Recent Research and Development Activities on Mg Alloys at CAAM

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Abstract. A brief review of recent research and development activities on light weight Mg alloys at the Center for Advanced Aerospace Materials (CAAM) is reported. Current research projects include various fields such as: (i) development of high strength/ductility Mg alloys; (ii) improvement in corrosion resistant of Mg alloys; (iii) semisolid state processing of Mg alloys and (iv) development of ultralight Mg alloys. For commercial utilization of Mg alloy parts, several problems, such as melting/casting, corrosion and recycling, have to be tackled. This review also contains a brief summary of the development project of Mg alloy parts for commercial application, mainly for automobile parts.

Keywords: Mg alloys, squeeze casting, semisolid processing, rapid solidification

1. Introduction

Lightweight alloys have had varying degree of importance in transportation systems. In aircraft and space industries, for example, the advances made in lightweight alloys have always provided the key to performance improvements. Moreover, recent strong demand for weight reduction of the vehicle has generated a considerable interest from the automotive industries as well. From these points of view, Mg alloys, the lightest commercial alloy developed so far, have great potential for high performance aerospace and automotive applications. However, there have been some major problems to be solved, for example, melting and casting under inert atmosphere, proper combination of strength, toughness and corrosion resistance, etc.

The Center for Advanced Aerospace Materials (CAAM) has been founded in 1990, and now is becoming one of the largest materials research institutes for aerospace and automobile industries in Korea. Development of lightweight alloys including Mg alloys is one of the most important research projects being performed at CAAM since its foundation. The research projects on Mg alloys at CAAM can be classified into two main areas: (i) process development and (ii) alloy design. Various processing techniques which include squeeze casting, semisolid processing and rapid solidification processing as well as conventional ingot casting are being investigated at CAAM. Development of corrosion resistant Mg alloys with high strength and toughness is one of the main areas concerned with the alloy design problems. Followings are examples of main projects on Mg alloys being performed at CAAM:

- Development of high strength/ductility Mg-Al-Si base alloys
- Improvement of corrosion resistance of Mg alloys
- Semisolid processing of Mg-Al-Zn alloys
- Fabrication of Mg alloy parts for automotive application
- Development of ultralight Mg-Li alloys
- Rapid solidification processing of Mg alloys
- Fabrication of Mg based composites by infiltration method

In the present paper, some of the above projects on Mg alloys are presented.

2. High strength/ductility Mg alloys [1, 2]

To improve the overall performance of Mg alloys, it is important to optimize the combination of various properties such as strength, ductility, corrosion resistance, etc. Recent studies indicate that addition of alloying elements such as Si and rare earth elements to Mg-Al-Zn alloys can produce substantial improvements in strength, toughness and corrosion resistance. Rare earth elements are very expensive and difficult to be alloyed homogeneously. On the other hand, Mg_2Si formed by the addition of Si is the very useful intermetallic compound that exhibits a high melting point, low density and a high elastic modulus. One of the main project on alloy development of Mg alloys at CAAM is concerned with the microstructural modification of AZ series of alloys by Si addition.

Figure 1 shows the representative microstructures of Si added Mg-Al-Zn alloys. It can be seen that Mg2Si particles are mainly in the form of a faceted polygonal shape in the

Figure 1. Optical micrographs of Mg-9Al-1Zn-0.7Si alloy: (a) ingot cast and (b) squeeze cast.

Figure 2. Optical micrographs of Mg-5Al-1Zn-0.7Si-X alloys: (a) Ca added and (b) P added.

conventional ingot cast alloy (figure $1(a)$). With the application of the pressure, however, Mg2Si particles become to have two types of morphology, i.e., chinese script type and faceted polygonal type (figure 1(b)). It has been shown that the amount of chinese script type Mg2Si particles decreases with an increase in Al content. In other words, increasing the Al content in Mg-Al-Zn-Si alloys has the effect of retarding the formation of chinese script type eutectic Mg2Si particles, thereby increasing the amount of primary polygonal type Mg_2 Si particles. Since the chinese script type Mg_2 Si particles are detrimental to ductility and toughness, Al content in the Mg-Al-Zn-Si alloys should be controlled at a proper level. However, increasing the Al content is not the proper approach to improve the combination of strength, toughness and corrosion resistance. It has been attempted to obtain advantageous distribution of Mg_2Si particles by Ca or P addition.

As shown in figures 2(a) and (b), both Ca and P additions refine the distribution of Mg_2Si particles in squeeze cast Mg-Al-Zn-Si alloys. Mg₂Si particles present in Ca and P containing alloys consist of several subgrains, which nucleate from the primary phases containing Ca and P. These results indicate the beneficial effect of Ca and P on modifying the morphology of Mg2Si particles. Tensile test of Mg-Al-Zn-Si-X alloys shows that the modification of microstructure improves the tensile properties, in particular, ductility. Another beneficial effect of P and Ca additions on the microstructure of Mg-Al-Zn-Si alloys is that the fine microstructure of squeeze cast alloys is retained after solution treatment.

3. Improvement in corrosion resistance of Mg alloys [3, 4]

Although Mg alloys have the lowest density among commercially available structural alloys along with excellent castability, workability and damping capacity, the poor corrosion resistance has limited wide-spread applications of Mg alloys. It is well known that the presence of impurities, e.g., Fe, Ni and Cu, decreases the corrosion resistance of Mg alloys. The high purity alloys such as the recently developed AZ91D show remarkably improved corrosion

resistance by minimization of impurity effects. However, in solutions containing Cl−, Br−, SO_4^{-2} and ClO_4^- ions, Mg alloys still show poor corrosion resistance. Therefore, there have been many attempts to improve the corrosion resistance of Mg alloys by appropriate surface treatment, heat treatment, alloying with rare-earth elements or refining microstructure with rapid solidification process.

The research programs at CAAM on improving the corrosion resistance of Mg alloys focus on the above mentioned areas. The main projects CAAM are concerned with include;

- Effect of $Mg_{17}Al_{12}$ on the corrosion behavior of AZ91
- Effect of rare earth element addition on the corrosion behavior of AZ91
- Corrosion behavior of rapidly solidified Mg alloys

As shown in figure 3, the corrosion potential of AZ91 is found to increase linearly as the volume fraction of $Mg_{17}Al_{12}$ increases from 0% to 10%. It is well known that the pitting is a dominant process at the initial stage of corrosion in Mg alloys. The corrosion rate determined from the salt spray test is shown in figure 4. The corrosion rate decreases linearly from 68 to 12 mpy as the volume fraction of $Mg_{17}Al_{12}$ increases from 0% to 10%. This is a remarkable improvement in corrosion resistance compared with the behavior of permanent mold cast AZ91 alloy with similar grain size. As the aging time increases, the

Figure 3. Change in corrosion potential as a function of the volume fraction of $Mg17Al12$ particles.

Figure 4. Corrosion rate as a function of the volume fraction of $Mg_{17}Al_{12}$ particles after salt spray tests.

corroded surfaces of specimens become more uniform and show lower degree of corrosion. This observation implies that the network structure of $Mg_{17}Al_{12}$ phase serves as an effective barrier against corrosion. In other words, the increase in the volume fraction of $Mg_{17}Al_{12}$ phase improves the corrosion resistance of AZ91 alloy.

4. Semisolid state processing of Mg alloys [5–9]

Semisolid state processing can produce sound and reliable castings and reduce micro- and macro-segregation. Because of low processing temperature and forming load, die and shot chamber life can also be extended. Furthermore, it can produce near net-shape casting and reduce post-cast treatments. Realization of such advantages of semisolid state processing has led to initiation of several projects on Mg alloy development. CAAM's main effort is currently on the fundamental understanding of microstructural evolution during semisolid state processing. The microstructural changes in the stir-cast alloys obtained with a stirring rate (V_s) of 200 rpm are shown in figure 5 as a function of isothermal stirring temperature. As the isothermal stirring temperature decreases, the solid volume fraction (f_s) increases and so does the collision among the primary solid particles. Therefore, the primary particle size increases with decreasing isothermal stirring temperature due to the coalescence of the primary solid particles by sintering and Ostwald ripening. The spherocity of the primary

Figure 5. Effect of stirring temperature on the microstructure of stir-cast alloy at V_s of 200 rpm: (a) 590°C $(f_s = 0.30)$, (b) 585°C($f_s = 0.38$), (c) 580°C ($f_s = 0.45$), and (d) 575°C ($f_s = 0.50$).

particles increases by the more effective abrasion. Figures 6(a) and (b) show the change in the tensile properties of the stir-cast alloys as a function of solid volume fraction at $V_s = 200$ rpm and of stirring rate with $f_s = 0.45$, respectively. With decreasing solid volume fraction or increasing stirring rate, the tensile strength of the stir-cast alloys increases as a result of decreased primary particle size. Also, the tensile elongation of the stir-cast alloys decreases with increasing solid volume fraction and stirring rate due to the increase in porosity level in the alloys. Since the variation of solid volume fraction is related with that of primary particle size, the modified rule of mixture has been applied in order to express the tensile strength of the stir-cast alloys in terms of the microstructural parameters such as the solid volume fraction and primary particle size as follows:

$$
\sigma_{\text{UTS}} \text{ (MPa)} = 124(1 - f_s) + \left[72 + 547d - \frac{1}{2}(\mu \text{m} - 1/2)\right] f_s \tag{1}
$$

where f_s is the solid volume fraction and d is the primary particle size. Figure 7 shows the interrelationship between the empirical and experimental tensile strengths. The result shows that the above empirical equation can predict the tensile strength of the stir-cast alloys quite well.

Figure 6. Effect of processing variables on the tensile properties of stir-cast alloy: (a) effect of solid volume fraction (V_s = 200 rpm) and (b) effect of stirring rate (f_s = 0.45).

Figure 7. Interrelationship between the empirical and experimental tensile strength of stir-cast alloy.

5. Fabrication of Mg alloy parts for automotive applications [10]

As emphasized earlier, the low density of Mg—approximately two-thirds of aluminium, one-fourth of zinc, and one-fifth of steel—makes it particularly attractive for applications in transportation systems where the weight reduction is critical. It has the best strengthto-weight ratio of any commercially available cast metals and alloys. In addition, Mg can offer many other advantages such as good damping capacity, castability and electromagnetic interference shielding properties.

These characteristics provide opportunities for the automotive industries to meet the current and future demands for fuel-efficient and low emission vehicles. As a result, increasing volumes of Mg alloys are being used in places such as North America, Europe and Japan. The automotive industries in Korea also have strong interest in the application of lightweight Mg alloy parts. Based on such large interest in Mg alloy parts, several large scale R&D projects are being undertaken by the consortium of automotive industries, government, research institutes and universities. Representative R&D projects are: (i) melting and casting technology; (ii) recycling; (iii) design of part and die; (iv) corrosion resistant surface treatment, and (v) development of high strength corrosion resistant alloys, all of which are important for practical application of Mg alloys as automotive parts. Figure 8 shows some typical examples developed as a part of the program.

(a)

(b)

Figure 8. Mg alloy automobile parts: (a) as-cast and (b) after coating treatment.

6. Rapid solidification processing of Mg alloys [11–14]

Rapid solidification processing (RSP) has the potential for substantially improving the strength, ductility and corrosion resistance of Mg alloys. Thus, many efforts to obtain the optimum combination of various properties have been made by using RSP and appropriate alloy design. Especially, rapid solidification of Mg alloys containing small amounts of rareearth elements such as Nd and Y forms Al-Nd or Al-Y intermetallic compounds with high themal stability. Researches at CAAM focus on the development of high strength corrosion resistant rapidly solidified Mg-RE-Al-Zn alloys and ultralight weight Mg-Li base alloys. The alloys are fabricated by using a melt spinning—(pulverization)—extrusion technique. Until now, microstructural characterization of the rapidly solidified alloys has been performed extensively. One of the important results is the formation of an Al-RE compound having a high melting temperature and high resistance to coarsening at high temperature. An example is shown in figure 9. Figure 9 shows a bright field TEM image of a transverse section of as-extruded Mg-5Al-5Zn-5Nd alloy. It reveals that the several nm size particles are present in the Mg matrix. Microdiffraction analysis as well as EDS analysis of the particle show that its nature is $A₁$ Nd. The experimental results show that the $A₁$ Nd particles are thermally stable after heat treatment at 350◦C for 24 hours. Due to the fine dispersion of Al2Nd particles only slight deterioration of mechanical property occurs after heat treatment. The results obtained so far imply that further investigations are needed to analyze the effects of various phases such as quasicrystal-related and $Al₁₁Nd₃$ -related phases, and to obtain the optimum alloy design conditions for rapid solidification processing of Mg alloys. The current research project on the rapid solidification processing of Mg alloy at CAAM is to investigate the characteristics of microstructure and mechanical properties in melt-spun and extruded rapidly solidified alloys wlth various alloy compositions

Figure 9. Bright field TEM image showing as-extruded microstructure of Mg-Al-Zn-Nd; and (insert) selected area electron diffraction pattern taken from the 10–15 nm size particles.

7. Other programs

Besides the above-mentioned research and development programs, there are several other programs currently being conducted at CAAM. These include (1) development of ultralight Mg-Li alloys, (2) rapid solidification processing of Mg alloys, (3) fabrication of Mg based composites by infiltration method, (4) modification of microstructure in Mg-Al-Mn alloys. All of these programs are conducted as collaborative research with national research institutes and related industries.

8. Summary

In this paper, a brief review of recent research and development efforts on Mg alloys at the Center for Advanced Aerospace Materials (CAAM) is reported. As mentioned above, the current projects at CAAM are concerned with both fundamental and practical issues needed for the successful utilization of Mg alloys in various applications. The interest in Mg alloys in Korea has been growing quite rapidly in recent years and it is expected that this will continue. In fact, Mg alloys are currently being considered for applications in high speed railway cars besides the current automotive applications and will find various applications in aerospace systems once the Korean aerospace industries become matured.

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