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# Effect of inoculation method of refiner on the grain refinement of AZ91 alloy

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## Abstract

Grain refinement involving inoculation of a grain refiner was investigated for application to a commercial Mg alloy. Cylindrical pellets composed of a mixture of $MnCO_3$ and carbon powder with several different ratios were plunged into a commercial AZ91 alloy. The results show that the addition of the mixed pellets can more efficiently refine AZ91 compared to the individual use of carbon powder or $MnCO_3$. In particular, the addition of mixed pellets with a 3:7 ratio between $MnCO_3$ and carbon provides an excellent refining efficiency, decreasing grain size from 460μm to 52μm of the AZ91 alloy. This is attributed to inoculation of $MnCO_3$ and carbon, which brings about the formation of heterogeneous nucleants such as MgO, $Al_4C_3$, and $Al_8Mn_5$ before solidification of α-Mg and also to melt agitation by the release of $CO_2$ gas

## Introduction

Grain refinement is an effective way to improve the mechanical properties of magnesium alloys. In general, refined microstructure in as-cast components leads to a more uniform distribution of solute elements, secondary phases and microporosity on a fine scale. It also provides superior extrudability and rollability, excellent resistance to hot tearing, good surface finish and other beneficial attributes, leading to considerable cost reduction in the production of wrought magnesium parts [1-4].

Many grain refining methods including Zr addition, super-heating, Elfinal or ferric chloride inoculation, carbon inoculation, direct addition of nucleant particles and so on have been developed for Mg-Al alloy systems [1-10]. Among them, the addition of carbon containing agents to the melt is known as the most effective way for grain refinement of aluminum containing magnesium base alloys because they offer some important practical advantages such as lower operating temperature, large melt volume, and less fading with long holding time [1, 2].

The addition of carbon-containing agents such as $C_2Cl_6$, SiC, $Al_4C_3$, and carbon powder have been reported to successfully refine Mg-Al based alloys [11-14]. Among them, $C_2Cl_6$ is the most useful grain refiner for commercial application; however, it is widely prohibited because it can cause serious environmental problems due to the release of toxic gas during refining. Other refining technologies also have accompanying problems, and the detailed refining mechanisms have not yet been clearly established. Accordingly, a reliable, effective and eco-friendly grain refiner should be developed.

We recently reported in a previous study [15] that manganese carbonate has excellent grain refining efficiency in Mg-9wt%Al alloys. Its refining effect is attributed to the inoculation of manganese carbonate, which brings about the formation of effective heterogeneous nucleant particles such as MgO, $Al_4C_3$ and $Al_8Mn_5$ in the melt as well as to melt agitation of carbon dioxide gas generated by the decomposition of manganese carbonate. However, direct inoculation of carbonate powder raises serious concerns regarding the safety of the magnesium foundry because carbonate powder is accompanied with an explosive reaction and the melt to be boiled. In addition, most of the reaction can occurs at the surface of the melt, which affects the efficiency of grain refinement. The present study investigates grain refinement of a commercial magnesium alloy by inoculation of a grain refiner of a pressed pellet comprising manganese carbonate and carbon powders in varying ratio. The microstructures and refining performance for an AZ91 alloy were studied.

## Experimental Procedure

Two types of refiners, carbon and manganese carbonate powders were used for grain refinement of a commercial AZ91 alloy. The average size of the carbon and manganese carbonate powders ranged from 3 to 5μm. The powders were mixed for 30 min with zirconia balls using a milling machine with varying ratios (Table 1). Next, the mixture of powders was pressed and formed to a cylindrical pellet shape.

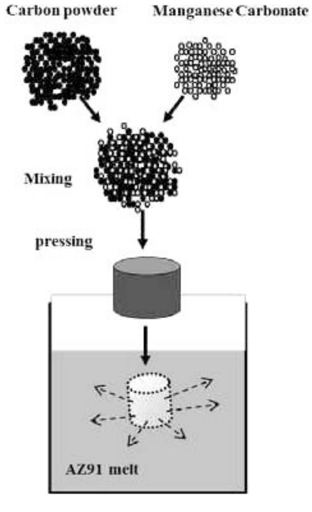

Figure 1. Schematic drawing of grain refining process using mixed pellets.

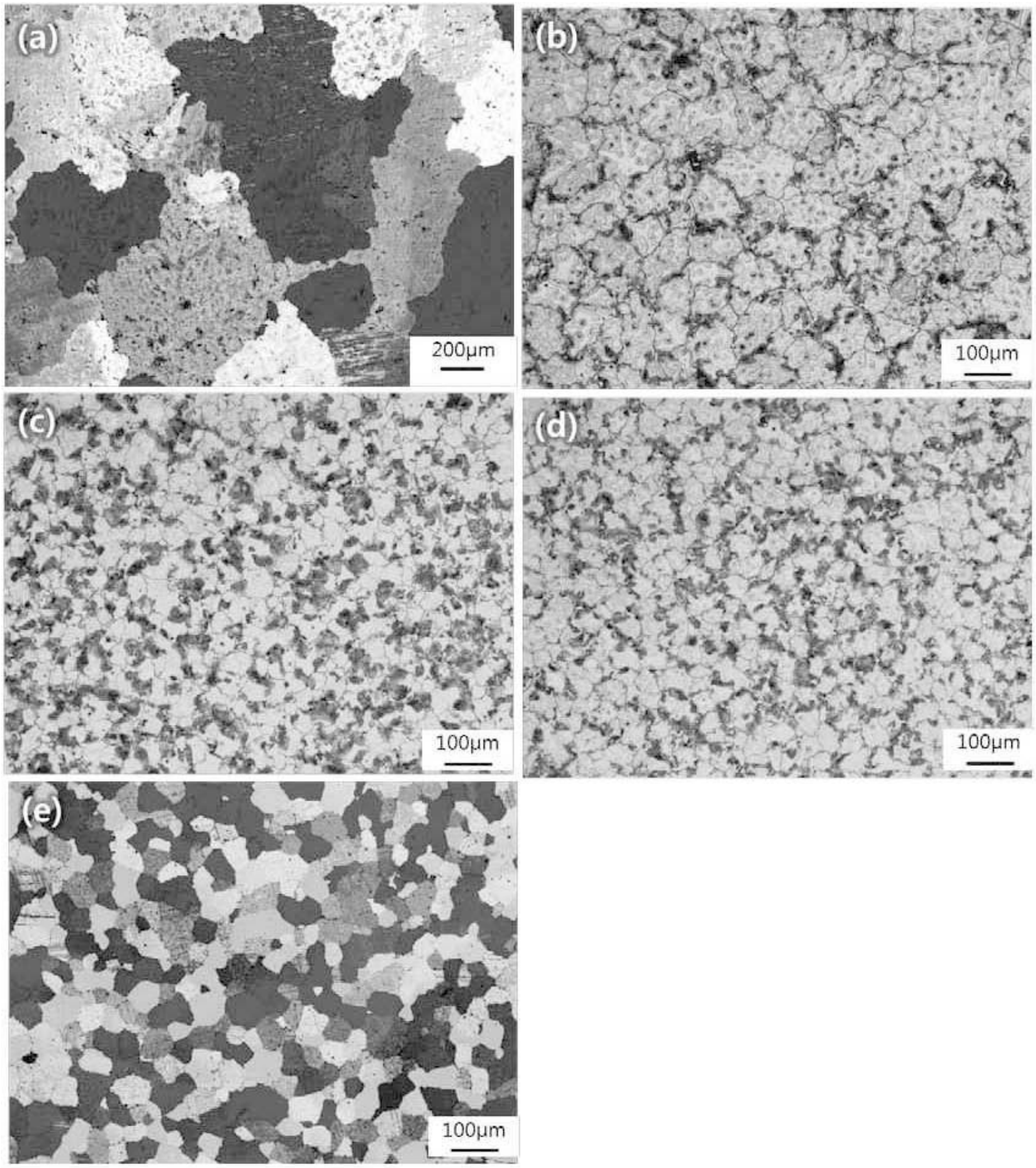

Figure 2. Microstructural changes of AZ91 alloys (a) without addition of the grain refiner and (b, c, d, e) with the addition of mixed pellet according to mixing ratio- (2, 3, 4, 5), respectively.

Table 1. Pellet mixing ratio of carbon and manganese carbonate

| Number | Mixing ratio (wt%) | |
|---|---|---|
| | Carbon | $MnCO_3$ |
| 1 | 100 | - |
| 2 | 10 | 90 |
| 3 | 30 | 70 |
| 4 | 50 | 50 |
| 5 | - | 100 |

Commercial AZ91 alloys supplied by DSM in Israel were prepared. They were melted in an electrical resistance furnace using a mild steel crucible under the protection of a mixed gas of $CO_2$ and $SF_6$. The mixed and pressed pellets, in an amount of 1wt% were plunged into the melt at 740°C. The melt was held at 740°C for 30 minutes and then poured into a permanent mould which was coated with BN and preheated to 200°C. During holding at the melting temperature, the melts were periodically stirred using steel rod. The schematic drawing presented in Figure 1 shows the sequential process of grain refinement of the magnesium alloy including the fabrication of the mixed pellets of refiners. Metallographic samples were cut from the same position, *i.e.* at 20mm from the bottom of the castings, and prepared according to a standard procedure. Samples for optical microscopy were etched with a solution of 1 ml acetic acid, 50 ml of water and 150 ml of ethyl alcohol. Grain size was measured by the linear intercept method from micrographs taken using polarized light in and optical microscope.

## Results and Discussion

Figure 2 shows the changes in the microstructure and grain sizes in grain refined as-cast AZ91 alloys using pellets with different ratios of manganese carbonate and carbon, in comparison to the un-refined AZ91 alloy. The average grain size of the AZ91 alloy without refining treatment was 460±40μm. The grain size decreased in all cases of treated grain refinement, notably, there was a significant decrease from 460±40μm to 52±3μm with the addition of mixed pellets having a 3:7 ratio between manganese carbonate and carbon powder, respectively.

The addition of more than 50% manganese carbonate, however, does not lead to further grain refinement as shown in Figure 3. In the case of using pellets composed 100% carbon, the grain refining ability was less (380±15μm) than that obtained with direct inoculation of carbon powder. Strongly pressed carbon powder cannot spread easily in the magnesium melt due to the poor wettability of the carbon pellet surface and the metal melt, and the powder has a tendency to agglomerate in the melt even with stirring. Pressed pellets composed solely of carbon powder thus have a detrimental effect on grain refinement of the Mg alloy. However, with the addition of manganese carbonate to the pellet, the grain size significantly decreased under the same casting conditions.

When the mixed pellet is plunged into the magnesium melt, manganese carbonate decomposes with the release of carbon dioxide gas and the melt is agitated. This facilitates the diffusion of the carbon powder in the magnesium melt at the same time. However, further addition of 50% manganese carbonate does not lead to a reduction of grain size, and the use of 100% manganese carbonate results in grain size of 70±2μm which is larger than that (under 60μm) obtained when using a 1:1 ratio of mixed refiners.

Normally, manganese carbonate decomposes with carbon dioxide at 200°C to give manganese oxide (MnO).

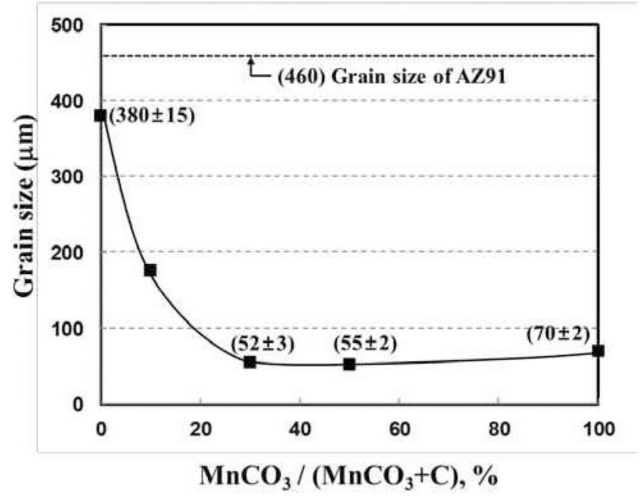

Figure 3. Changes in average grain size of AZ91 alloy with the addition of pellets mixed with different ratios.

However, when manganese carbonate is added into a commercial AZ91 alloy melt at 740°C, magnesium oxide (MgO) is formed by the following reaction instead of MnO (1):

$$89.9\,Mg + 9.0Al + 0.8Zn + 0.3Mn + 1MnCO_3 \rightarrow \text{Liquid} + MgO + Al_4C_3 \text{ (at 1013K)} \quad (1)$$

It is observed that there is no $CO_2$ gas at the equilibrium condition as the the excess Mg can consume $CO_2$ gas completely. At the same time, an $Al_4C_3$ phase can be formed by the reaction of carbon dioxide gas and aluminum atoms dissolved in the magnesium melt. Figure 4 shows the results of the thermodynamic calculation showing the solidification behavior of the AZ91 alloy with the addition of 1wt% $MnCO_3$.

In the actual process, carbon dioxide gas bubbles rise to the surface of the melt, and there is not sufficient time to react completely of carbon dioxide gas and aluminum, magnesium atoms dissolved in magnesium melt. The efficiency of refinement cannot be controlled easily, as the actual amounts of $Al_4C_3$ and MgO which are effective nucleants in this system are lower than the predicted values, as seen in Figure 4. The addition of carbon to manganese carbonate compensates for the loss of C from the released $CO_2$ gas without reaction with aluminum atoms.

According to previous reports, MgO, $Al_4C_3$ and $Al_8Mn_5$ phases can have beneficial effects on grain refinement of Al contained magnesium alloys. $Al_4C_3$ is known to be an excellent grain refiner due to its thermodynamic stability at the melting temperature of magnesium and crystallographic similarity with α-Mg; however, there have been no decisive experimental findings supporting this [13-19].

The fact that carbon addition leads to the formation of globular type $Al_8(Mn,Fe)_5$ particles causing the grain refinement in Mg-Al base alloys instead of $Al_4C_3$ particles is possibly conflicted with the $Al_4C_3$ nuclei hypothesis commonly accepted by many researchers. Although $Al_4C_3$ particles are known to provide more effective heterogeneous nucleation sites than $Al_8Mn_5$ particles in terms of crystallographic features [20], such a comparison of which one is better or worse is indeed meaningless in the melt where solute atoms can easily diffuse to long distance unlike solid-solid transformation. As far as crystallographic coherency

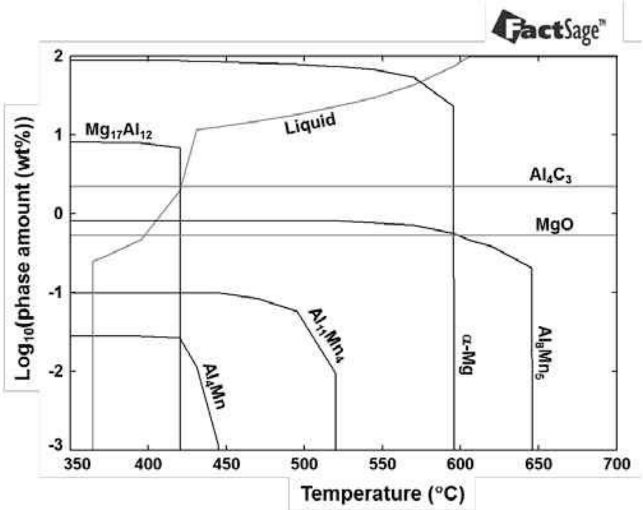

Figure 4. Thermodynamic calculation showing the sequence of microstructural evolution during solidification of manganese carbonate and carbon added in AZ91 alloy.

between magnesium matrix and heterogeneous nuclei is somewhat satisfied, other factors such as affinity between them, particle size and so on become more important. The existence of other particles such as Mg-rich Mg-Al-C ternary carbide in the melt must be not ignored. Although thermodynamic data for magnesium carbide are not sufficient yet, Viala [21] and Feldhoff [22] already reported that $Al_2MgC_2$ carbides were found in the interfaces between carbon fibers and magnesium alloys containing from 0.6 to 19%Al.

Experimental results by Kim et al show that carbon inoculation through the addition of 0.6wt% $C_2Cl_6$ lead to considerable grain refinement of commercial AZ91 with 0.25wt% Mn and Mg-9Al-0.3Mn alloys [23]. This indicates that the presence of Mn in Mg-Al alloy is necessary to acquire considerable grain refinement by carbon inoculation. Kim et al proposed a duplex nucleation theory, outlined as follows: (1) the formation of $Al_4C_3$ (R-3m, a=3.335Å, c=24.967Å) particles after carbon addition; (2) an $Al_8Mn_5$ (R3m, a=12.64Å, c=15.855Å) layer is formed on the surfaces of $Al_4C_3$ particles; and (3) α-Mg ($P6_3$/mmc, a=3.209Å, c=5.211Å) phases nucleate on the surfaces of $Al_8Mn_5$ particles. This concept was originally proposed for magnesium alloys by Mahoney *et. al.* [8] and has been known as a kind of grain refining mechanism in aluminum alloys [24, 25]. Similarly, Schumacher and Greer [25] also suggested that the $TiB_2$ particles were surrounded by $Ti_3Al$ layer which in turn was surrounded by α-Al. That was same phenomenon as shown in this research.

Based on the above results in this research, therefore, the grain refining mechanism by carbon addition can be suggested as followed; after carbon inoculation, carbides containing aluminum are formed in magnesium melt and Al and Mn solute atoms in the magnesium melt segregate to the melt-carbides interfaces, and then globular type $Al_8Mn_5$ particles are nucleated on the surfaces of the carbides and enclose them before the formation of α-Mg phase as temperature decreases. Finally α-Mg phases are nucleated on the surfaces of $Al_8Mn_5$ particles. This is supported by a previous finding that the direct addition of fine $Al_4C_3$ powders into an AZ91 alloy melt led to the formation of polygonal $Al_8Mn_5$ particles, but $Al_4C_3$ particles could not be found. When 1.0%$Al_4C_3$ powders with average particle size of 13.7μm were directly plunged into the AZ91 alloy melt at 740°C, all the particles observed except β phases were globular type $Al_8(Mn,Fe)_5$ particles as shown in Figure 5, while $Al_4C_3$ particle was not found even in the sample poured just after addition of $Al_4C_3$ powders (Figure 5(a)). It implies that $Al_4C_3$ plays a role of heterogeneous nucleation site for $Al_8(Mn,Fe)_5$ particle instead of α-Mg phase [26].

The addition of $MnCO_3$ in the magnesium melt provides an additional advantage, the melt agitation effect of carbon dioxide gas generated with agitation of the melt. Although the effect of melt agitation on grain refinement of Mg-Al based alloys in not yet fully understood, it has been reported that melt agitation by gas bubbling leads to a grain refinement. Besides, decomposition of $MnCO_3$ provides additional Mn elements, and also contributes to the formation of additional $Al_8Mn_5$ particles leading to a positive grain refining effect.

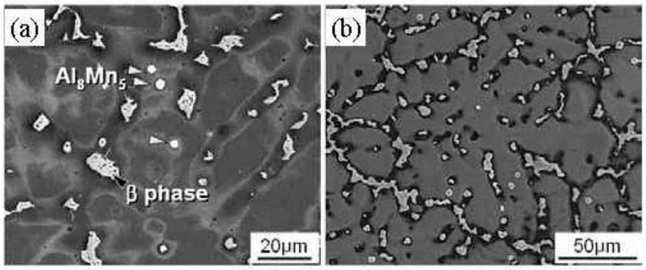

Fig. 5. SEM micrographs of the samples held for (a) 0min and (b) 30min after adding 1.0%$Al_4C_3$ powders into AZ91 alloy at 740°C. [26]

## Conclusions

In the present research, the grain refining efficiency of pressed pellets composed of manganese carbonate and carbon powder for a commercial AZ91 alloy were investigated. Mixed pellets with a ratio of 3:7 of manganese carbonate and carbon powder showed excellent grain refining efficiency in the AZ91 alloy, and a decrease of up to 52μm in the average grain size was obtained with the addition of 1wt% mixed pellet. The addition of pellets composed solely of carbon has detrimental effects as compared to direct inoculation or other methods. Mixed pellets with manganese carbonate and carbon powder bring about the formation of effective heterogeneous nucleant particles such as MgO, $Al_4C_3$ and $Al_8Mn_5$ in the melt as well as to melt agitation of carbon dioxide gas generated by the decomposition of manganese carbonate. These factors contribute to the diffusion of the carbon powder in the melt. The pellets also provide additional Mn which is the source element for the formation of $Al_8Mn_5$ nucleant. Therefore, mixed pellets with manganese carbonate and carbon powder offer several effective heterogeneous nucleant and refining mechanism, and are expected to provide the best refining performance among grain refiners developed thus far.

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