THERMAL EFFECTS OF CALCIUM AND YTTRIUM ADDITIONS ON THE SINTERING OF MAGNESIUM POWDER

Paul Burke[1], Chloe Petit[2], Sonia Yakoubi[2] and Georges J. Kipouros[1]

[1] Dalhousie University, 1360 Barrington Street, PO Box 1000, Halifax, NS, Canada, B3J 2X4

[2] ICAM, 75 avenue de Grande-Bretagne, 31 300 Toulouse, France

Keywords: magnesium powders, magnesium powder metallurgy, sintering phenomena

Abstract

The low density and good mechanical properties make magnesium and its alloys attractive materials for use in automotive and aerospace applications. Powder metallurgy P/M can be used to alleviate the formability problem through near-net-shape processing, and also allows unique chemical compositions that can lead to new alloys with novel properties. However, the surface layer formed on the Mg powders during processing acts as a barrier to diffusion and sintering is problematic. The layer, characterized using focused ion beam milling and transmission electron microscopy (FIB-TMS), as well as x-ray photoelectron spectroscopy (XPS), contains oxides, hydroxides and carbonates of magnesium, formed by reactions with the atmosphere. To overcome this barrier, small additions were made of calcium and yttrium the oxides of which are thermodynamically more stable than magnesium oxide. The present work reports on the thermal effect of Ca and Y additions to magnesium powder during sintering, utilizing differential scanning calorimetry (DSC).

Introduction

In the past quarter of a century the increasing cost of energy and increased environmental awareness have lead to a global requirement for the reduction of automotive emissions. One strategy for the reduction of emissions is to reduce the gross weight of vehicles. As the weight is decreased, less fuel is consumed to propel the vehicle. The average vehicle in 1977 had a mass of 3665.5 lb, and in 2001 the average weight had been reduced to 3309.0 lb; an over 300 lb reduction [1]. Among the principal reasons for the weight reduction was the increased use of lightweight materials, especially aluminum. In the same 24 year period, the average amount of Al utilized per automobile climbed from 97 lb to 256.6 lb. The driving force behind the increased usage can be attributed to the intense research effort put forth to provide over 1600 aluminum alloys from multi-component systems and numerous production and fabrication improvements. More recently, aluminum products processed via powder metallurgy (P/M) routes have shown excellent properties and are increasing in utilization.

Magnesium, which has the lowest density of all structural metals, has not enjoyed the phenomenal increase in average mass per vehicle that aluminum has, but had an exceptional growth of 850%. Unfortunately, the actual amounts went from under 1 lb in 1977 to 8.5 lb in 2001. Aside for low density, magnesium has a number of other advantageous properties: Its stiffness to weight ratio is very high; one pound of magnesium is as stiff as 1.8 lb of aluminum and 2.1 lb of steel; the dimensional stability and damping capacity are high, it is easily machined and can be readily recycled [2]. For magnesium to penetrate the automotive industry as a structural material several requirements need to be met [3].

Magnesium has poor corrosion resistance due to heavy metal contamination [4] and lacks a catalogue of developed alloys [5]. The use of magnesium in under the hood components is also hindered by the low creep resistance of existing commercial alloys [2]. Also, magnesium has a hexagonal close packed (HCP) crystal structure, which leads to difficulty in forming, especially at room temperature [5].

Magnesium Powder Metallurgy

Powder metallurgy can be used to alleviate one of the largest problems with magnesium utilization, formability, with its inherent near-net-shape processing. Raw magnesium powders of a 75 μm typical size are blended with alloying elements and compacted in a die at high pressure. The "green" compacts are then sintered in a controlled atmosphere at a temperature lower than the melting point, but high enough to allow rapid diffusion between the powder particles. The method in which powders are produced allows unique chemical compositions that can lead to new alloys with novel properties [6, 7].

For magnesium P/M to compete on a level with aluminum P/M, simple, industrially relevant processing using existing P/M equipment is necessary. Because the economics of P/M require high volume, a robust process utilizing uni-axial compaction and mesh belt furnaces is needed to compete with established magnesium production methods like die casting.

The major issue in the development of the magnesium P/M is the availability of commercial magnesium powders. Unlike aluminum most commercial magnesium powders are produced by mechanical grinding. The low cost and less restrictive requirements for the main intended use of magnesium as a reactant make grinding attractive. For P/M applications the angular morphology of the powder gives good green strength because of mechanical interlocking, but the powder particles are typically covered by a thick surface layer. The layer is hypothesized to contain primarily oxides, but hydroxides, carbonates and hydrates are possible due to long exposure to atmospheric conditions during the grinding process. Recently magnesium powder was also produced commercially by centrifugal inert gas atomization by a small number of companies. The product has very little surface oxidation due to the inert conditions maintained during production and shipment, but the spherical morphology gives poor green strength. No fundamental studies of the sintering behaviour of magnesium powders have been completed to date, but preliminary studies have been reported [8, 9, 10, 11]. The goal of the present study is to determine if the surface layer is in fact the main obstacle to producing magnesium P/M parts without the addition of secondary hot working, by looking solely at solid state sintering

of pure magnesium powders. A new surface characterization technique, focused ion beam/transmission electron microscopy (FIB/TEM), was applied to identify the nature of the surface layer [10] with very promising results.

A method for disrupting the surface layer is to add a small amount of a more reactive metal. During sintering, the additive reacts with the surface of the surrounding base powder, reducing the oxides of the base to pure metal and forming its own oxide. While the total amount of oxide is still the same, the cohesive layer that was the barrier to diffusion has been disrupted, providing pathways for unimpeded diffusion. This technique is used successfully in aluminum P/M [12], where a small amount of magnesium results in an increase in density and mechanical properties. In the case of magnesium P/M, calcium has shown promise as a surface layer reducing alloy addition [11]. Yttrium has also been identified as a possible reductant.

If the alloy being sintered has one or more lower melting point additions, a liquid phase forms during sintering. The liquid flows through the inter-granular space, and if the matrix is soluble in the liquid, the liquid acts as a diffusion bridge between adjacent powder particles. The presence of the liquid phase can make use of cracks or pores in the surface layer that may not have been located at a point contact. Because of this, there are many more areas for diffusion to proceed, and sintering is much more rapid. However, if the liquid is also soluble in the matrix, the liquid phase is termed transient, and will be absorbed into the matrix at some point and can no longer assist the sintering. Previous studies have shown that Ca [11] and Al [13] have the ability to form transient liquid phases during the sintering of Mg P/M, with Ca having the additional benefit of disrupting the surface layer of Mg. According to phase diagrams yttrium will also form a transient liquid during sintering, and enjoys the dual benefit of surface layer disruption. In the case of Ca and Y, transient behaviour is preferred because solubility in the Mg matrix will allow greater mobility and therefore interaction with the surface layer.

Traditionally sintering of P/M magnesium alloys has been completed in inert argon environments to provide the best protection from oxidation during the time at high temperature [8, 9, 10, 11]. However, it has been shown that in the case of aluminum P/M alloys [14], sintering in semi-inert nitrogen is beneficial because gases trapped in pores to react with Al to form nitrides, which then lowers the partial pressure of gases inside the pore. This reduced pressure allows the pore to be filled during sintering, and increases the final density. It was also found that the nitride formed on grains was more readily wet by the liquid phase allowing the liquid phase to travel more easily. If similarly beneficial nitrides are formed during the sintering of P/M Mg alloys, perhaps superior properties can be achieved by sintering in nitrogen.

The objective of this research is to improve the attractiveness of magnesium through non-traditional processing, by producing magnesium alloys via powder metallurgy utilizing the industrially dominant process of cold die compaction and controlled atmosphere sintering. The addition of calcium and yttrium to the base Mg powder has the potential to reduce oxides in the surface layer and create pathways for rapid diffusion, as well as assisting sintering with the formation of a liquid phase. Sintering under a nitrogen atmosphere may allow the formation of beneficial nitrides, resulting in improved densification. This work focuses on the initial steps of investigating the effects of Ca and Y additions, and a N_2 atmosphere by simulating sintering conditions and tracking thermal response utilizing a differential scanning calorimeter (DSC)

Experimental

Materials

Tangshan Weihao Magnesium Powders supplied the centrifugally atomized pure magnesium powder of 98.02 % active magnesium content, which had an average particle size of 38 μm. Pure calcium granules 99% were supplied by Acros Organics, and had an average particle size of 2mm. The granules where reduced to 100 μm through grinding a screening under inert conditions. Acros Organics was the manufacturer of the Y powder, which was -325 mesh size. All powders were characterized by laser Malvern size analyzer in water to determine the size distribution.

Methodology

Blending. Calcium and yttrium containing Mg alloy powders were mixed under a controlled atmosphere and sealed in an appropriate container. Blending was done in a Turbula mixer/shaker for 10 minutes.

Differential Scanning Calorimetery. Tests were completed using a SDT – Q600 DSC/TGA manufactured by TA instruments. All specimens were heated from room temperature to 600°C at a rate of 10°C/min under flowing nitrogen (100ml/min). Experiments were run with loose powder settled in the crucibles by light tapping.

Crucibles. Standard crucibles used for the DSC are alumina, and will be reduced by the highly reactive Mg, Ca and Y metals. Crucibles were gold coated by sputtering to minimize any interaction at temperatures of interest, and used for both the empty reference and sample containing crucibles.

Results and Discussion

There are several possible reactions between magnesium and atmospheric gases that may form compounds found in the surface layer covering Mg powders. Using FACTSage thermodynamic software, the plausible reactions are:

$$Mg + O_2 = MgO$$

$$Mg + CO_2 = MgCO_3$$

$$Mg + H_2O = Mg(OH)_2$$
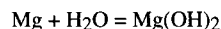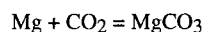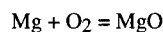
Of those compounds formed, $MgCO_3$ and $Mg(OH)_2$ have decomposition reactions that become spontaneous below the melting point of magnesium. FACTSage was utilized to estimate the decomposition temperatures:

$$Mg(OH)_2 = MgO + H_2O \qquad \sim 260°C$$

$$MgCO_3 = MgO + CO_2 \qquad \sim 450°C$$

Reduction to elemental Mg would be more beneficial, but is not possible below the melting temperature of Mg. However, the

disruption to the surface layer caused by the decomposition may well expose areas of Mg underneath the layer, allowing for better diffusion between adjacent particles during sintering of P/M parts.

Pure Magnesium

The DSC trace of pure magnesium powder is shown in Figure 1. Area (A) shows a slight decrease in slope begging around 260°C, indication that an exothermic reaction is taking place. This co-insides with the FACTSage estimated decomposition of $Mg(OH)_2$. Area (B) shows a larger exothermic peak at ~450°C, the estimated decomposition temperature of $MgCO_3$. Although **area (C) is beyond the temperature of interest, it is prudent to note** that the large endothermic peak starting at ~540°C is likely the formation of Mg-Au compounds from the sample reacting with the gold crucible coating, and the inflection at 575°C corresponds to the eutectic liquid formation of Mg-Au.
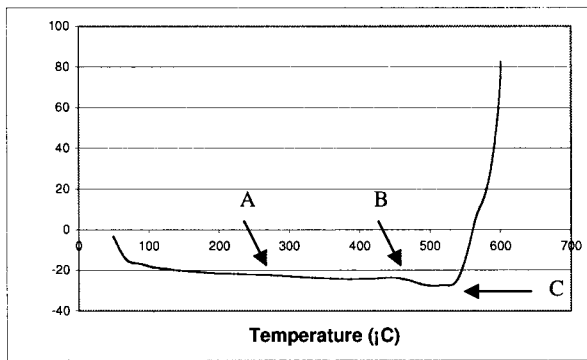
Figure 1 – DSC trace of pure magnesium powder heated from ambient to 600°C at 10°C/min. Area (A) represents hydroxide decomposition, area (B) carbonate decomposition. Area (C) is the formation of Mg-Au compounds followed by Mg-Au eutectic liquid formation.

Magnesium + 1wt% Calcium

Figure 2 shows the DSC trace of magnesium with a 1wt% addition of calcium. The presence of calcium, which is a more reactive metal than magnesium, disrupts magnesium surface layer through the following reactions:

$$MgO + Ca = Mg + CaO$$

$$Mg(OH)_2 + Ca = Mg + Ca(OH)_2$$

$$MgCO_3 + Ca = Mg + CaCO_3$$
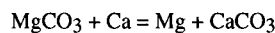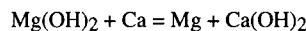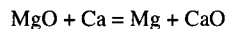
In this case, not only do the reaction disrupt the cohesiveness of the surface layer, but the product is elemental Mg. The total amount of impurity does stay the same as now Ca is taking the place of Mg with the impurities. Since these reactions are spontaneous at any temperature, they are controlled by kinetics and are more difficult to estimate.

Area (A) at ~120°C indicates a slope decrease similar to that of the hydroxide decomposition for the pure Mg samples that may be the conversion of $Mg(OH)_2$ to $Ca(OH)_2$. The decomposition

reaction for calcium hydroxide is possible below the melting temperature, but at relatively high temperature of 516°C. Area (B) indicates the possible Mg to Ca carbonate reaction at roughly 310°C. Area (C) corresponds to the lowest melting Mg-Ca eutectic at 445°C. Beyond that temperature, there is another Mg-Ca eutectic at 516°C and also the same Mg-Au reactions with the crucible are possible. The larger endothermic heat flow at 600°C compared to the pure Mg samples points to the combination of a ternary Mg, Ca and Au melting.

Magnesium + 2wt% Yttrium

Figure 3 shows the DSC trace of a mixture of pure magnesium with 2wt% yttrium. The $Mg-O_2-H_2O-CO_2-Y$ system is different from the Ca system because Y it is more reactive than Ca, and also it has only the ability to decompose the oxide of magnesium, but not the hydroxide or carbonate.

Examining Figure 3 shows little is happening up to 500°C. There are no exothermic peaks indicating hydroxide or carbonate decomposition, whether they stem from the effect of yttrium or are the basic reaction as shown in the pure magnesium case. It would seem that the presence of yttrium may be detrimental in this case, as it does not allow the surface layer disruption caused by the decomposition of magnesium hydroxide and carbonate to MgO. Beyond 500°C, there is a Mg-Y eutectic at 567°C, and the Mg-Au eutectic that contribute to the large endothermic peak in that area.
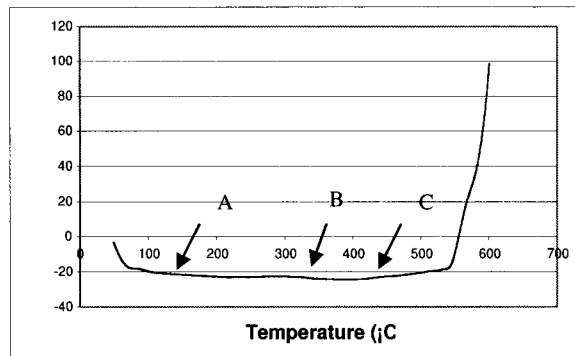
Figure 2 – DSC trace of magnesium with 1wt% calcium heated from ambient to 600°C at 10°C/min. Area (A) represents hydroxide decomposition, area (B) carbonate decomposition. Area (C) is the Mg-Ca eutectic liquid formation.

483
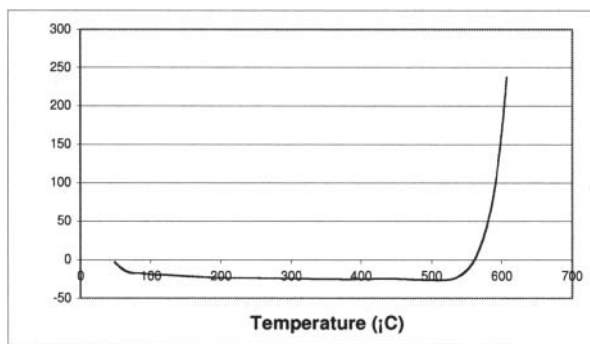
Figure 3 - An optical microscopy micrograph of the boundary between the eutectic liquid and the equi-axed regions. Calcium rich area at left.

Conclusions

In this work, differential scanning calorimetry was used to simulate sintering conditions to examine the thermal effects on the magnesium surface layer, with and without the sintering aids calcium and yttrium. Estimations using the FACTSage software suggested the presence of oxides, carbonates and hydroxides of magnesium. It was found that the process of heating the pure magnesium powder from room temperature to 600°C allowed for the spontaneous decomposition of the hydroxide and carbonate to oxide, which may disrupt the cohesiveness of the layer and allow better diffusion between particles.

Additions of calcium allow earlier and more complete surface layer disruption by forming calcium hydroxide and carbonate in the place of the original magnesium hydroxide and carbonate.

Yttrium additions, while having the greatest potential to reduce the oxide of magnesium, do not react with magnesium hydroxide or carbonate, and it appears to prohibit the decomposition of those compounds to MgO as well.

Acknowledgments

References

1. "State of the North American P/M industry", International Journal of Powder Metallurgy, 37, 2001, 36.

2. M.M. Avedesian and H. Baker, Editors, "ASM specialty handbook, magnesium and magnesium alloys", ASM International, Materials Park, OH, 1999.

3. G.J. Kipouros, "Bringing Magnesium to Automobiles", Materials Solutions for Environmental Problems, The Metallurgical Society, The Canadian Institute of Mining, Metallurgy and Petroleum , Ed.H. Mostaghasi, Sudbury, Ontario, Canada, August 17-20, 1997, 265-267.

4. E. Ghali, W. Dietzel and K-U. Kainer, "General and Localized Corrosion of Magnesium Alloys: A Critical Review", Journal of Materials Engineering & Performance, 13, 2004, 7-23.

5. C.J. Bettles and M.A. Gibson, "Current wrought magnesium alloys: strengths and weaknesses", Journal of Metals, 57, 5, 2005, 46-49.

6. C.W. Hennessey, W.F. Caley, G.J. Kipouros and D.P. Bishop, "Development of Al-Si-Base P/M Alloys", International Journal of Powder Metallurgy, 41, 2005, 50-63.

7. G.J. Kipouros, W.F. Caley, and D.P. Bishop, "On the Advantages of Using Powder Metallurgy in New Light Metal Alloy Design", Metallurgical and Materials Transactions A, 37A, 12, 2006, 3429-3436.

8. P. Burke, D. Fancelli and G. J. Kipouros, "Investigation of the Sintering Fundamentals of Magnesium Powders", Ed. M.O. Pekguleryuz, Light Metals in Transport Applications, COM 2007, Toronto, 2007, 183-195.

9. P. Burke, D. Fancelli. V. Laverdiere and G. J. Kipouros, "Sintering Fundamentals of Magnesium Powders", Canadian Metallurgical Quarterly, 48, (2), 2009, 123-132.

10. J. Li, G.J. Kipouros, P. Burke and C. Bibby, "Investigation of surface film Formed on Fine Mg Pacrticles", Microscopy & Microanalysis, VA, USA, July 26-30, 2009.

11. P. Burke and G.J. Kipouros, "Powder Metallurgy of Magnesium: Is it Feasible?", Ed. Sean R. Agnew, Magnesium Technology 2010, TMS 2010, Seattle, 2010, 115-120.

12. Lumley, R. N., Sercombe, T. B. and Schaffer, G. B. "Surface oxide and the role of magnesium during the sintering of aluminum". Metallurgical and Materials Transactions A, 30, 2, 1999, 457-463.

13. P. Burke, "Development of Magnesium Powder Metallurgy AZ31 Alloy Using Commercially Available Powders", M.A.Sc. Thesis, Dalhousie University, Halifax, NS, Canada, 2008.

14. G.B. Schaffer, B.J. Hall, S.J. Bonner, S.H. Huo, T.B. Sercombe, "The effect of the atmosphere and the role of pore filling on the sintering of aluminium", Acta Materialia, 54, 1, 2006, 131-138