Magnesium Technology 2011
Edited by: Wim H. Sillekens, Sean R. Agnew, Neale R. Neelameggham, and Suveen N. Mathaudhu
TMS (The Minerals, Metals & Materials Society), 2011

PROPORTIONAL STRENGTH-DUCTILITY RELATIONSHIP OF NON-SF6 DIECAST AZ91D ECO-MG ALLOYS

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Keywords: Mg alloys, Diecasting, CaO, Non-SF_6, Strength, Ductility

Abstract

SF_6 gas has been generally used for Mg alloys during melting and casting as a cover gas. The use of SF_6 gas, however, will be limited owing to its significant impact on global warming. Non-SF_6 process during melting and casting in diecasting industry has been proved with Eco-Mg alloys by a simple addition of small amount of CaO into AZ91D and AM60B Mg alloys. This paper will show non-SF_6 diecasting procedures for AZ91D Eco-Mg alloys. Cold-chamber and hot-chamber diecasting mass productions were performed by using a Toshiba 135-ton cold chamber and a Frech 200-ton hot chamber diecasting machines under CO_2 atmosphere without SF_6 gas. An emphasis will be on proportional strength and ductility relationship of Eco-Mg alloys, in part, due to a high-quality melt, refined grain size and Al_2Ca second phase strengthening. Microstructures and mechanical properties of AZ91D Eco-Mg alloys will be evaluated in comparison with those of conventional AZ91D Mg alloy.

Introduction

Molten Mg alloys react with ambient atmosphere without the melt protective gases during melting and casting process due to their chemical unstability [1]. Oxides and inclusions formed by this reaction decrease the quality of melt and safety of work. SF_6 gas is generally used for Mg alloys during melting and casting as a cover gas and has proved to be a successful inhibitor. The use of SF_6 gas, however, will be limited owing to its significant impact on global warming. SF_6 gas has recognized as a very potent greenhouse gas with a high global warming potential (GWP) value of 23,900 compared with CO_2 and has a long atmospheric lifetime of 3,200 years [2]. For the expansion of Mg diecasting industry, non-SF_6 process is necessary. The one simple and effective way of non-SF_6 process is to improve oxidation resistance of Mg alloys without change of original Mg alloys properties. The automotive industry accounts for 90% of the casting demand, and diecasting is the dominant commercial fabrication process. The high-pressure die-cast (HPDC) Mg-alloys contain a considerable amount of casting defects such as oxides, inclusions and micro-porosity which adversely affect the mechanical properties of cast Mg alloys [3-5]. Although the SF_6 gas is used to protect the melt from oxidation in diecasting process, the surface of Mg alloys melts is only protected from oxidation in SF_6 gas affected zone such as melting furnace. The diecasting defects, in spite of using SF_6 gas, still exist and decrease the quality of diecast Mg alloys. So, the mechanical properties of diecast Mg alloys will be able to increase by improvement of oxidation resistance of Mg alloys.

The total vehicle weight can be reduced by using magnesium alloy components. The automotive part that may be subjected to deformation during crash must withstand a certain degree of deformation and absorb a certain amount of energy without fracture for safety. AZ91D alloys are the most widely used diecasting magnesium alloy in automotive applications due to their excellent castability and good room-temperature mechanical properties. But AZ91D alloys have poor elongation due to presence of brittle β-$Mg_{17}Al_{12}$. The enhancement of the ductility and strength of Mg alloys by alloying elements is very difficult but required for increased application of Mg alloys in automotive parts. Recently, the non-SF_6 process during melting and casting in diecasting industry and enhancement of the ductility and strength of Mg alloys have been proved with Eco-Mg alloys, a simple addition of small amount of CaO into AZ91D and AM60B Mg alloys. CaO added into the Mg melt does not exist as CaO itself in the solidified state. By the reactive phase formation, Mg_2Ca (C14) in pure Mg and Al_2Ca (C15) or $(Mg, Al)_2Ca$ (C36) in Al-bearing Mg alloys are formed only in the grain or sub-grain boundary region. The distinguished difference is that CaO does not form α-phase (solid solution phase) in pure Mg regardless of content and process conditions. The effect of CaO on Mg alloys has been already demonstrated in previous studies. Eco-Mg is characterized by (1) non-SF_6 processing, (2) Be elimination, (3) improved melt cleanliness, (4) ensuring original process abilities for casting, forming, joining as well as surface treatment, (5) improved mechanical properties by grain refinement and internal soundness, (6) ensured safety during manufacturing and application by raising oxidation and ignition resistances, (7) improved recyclability, and (8) cost reduction [8-14].

In this paper, the effect of CaO addition to AZ91D Mg alloy on non-SF_6 diecasting procedures and tensile properties has been investigated, with focus on proportional strength and ductility relationship. Cold-chamber and hot-chamber diecasting mass productions were performed by using a Toshiba 135-ton cold chamber and a Frech 200-ton hot chamber diecasting machines under CO_2 atmosphere without SF_6 gas. Microstructures and mechanical properties of AZ91D Eco-Mg alloys will be evaluated in comparison with those of conventional AZ91D Mg alloy.

Experimental Procedures

For diecasting procedure, AZ91D Mg alloy ingot was melted under SF_6 and CO_2 gases; on the other hand, The pre-made 0.3wt.%CaO added AZ91D Mg alloys and 0.7wt.%CaO added AZ91D Mg alloys ingot was melted respectively under CO_2 atmosphere without SF_6 gas in a steel crucible heated to 720°C. The diecasting was performed by using a Toshiba 135-ton cold chamber and a Frech 200-ton hot chamber diecasting machines as shown in Fig. 1. The metallic mold was designed for cellular phone case and preheated at 200°C. The metallic mold for tensile test specimen was prepared specifically. Fig. 2 (a) and Fig. 2 (b) show the hot chamber diecasting process for the cell phone casing and tensile test specimen under nitrogen atmosphere without protective gas, respectively. The temperature of melt was 690°C. Chemical composition analysis was performed by ICP-mass spectrometer. In order to observe the change of the microstructures by CaO addition, the cast billets were polished and observed using an Olympus PME3 microscopy. Tensile test was carried out at room temperature. Cross-head movement speed was determined as 1 mm/min. The obtained values of tensile properties were based on the average of 3 times. Tensile specimen had a gauge length of 30mm and a diameter of 6mm as shown in Fig. 7.

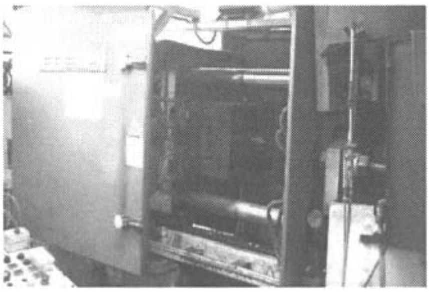
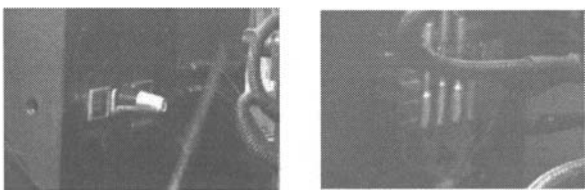


Figure 1. Photograph of Frech 200-ton hot chamber diecasting machine.



(a) (b)

Figure 2. Diecastings of CaO added AZ91D Mg alloy under nitrogen atmosphere without protective gas; (a) cell phone case and (b) tensile test specimen.

Results and Discussions

The results of tests to demonstrate the effect of small amount of CaO on non-SF_6 processing for AZ91D Mg alloys are shown in Fig. 3. The each melt, under the same melting conditions, is poured into large circular mold though slide for vigorous reaction with ambient atmosphere. Fig. 3 (a) shows the surfaces of AZ91D Mg alloy melt during casting and solidification under an ambient atmosphere without protective gas. Terrible oxidation began and the melt surface became tarnished in 10 seconds just after being poured. Severe burning started in 30 seconds and continued even with white flame to the point until the melt was consumed by burning. It is well known that continuous oxidation and resultant burning of Mg alloy at high temperature over 500℃ is due to the porous surface MgO oxide films that do not act as a protective layer to prevent further oxidation and burning. The experiment with 0.1wt.%CaO added AZ91D Mg alloy was carried out to investigated the minimum amount of CaO for non-SF_6 processing. The oxidation and burning occurred at melt surface a little. The result showed that 0.1wt.%CaO addition was not enough to be processed in an ambient atmosphere without protective gas. Fig. 3 (c) shows the change of surfaces of 0.3wt.%CaO added AZ91D Mg alloy during casting and solidification under an ambient atmosphere without a protective gas. No oxidation and burning appeared and shiny surfaces were maintained until the solidification completely finished. The small addition of 0.3wt.%CaO can prevent the oxidation and burning of AZ91D Mg alloys melt without any protective gas.

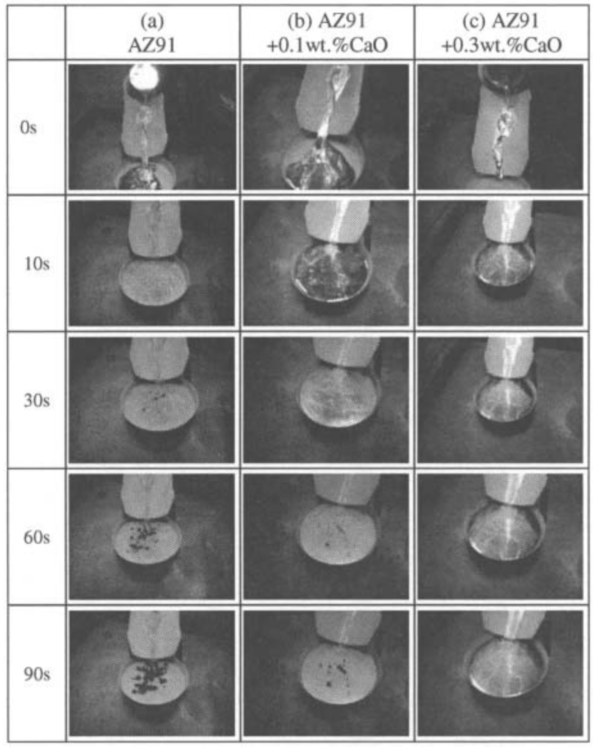
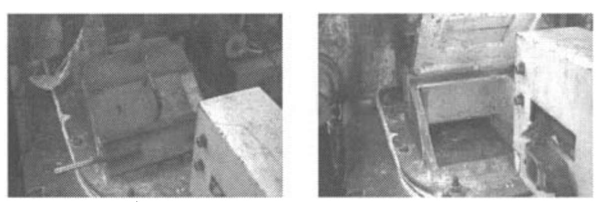


Figure 3. The melt surface change of the (a) AZ91, (b) AZ91+0.1wt.%CaO, and (c) AZ91D+0.3wt.%CaO alloys during casting and solidification under an ambient atmosphere without protective gas.

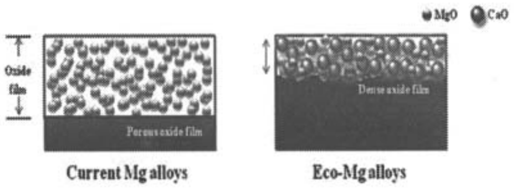
Fig. 4 shows the non-SF_6 diecasting process for 0.3wt.%CaO added AZ91D under nitrogen atmosphere without protective gas in the furnace. Fig. 4 (b) shows clean surface of 0.3wt.%CaO added AZ91D Mg alloy melt. There is no visible oxidation and burning on melt surface. The result showed that 0.3wt.%CaO was enough to be processed in non-SF_6 atmosphere.



(a) (b)

Figure 4. Non-SF_6 diecasting furnace for 0.3wt.%CaO added AZ91D Mg alloy under nitrogen atmosphere without protective gas; (a) closed furnace door and (b) melt surface in furnace.

Fig. 5 explains the reason of the non-SF_6 process of Eco-Mg schematically. The surface oxide film of Eco-Mg is denser than that of current Mg alloys because it consists of oxides mixture of MgO and CaO. The CaO existing in surface layer is not CaO added into Mg melt itself. That is reproduced CaO after reduction in Mg melt. Due to the dense complex surface oxide film, the casting and solidification of Mg alloys is possible without any protective gas.



(a) (b)

Figure 5. Schematic illustration of surface oxide film for (a) current Mg alloys and (b) Eco-Mg alloys.

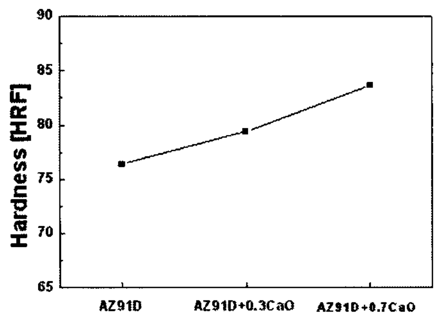
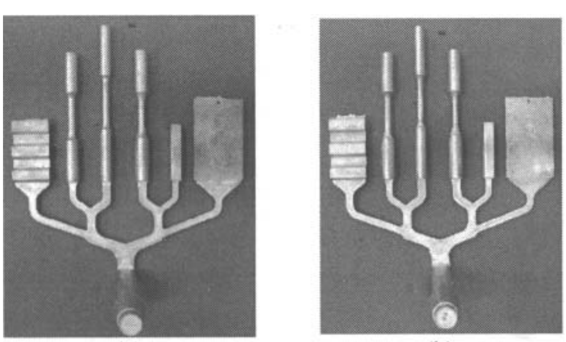


Figure 6. Rockwell hardness values of cellular phone case produced by cold chamber diecasting of AZ91D under SF_6 and CaO added AZ91D Mg alloys without SF_6 gas.

Fig. 6 shows the hardness values of cellular phone case produced by cold chamber diecasting AZ91D under SF6, 0.3wt.%CaO added AZ91D Mg alloys without SF6 gas and 0.7wt.%CaO added AZ91D Mg alloys without SF6 gas. Hardness tests were conducted using the Rockwell hardness tester. The Rockwell hardness values of AZ91D, 0.3wt.%CaO added AZ91D Mg alloys and 0.7wt.%CaO added AZ91D Mg alloys were 76.4, 79.4 and 83.6, respectively. The Rockwell hardness value of 0.3wt.%CaO added AZ91D Mg alloy was little higher than that of AZ91D Mg alloy. The Rockwell hardness value of 0.7wt.%CaO added AZ91D Mg alloy was highest.



(a) (b)

Figure 7. Tensile test specimen produced by hot chamber diecasting of (a) AZ91D under SF_6 gas and (b) CaO added AZ91D without SF_6 gas

Fig. 7 (a) shows the tensile test specimen produced by hot chamber diecasting of AZ91D Mg alloy under SF_6 and CO_2 protective gas. Fig. 7 (b) shows the mechanical property specimen produced by hot chamber diecasting of CaO added AZ91D Mg alloy under only nitrogen atmospheres without protective gas.

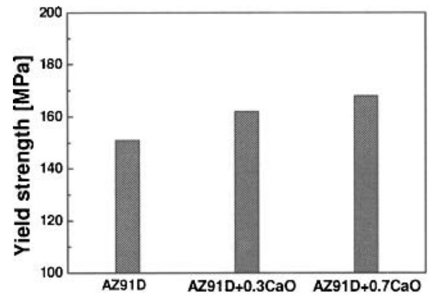


Figure 8. Yield strength of tensile test specimen produced hot-chamber diecasting of AZ91D under SF_6 gas and CaO added AZ91D Mg alloys without SF_6 gas.

Fig. 8 shows the yield strength of tensile test specimen produced by hot chamber diecasting of AZ91D under SF_6 and CO_2 protective gas and CaO added AZ91D Mg alloys without SF_6 gas. The yield strength of AZ91D, 0.3wt.%CaO added AZ91D Mg alloys and 0.7wt.%CaO added AZ91D Mg alloys were 151 MPa, 162 MPa and 168 MPa respectively. The yield strength of CaO added AZ91D Mg alloy, in spite of non-SF_6 process, was higher than that of AZ91D Mg alloy.

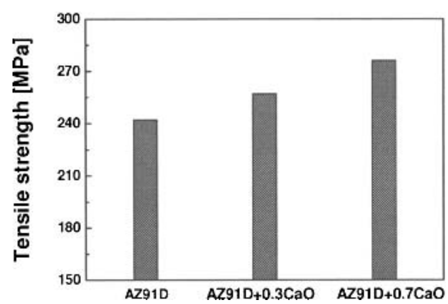


Figure 9. Tensile strength of tensile test specimen produced by hot-chamber diecasting of AZ91D under SF_6 and CaO added AZ91D Mg alloys without SF_6 gas.

Fig. 9 shows the tensile strength of tensile test specimen produced by hot chamber diecasting of AZ91D under SF_6 and CO_2 protective gas and CaO added AZ91D Mg alloys without SF_6 gas. The tensile strength of AZ91D, 0.3wt.%CaO added AZ91D Mg alloys and 0.7wt.%CaO added AZ91D Mg alloys were 242 MPa, 257 MPa and 276 MPa, respectively. The tensile strength of CaO added AZ91D Mg alloy was higher than that of AZ91D Mg alloy.

Fig. 10 shows the elongation of tensile test specimen produced by hot chamber diecasting of AZ91D under SF_6 and CO_2 protective

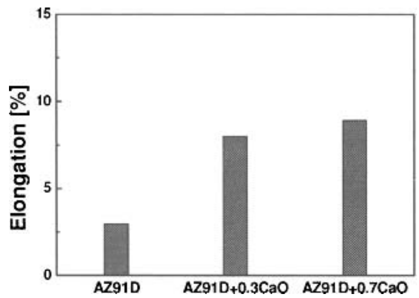


Figure 10. Elongation of tensile test specimen produced by hot-chamber diecasting of AZ91D under SF_6 and CaO added AZ91D Mg alloys without SF_6 gas.

gas and CaO added AZ91D Mg alloys without SF_6 gas. The elongation of AZ91D, 0.3wt.%CaO added AZ91D Mg alloys and 0.7wt.%CaO added AZ91D Mg alloys were 2.96 %, 8 % and 8.91 %, respectively. The elongation of CaO added AZ91D Mg alloy, in spite of non-SF_6 process, was much higher than that of AZ91D Mg alloy.

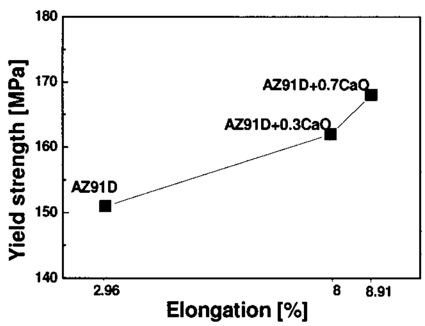


Figure 11. Proportional strength-ductility relationship of non- SF_6 Diecast AZ91D Eco-Mg Alloys.

This leads to a conclusion that additions of CaO to the AZ91D Mg alloys, in spite of non-SF_6 process, improve the ductility as well as UTS and TYS. It is usually experienced that optimizing one property by alloying reaches the expense of one or more other properties. The relationship between yield strength and ductility is a typical example. In order to increase yield strength significantly, some ductility has to be sacrificed. However, tensile yield strength and ductility are all increased by CaO addition. The proportional strength-ductility relation results from high-quality melt, refined grain size and Al_2Ca second phase strengthening. This is illustrated in Fig. 11. Fig. 12 shows another example of the proportional strength-ductility relationship of non-SF_6 diecast Eco-Mg alloys. As the CaO content added into Mg alloys increases from 0.25 to 0.65 wt.% the strength and ductility of Mg alloys improve at the same time proportionally. The strength - ductility relationship of conventional Mg-Al alloys such as AM and AZ series Mg alloys, however, is in inversely proportional with joining Al contents [15].

The alloying element Al increases the strength and castability of Mg alloys but the ductility decreases sharply due to brittle β-$Mg_{17}Al_{12}$ phase formation. In order to significantly improve the

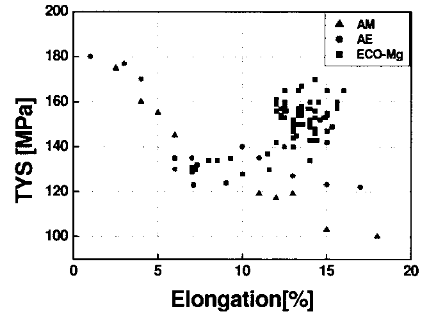


Figure 12. Relationship of strength and elongation of Eco-Mg alloys, compared with those of conventional Mg-Al alloys.

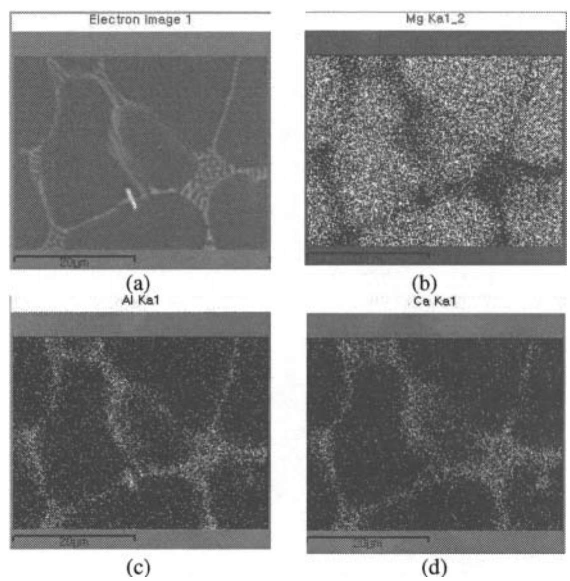
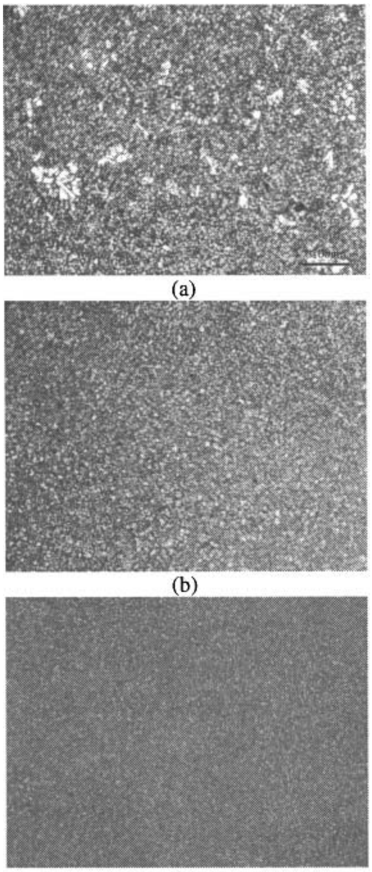


Figure 13. Comparison of elemental mapping images of (a) BSE image, (b) Mg, (c) Al, and (d) Ca by EDS for CaO added AZ91D Mg alloy .

ductility of Mg-Al based diecasting Mg alloys with high Al contents, the brittle effect of the β-$Mg_{17}Al_{12}$ phase needs to be reduced.

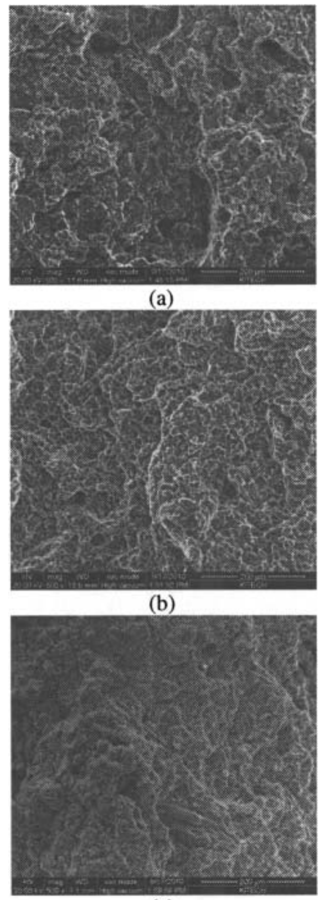
Fig. 13 shows comparison of elemental mapping images of (b) Mg, (c) Al, and (d) Ca by EDS for CaO added AZ91D Mg alloy. Fig. 13 (a) shows BSE (back scattered electron) image for CaO added AZ91D Mg alloy. Ca was distributed on the grain boundary. But O was not detected. CaO did not exist as CaO itself in the solidified state. Ca reduced from CaO forms intermetallic compound with Al. By reactive phase formation, Al_2Ca phase was formed mostly in the grain or sub-grain boundary region. The distinguished difference is that CaO did not forms solid solution phase. Although Ca has a strong segregation tendency, Ca added Mg alloys solidified first as solid solution phase and then as divorce eutectic phase. The brittle β-$Mg_{17}Al_{12}$ phase formation grows down due to Al_2Ca phase formation. The Al_2Ca phase has a lamellar structure with a relatively large extension from the grain boundaries. The formation of Al_2Ca suppresses the formation of brittle β-$Mg_{17}Al_{12}$ by binding up Al. The effect of second phase strenghening increases due to Al_2Ca phase in the grain or sub-grain boundary region. Also, the strength is improved due to grain refinement by Al_2Ca phase formation. So, the ductility and strength are enhanced at the same time by CaO addition.



(a) (b) (c)

Figure 14. Microstructures of a cell phone case produced by cold chamber diecasting of (a) AZ91D under SF_6, (b) 0.3wt.%CaO added AZ91D without SF_6 gas and (c) 0.7wt.%CaO added AZ91D without SF_6 gas.

Fig. 14 shows the microstructures of a cell phone case produced by cold chamber diecasting of AZ91D under SF_6 gas, 0.3wt.%CaO added AZ91D Mg alloys without SF_6 gas and 0.7wt.%CaO added AZ91D Mg alloys without SF_6 gas. The microstructure of AZ91D has porosity and coarse grain as shown in Fig. 14 (a). The phase distribution of AZ91D is irregular. Figure 14 (b) shows the microstructure of 0.3wt.%CaO added AZ91D Mg alloy. The grain of 0.3wt.%CaO added AZ91D Mg alloy is refined with little porosity in spite of non-SF_6 process. This tendency is more prominent in 0.7wt.%CaO added AZ91D Mg alloy as seen in Fig. 14 (c). The microstructure of Eco-Mg alloys is refined by Al_2Ca phase formation by CaO addition. The Al_2Ca phase is distributed uniformly. The grain refinement and regular distribution of phase contribute to simultaneous enhancement of ductility and strength of AZ91D Mg alloys.



(a) (b) (c)

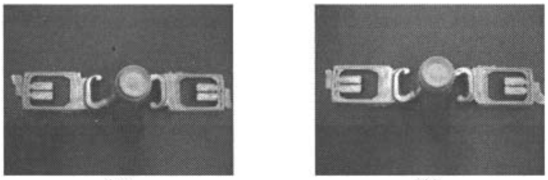
Figure 15. SEM images of the fracture surface of a tensile test specimen of (a) AZ91D under SF_6, (b) 0.3wt.%CaO added AZ91D without SF_6 gas and (c) 0.7wt.%CaO added AZ91D without SF_6 gas.

There is a close correlation between the tensile ductility and quality of castings such as the area fraction of the porosity and inclusions. The fracture beginning preferentially goes through the regions containing concentrated pores or inclusions [16].

Fig. 15 shows the fracture surfaces of tensile bars of hot chamber diecasting of AZ91D under SF_6 gas and CaO added AZ91D Mg alloys without SF_6 gas. In Fig. 15 (a) corresponding to brittle AZ91D alloys, the cleavage planes are prominently observed inside the grains that also contain evidence of void formation. In CaO added AZ91D Mg alloys samples, on the other hand, cleavage is rarely seen. The dimples on the fracture surface of the CaO added AZ91D Mg alloys sample are demarcated by intense slip at the boundary region. The area fraction of porosity in the fracture surface is high in brittle AZ91D alloys. But in

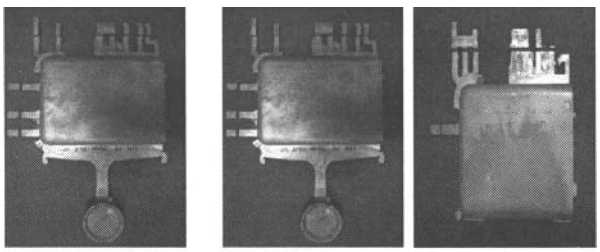
0.7wt.%CaO added AZ91D Mg alloys, it decreased sharply as shown in Fig. 15 (c).

Fig. 16 (a) shows the small cell phone case produced by hot chamber diecasting of AZ91D Mg alloy under SF_6 and CO_2 atmospheres. Fig. 16 (b) shows the cell phone case produced by hot chamber diecasting of 0.3wt.%CaO added AZ91D Mg alloy under nitrogen atmospheres without protective gas.



(a) (b)

Figure 16. Photograph of a cell phone case produced by hot chamber diecasting of (a) AZ91D under SF_6 and (b) 0.3wt.%CaO added AZ91D without SF_6 gas.



(a) (b) (c)

Figure 17. Photograph of cell phone case produced by cold chamber diecasting of (a) AZ91D under SF6 , (b) 0.3wt.%CaO added AZ91D without SF6 gas and (c) 0.7wt.%CaO added AZ91D.

Fig. 17 shows another larger cell phone cases produced by cold chamber diecasting. Fig. 17 (a) shows cell phone cases produced by cold chamber diecasting of AZ91D under SF_6 and Fig. 17 (b) and (c) show cell phone cases produced by cold chamber diecasting of 0.3wt.%CaO added AZ91D and 0.7wt.%CaO added AZ91D without SF6 gas, respectively. In spite of non-SF_6 process, CaO added AZ91D are well produced by hot chamber diecasting and cold chamber diecasting. It means that non-SF_6 CaO added AZ91D has good diecastability. A possible explanation of the good diecastability of Eco-Mg alloys can be the suppression of the formation of β-$Mg_{17}Al_{12}$, combined with reduced casting defects like inclusions and porosity.

Conclusions

Without SF_6 gas, the 0.3wt.%CaO added AZ91D Mg alloy and 0.7wt.%CaO added AZ91D Mg alloy could be well manufactured by hot chamber diecasting and cold chamber diecasting. This is because oxidation resistance of Mg alloys is improved by dense complex surface oxide film which consists of oxides mixture of MgO and CaO. That lead to melt soundness and improvement of mechanical properties. The Rockwell hardness value of AZ91D Mg alloy increases with CaO contents up. Yield strength and tensile strength of CaO added AZ91D Mg alloy was higher than that of AZ91D Mg alloy. The elongation of CaO added AZ91D Mg alloy was much higher than that of AZ91D Mg alloy. It is remarkable that in spite of ductility improvement, the tensile yield strength is improved and ultimate tensile strength is increased. Addition of CaO results in the formation of Al_2Ca phase (C15 phase) on the grain boundaries. This phase formed by the red uction of CaO leads to the refinement of grain structure and dispersion strengthening. As a result, strength and ductility improve proportionally. The suppression of formation of brittle β-$Mg_{17}Al_{12}$ phase and decrease of fracture surface porosity and other casting defect caused by melt soundness also contribute to enhancement of ductility and strength of AZ91D Mg alloy. The proportional strength-ductility relationship results from high-quality melt, refined grain size and Al_2Ca second phase strengthening.

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