equations to reliably predict grain size [26].

5. Conclusion

Some techniques used for years have a mechanism for refining grains. However, consequently, more research is required to comprehend the mechanisms of current methods and to uncover some fresh approaches to improving the microstructure of magnesium alloys. Grain refinement, which entails the formation of small, equiaxed grains in the presence of dendrites and is connected to forming intermetallic phases as a coating on the nuclei, can enhance an alloy's mechanical properties. There are several ways to refine the grains of the AZ91 magnesium alloy, including superheating, C inoculation, vibration, the Elfinal process, and the addition of solutes. Their mechanisms involve both physical and chemical processes. In general, from the earlier research about various methods. Generally speaking, results from earlier studies on various methods of grain refinement for AZ91Mg alloy lead to an improvement in the material's mechanical properties and grain size of the microstructure

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