JMEPEG (2008) 17:297–301
DOI: 10.1007/s11665-008-9201-0

1059-9495/$19.00

Magnesium Powder Metallurgy: Process and Materials Opportunities

Colleen J. Bettles

(Submitted October 24, 2007)

The major efforts in magnesium alloy development for automotive applications have concentrated on creep resistant alloys produced by permanent mould and high-pressure die casting routes. While large components, such as crankcases, will never be produced by powder metallurgy, there are smaller components in and around the powertrain which could be fabricated from powder precursors. This article will explore the potential of some of the more recent powder compaction developments, and discuss the alloy development strategies that emerge for magnesium-based components as a consequence of these process developments. In particular, the viability of direct powder extrusion of semi-finished product, using conventional extrusion or equal channel angular processing, combined with T6 heat treatments, will be considered.

Keywords magnesium, powder metallurgy, precipitation

1. Introduction

In the development of new alloys for specific end applications the researcher draws on his/her knowledge of microstructure/property interactions, which define the various elements of a microstructure that contribute to the development of an optimized mechanical response. In the case of strength and creep properties it is necessary to consider the deformation behavior at both grain boundaries and within the grains.

The strengthening mechanisms in metals are generally concerned with impeding the motion of dislocations. This is achieved by:

- Solid solution strengthening,
- The formation of either coherent, shearable precipitates or non-deformable particles in the matrix (Orowan strengthening), and
- Increasing the number of grain boundaries (i.e., grain refinement which invokes the Hall-Petch effect).

The first two mechanisms rely on controlling the composition and distribution of both the precipitate and matrix phases. This is achieved by manipulating the thermal treatments to promote the best age hardening response possible.

To ensure adequate creep resistance these improvements in strength must be maintained for long periods at elevated temperatures. This could be through a stable size and number of strengthening precipitates, or a suppression of grain growth. In addition, the nature of the grain boundary is important for creep resistance, with grain boundary sliding often being the creep-limiting mechanism in metals such as magnesium, which have a hexagonal crystal structure. This mobility may be impeded by the presence of large intermetallic phases at triple points and along grain boundaries and arrays of fine precipitates on the interfacial dislocations within the boundaries.

Designing a microstructure for both strength and creep resistance is often an exercise in multiple compromises. This is most apparent when considering the grain boundary effects. A decrease in grain size, to improve strength, brings with it an increase in the length of grain boundary in the structure, which, as has been mentioned, may be deleterious to creep behavior. It is extremely difficult to include all these features in any one microstructure, and it is the role of the alloy developer to make best use of the processing route to bring the microstructure as close as possible to the ideal. Traditionally, the application of these alloy design steps to magnesium alloys has concentrated on those processing routes that rely on a molten metal feedstock, and which may or may not lend themselves to solutionizing and aging heat treatments. Conventional age hardening relies on the presence of a super saturated solid solution at elevated temperature, and the precipitation of an intermetallic phase at the aging temperature due to the reduced solubility of the solute element at the lower aging temperature. It is often the case that the most thermodynamically stable phases form during solidification from the melt, and it is not possible to control the morphology and/or distribution of these phases during cooling. Additionally, the stability is such that a solution heat treatment has no effect on these phases, and age hardening is not possible.

Powder metallurgical processing can avoid some of these problems, but can have limitations of its own primarily related to residual porosity. Voids, even at the submicron level, can interfere with diffusion processes and thus impede any age hardening treatment. There are several conventional routes to achieve full densification, some of which rely on the application of external pressure. In the pressureless environment, sintering of the compact to full density is dependent on the

---

This article was presented at Materials Science & Technology 2007, Automotive and Ground Vehicles symposium held September 16-20, 2007, in Detroit, MI.

Colleen J. Bettles, ARC Centre of Excellence for Design in Light Metals, Materials Engineering, Monash University, Clayton, Victoria 3800, Australia. Contact e-mail: colleen.bettles@eng.monash.edu.au.

provision of good diffusion paths—this may be facilitated by the presence of a transient minority liquid phase. In magnesium-based materials this route has its limitations due to the reactive nature of molten magnesium. The alternatives to pressureless sintering are hot pressing and hot isostatic pressing (HIP). HIP in particular is an expensive and relatively time-consuming process, but it can possibly double as the first stage of a solutionizing or aging heat treatment.

The critical requirement for any solution/precipitation reaction is the provision of good diffusion paths, be they along grain boundaries or through the bulk of the material. Some of the less conventional powder compaction techniques, especially those involving the generation of high strains in the materials during processing, can produce compacts with very high green densities and intimate particle-particle bonding. It is these processes that provide the opportunities for the application of microstructural design concepts previously perhaps considered the domain of the molten processing routes.

At this point, the concept of Interference Hardening (Ref 1, 2) should be introduced. When different elements are combined together intimately in the solid state and heating is applied to allow diffusion to take place, concentration gradients can be produced. It may then be possible to generate at least temporarily all phases in the phase diagram, and unusual properties may result. These two effects, when combined, can lead to extensive precipitation with an associated modification of the material properties. The precipitates may also be those that would, under molten processing routes, form during solidification and would be thermally stable during any subsequent heat treatment.

This article will present the opportunities afforded by these less conventional routes, using the Mg-Al-rare earth (AE) alloy systems, to demonstrate the concepts in more detail. The microstructural limitations imposed by the molten routes will be discussed first, as background information to the newer developments. The AE system was chosen over some of the other well-known creep-resistant Mg-alloy compositions for its relative economic advantage. The principles described are, however, not necessarily restricted to those alloys containing aluminum.

2. AE Alloys Processed from Molten Feedstock

The AE family of alloys (AE42 and AE44 in particular) are some of the most creep resistant of the magnesium alloys containing aluminum. The preferred production route for components is high-pressure die casting (HPDC), and this is as much for property development reasons as it is economic. HPDC has a fast cooling rate, which ensures some refinement of the microstructure but even so, in the AE alloys, the microstructure is characterized by relatively equiaxed grains (rather than the strongly dendritic structure associated with Al HPDC alloys) with large intermetallic phases at the boundaries. In HPDC it is possible to form localized closed porosity, which expands on heating often causing blistering, and therefore components are normally used in the as-cast condition. Thus the mechanical properties must be achieved during the casting process. This is in contrast to magnesium-rare earth alloys which can be gravity and permanent mould cast and heat-treated to form a fine dispersion of strengthening precipitates within the magnesium matrix. It is the rare earth-aluminum intermetallic phases in the AE alloys, which form along some boundaries and often appear as eutectic-type structures at triple points, that provide the strength and creep resistance to the alloy. Figure 1 shows the microstructure of HPDC AE42, where the rare earth used is a cerium-rich misch metal. The bulk intermetallic phase (A) is an $Al_{11}RE_3$ phase which, over time at elevated temperatures, decomposes into the more thermally stable Al_2RE and the deleterious $Mg_{17}Al_{12}$. The creep resistance is adversely affected by this decomposition reaction. It has been shown by Powell et al. (Ref 3) that the formation of the $Al_{11}RE_3$ phase is related to the level of Nd in the alloy. If the Nd level is increased at the expense of the La, the primary intermetallic phase can become Al_2RE. The matrix material in either case contains the excess aluminum. Porosity issues aside, if it was possible to carry out a T6 heat treatment, there is little opportunity to further enhance the mechanical properties by the formation of precipitates within the grains, as the intermetallic phases are stable over the times and temperatures usually associated with standard heat treatments, and super saturated solid solutions, which are the prerequisite for age hardening, are not generated.

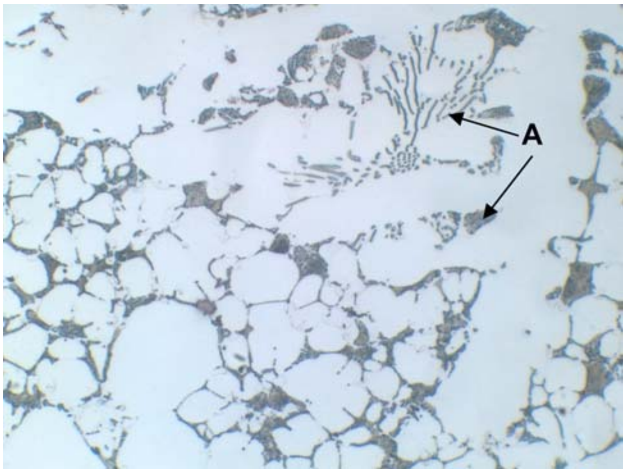

Fig. 1 The microstructure of HPDC AE42 showing the Al-RE intermetallic phases (A) at boundaries

Therefore, to obtain a dispersion of fine precipitates throughout the microstructure in this alloy system, it is necessary to avoid the formation of the stable intermetallic phases during the initial processing. This can only be achieved by solid-state powder metallurgical processing routes.

3. Novel Powder Metallurgical Processing Routes

As already indicated, for powder metallurgical parts to have microstructural integrity it is necessary to have a fully dense material. In conventional processing the green compact, with a relative density of up to 85%, is sintered to realize full densification. Powder surfaces must be clean, or at least able to be cleaned during sintering by say dissolution in the liquid phase or reduction of oxides by appropriate selection of sintering atmosphere. An alternative to sintering is the application of a direct pressure or shear stress to the particles during processing—this can in extreme cases result in cold welding of the particles, but is usually restricted to the formation of an intimate interfacial bond between adjacent particles across which a diffusion path may form. It is this structure that lends itself to novel alloying opportunities. Extrusion is one such processing path where high strains are generated during the processing, and where the surface film on powder particles is broken by the shearing action and highly reactive surfaces are produced. It has been reported that in conventional extrusion, it is usually necessary to have an extrusion ratio (ER) greater than 10 to ensure a fully coherent product (Ref 4). Even higher ratios may be needed to encourage diffusion. The relationship between the ER (initial area/final area) and the homogenized strain resulting from that extrusion is a logarithmic one so that as the desired strain is increased the required ER must increase exponentially. As a consequence of this, the loads that are required also increase dramatically if the final part size is to be maintained. Equal channel angular processing (ECAP) is a relatively new process that can impart a strain of 1.15 as material is deformed by simple shear in a thin layer as it passes from a vertical to a horizontal extrusion channel. In this process the cross-sectional area is maintained throughout. This is currently a batch process and repetitive passes accumulate the strain in the body; however, the loads required are significantly lower than those required for conventional extrusion. The ECAP technique has already been explored in the field of powder compaction (Ref 5-9) and has been found to be very successful in obtaining a high degree of compaction with various metals and alloys at lower temperatures and pressures than those required by conventional compaction techniques. Moss (Ref 10) has shown that magnesium powders can be successfully ECAPed to full density at intermediate temperatures (150 °C) and back pressures, ideally using a powder with an irregular morphology (rather than spherical, as would be obtained by a gas atomization process).

Figure 2 shows the strain intensification and its exponential relationship to the ER for forward extrusion. The line of small circles at an ER of approximately 3 (strain of 1.15, which is achieved in an ECAP die with a 90° internal angle) shows the accumulating strain from successive ECAP passes for comparison. The two circles, at a strain of 4.6, represent the loads required by each process to achieve the final strain. Clearly, the loads for ECAP are significantly lower than those for direct extrusion, and consequently, even though ECAP is a repetitive batch process, the capital cost of the equipment is significantly lower than that required for high ER extrusion processes.

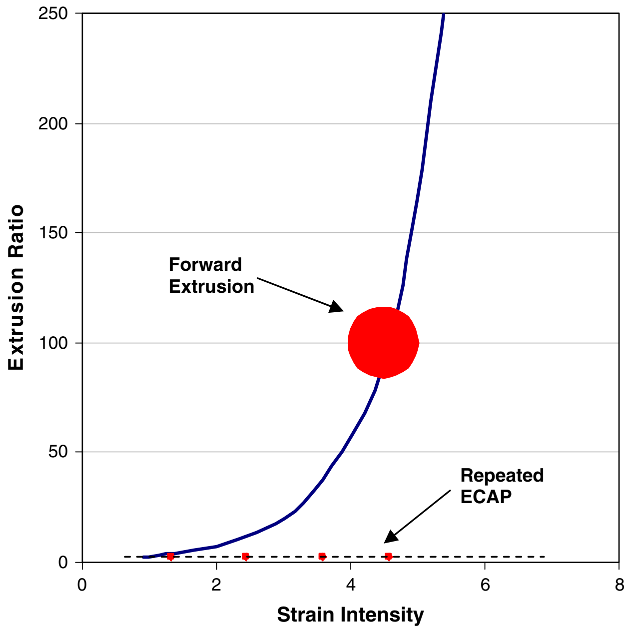

Fig. 2 Relationship between the extrusion ratio and the strain intensity for conventional forward extrusion under ideal conditions

4. Alloy Design Concept

With the emergence of these newer processing routes, alloy design based on interference hardening may become a reality. Consider a model three element system, with a matrix and two alloying additions contained within two solid powder precursor materials. The majority material is an Mg solid solution containing a single solute, X. The minor powder phase is the second alloying addition, Y, present either as the pure element or more preferably as an Mg-rich material. In the selection of Y, the criteria are:

- High solubility in Mg, and
- The diffusion of Y in Mg should not be vastly different to Mg self-diffusion, to minimize any Kirkendall effect. This is an ideal, and there are other strategies to overcome Kirkendall behavior, but an equalization of diffusion should negate the need for these alternatives.There are only a few possibilities for Y, with Al being one of the preferred options.

In considering the third element addition, X, the criteria are:

- A finite solubility in Mg
- (Solubility in Mg)/(Solubility in Y) > 5. This should also mean that as Y diffuses into the Mg solid solution, the solubility of X in Mg will decrease and increase the driving force for precipitation.
- There must be intermetallic phases formed between X and Y.
- (Melting Point Y-X phase)/(Melting point Mg-X phase) > 1.25 (based on the assumption that the higher melting point phase will be the most stable and that interaction forces between X and Y will be greater than those between Mg and X, so that X-Y phase forms preferentially).It is not essential that the precipitation of the Mg-X phase (should it exist) is totally suppressed. There may be cases where the final microstructure will benefit from a mixture of Mg-X and Y-X phases—this depends largely on the final properties demanded by the application.

5. Selecting an Example System and Experimental Validation

Let us now consider the selection of element X. Figure 3 plots both the solubility ratio and the melting point ratio for all elements against atomic number. Both criteria must be met, and in this case those elements meeting both are shown as linked. Fourteen options are possible, with the majority being found between the atomic numbers of 55 and 72 (i.e., the lanthanides).

As an example, alloys in the Mg-Al-Nd system were prepared from powder precursors by ECAP. In this case, there are several Al-Nd intermetallic phases which could possibly form (based on the known phase diagram): Al_2Nd, Al_3Nd, $Al_{11}Nd_3$, AlNd, Nd_2Al, and Nd_3Al. The composition selected, Mg-5wt.%Al-(1 or 2)wt.%Nd, is Al-rich and the most likely phases to precipitate are the first three. The two powder compositions used were Mg-(1 or 2)wt.%Nd and Mg-35wt.%Al (the eutectic composition Mg + $Mg_{17}Al_{12}$). The powders were prepared from solid ingots by filing (irregular morphology, grain size −45 μm)—the Mg-Nd ingot had been solution treated to ensure that all the Nd was in solid solution. The powders were mixed for 10 min prior to ECAPing at 150 °C. The subsequent heat treatments have been at various temperatures, above and below that which could induce incipient melting, for times ranging from 2 to 24 h.

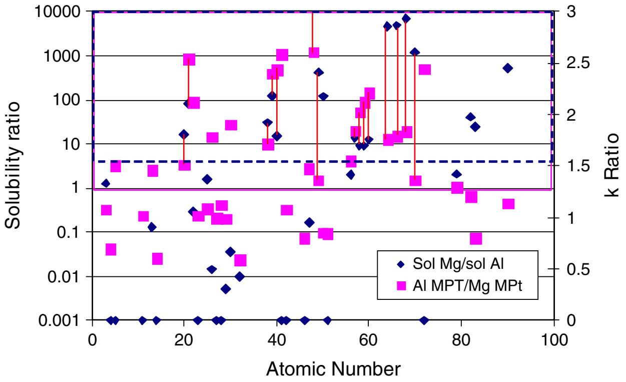

Fig. 3 Plot of solubility ratio and K ratio against atomic number for all possible X alloying elements

Preliminary results obtained from this system are encouraging. A single ECAP pass resulted in relative densities of the order of 99%, with the primary cause of porosity being inadequate bonding between the relatively ductile Mg matrix and the largest hard Mg-Al particles. Solution treatment, therefore, did not reduce the level of porosity. However, where adequate bonding was achieved the solution treatment resulted in dissolution of the Mg-Al particles and diffusion of Al into the Mg-Nd particles. The Al was distributed uniformly throughout, indicating that diffusion was possible not only at Mg-Al/Mg-Nd interfaces but also at Mg-Nd/Mg-Nd interfaces (where oxide layers could conceivably exist). Further ECAP passes and modifications to particle size distributions are being examined at the present time.

The transmission electron microscope (TEM) micrographs of Fig. 4(a)-(c) are taken from some of this preliminary work. Figure 4(a) and (b) are after a treatment at 500 °C, which did result in increased porosity due to a small amount of melting. The beam directions are ⟨10-10⟩ and ⟨11-20⟩ respectively. Whilst these directions are 30° apart, they are both contained within the basal plane of the Mg matrix and therefore any precipitates with a basal habit will be viewed “edge on” in

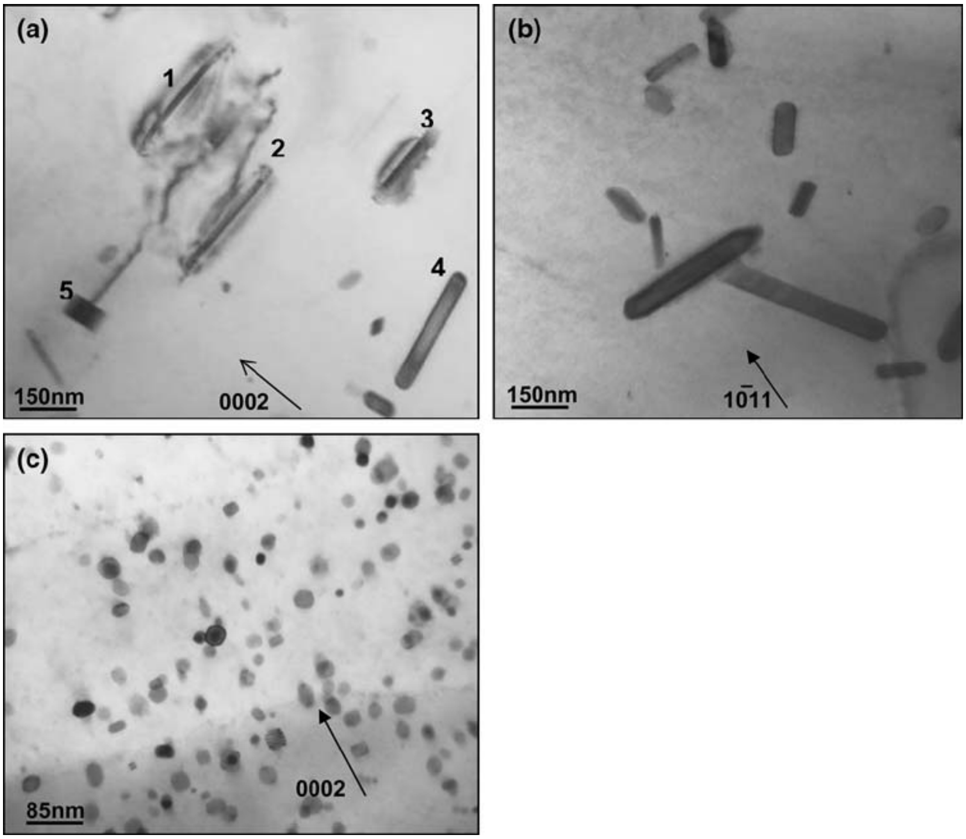

Fig. 4 TEM micrographs showing various precipitate morphologies: (a) 500 °C treatment, beam direction approximately ⟨10-10⟩; (b) 500 °C treatment, beam direction approximately ⟨11-20⟩; and (c) 420 °C treatment, beam direction approximately ⟨11-20⟩

these two micrographs. In Fig. 4(a) precipitates 1-3 are all parallel, lying on the basal plane, and have an aspect ratio (AR) of greater than 10 and a length of between 150 and 300 nm. Precipitate 4 has a different AR, and does not have the conventional basal habit, and precipitate 5 is indeed lying at 90° to this. Figure 4(b) is confirmation that the precipitates formed have several distinctly different habit planes and growth directions—unlike most more conventional precipitation hardening systems where a single family of precipitate predominates. Not all the precipitate types have been identified at present. The majority can be identified as Al_3Nd, but the orientation relationships are many and complex. Figure 4(c) is an image of a sample treated at 420 °C for 24 h. The precipitate density is significantly increased, and the size of the precipitates has reduced by a factor of approximately 10. This refinement of the precipitating phases is beneficial in terms of mechanical property development.

This microstructure is totally different to that generated through HPDC. There are no large intermetallic particles at boundaries, other than those which may be retained after the solution treatment of the Mg-Nd powder prior to processing, and in this case the phase would most likely be $Mg_{12}Nd$. The grain boundaries have not been investigated in detail at this time, and it is therefore not known whether there is a precipitating phase at the boundaries that can suppress sliding during any deformation process.

6. Discussion

Interference hardening was reported more than 50 years ago and it is time that its application to current powder metallurgy techniques is reassessed. In the initial work, a high ER process was required, presumably to ensure adequate densification and to supply a sufficiently high dislocation density to facilitate diffusion of the alloying elements. ECAP is currently a batch process, but has the advantage over direct extrusion that initial dimensions are retained and high strains are induced into the microstructure with each pass. Whilst multiple passes are needed to achieve the same nominal strain as the direct extrusion process (ER = 40), it has been shown that even a single ECAP pass will give porosities of less than 1% and also provide adequate diffusion for precipitation hardening to occur. The example system, Mg-Al-Nd, provided a range of precipitate morphologies and orientation relationships without undue optimization of the heat treatment cycles. It should be possible, therefore, to generate microstructures with multiple precipitating phases, leading to optimized morphologies and number densities, by judicious selection of the alloying elements and heat treatments. The ECAP process is currently restricted to semi-finished product for the manufacture of small components, and its being a batch process is likely to restrict scale up to larger components. However, there are processes available that produce a similar strain distribution and are considered to be continuous in nature. It is the application of interference hardening to these processes that is of most interest, and which could lead to the wider acceptance of PM Mg components.

Acknowledgment

The author wishes to thank M. Moss for the preparation of the ECAPed samples.

References

1. R.S. Busk and T.E. Leontis, The Extrusion of Powdered Magnesium Alloys, *Trans. AIME*, 1950, **188**, p 297–306
2. G.S. Foerster, Dispersion Hardening of Magnesium, *Met. Eng. Quart.*, 1972, **12**(1), p 22–27
3. B.R. Powell, V. Rezhets, M.P. Balogh, and R.A. Waldo, Microstructure and Creep Behavior in AE42 Magnesium Die-casting Alloy, *JOM*, 2002, **54**(8), p 34–38
4. U. Stahlberg and H. Keife, A Powder-compaction Model and its Application to Extrusion, *J. Mater. Proc. Technol.*, 1992, **30**, p 143–157
5. K. Matsuki, T. Aida, T. Takeuchi, J. Kusui, and K. Yokoe, Microstructural Characteristics and Superplastic-like Behavior in Aluminum Powder Alloy Consolidated by Equal-channel Angular Pressing, *Acta Mater.*, 2000, **48**, p 2625–2632
6. K. Xia and X. Wu, Back Pressure Equal Channel Angular Consolidation of Pure Al Particles, *Scripta Mater.*, 2005, **53**, p 1225–1229
7. O.N. Senkov, S.V. Senkova, J.M. Scott, and D.B. Miracle, Compaction of Amorphous Aluminum Alloy Powder by Direct Extrusion and Equal Channel Angular Extrusion, *Mater. Sci. Eng. A*, 2005, **393**, p 12–21
8. R. Lapovok, D. Tomus, and B.C. Muddle, Compaction of Ti-6Al-4V Powder by ECAE with Back Pressure, *Proceedings of 4th International Conference on Advanced Materials and Processing*, Hamilton, New Zealand, 2006
9. S. Xiang, K. Matsuki, N. Takatsuji, M. Tokizawa, T. Yokote, J. Kusui, and K. Yokoe, Microstructure and Mechanical Properties of PM 2024Al-3Fe-5Ni Alloy Consolidated by a New Process, Equal Channel Angular Pressing, *J. Mater. Sci. Lett.*, 1997, **16**, p 1725–1727
10. M. Moss, R. Lapovok, and C.J. Bettles, The ECAP of Magnesium and Magnesium Alloy Powders, *JOM*, 2007, **59**(8), p 54–57