

The Effect of Composition and Milling Conditions on the Structure of Mechanically Alloyed Mg-Al Based Alloys

ABSTRACT

Mg-Al based alloys were mechanically alloyed under varying conditions. Elemental reaction times correlated with known diffusion coefficients and elemental hardness, but milling temperature had almost no effect over a 200 °C range. Increasing impact energy caused the steady state level of crystallinity to increase. Alloys with up to 6 at% of Ti, Y, Ca, Zr, V, Er, or Pr yielded amorphous alloys near the composition Mg₄₀Al₆₀. Certain phases were suppressed by mechanical alloying, while others became more dominant than in the equilibrium phase diagram. These effects are explained by DSC results which indicate they are growth rate controlled during mechanical alloying. Hard elements such as Cr and Mo with positive free energy of mixing did not react completely even after relatively long milling times.

I. INTRODUCTION

There has recently been growing interest in Mg-containing amorphous^{1,2,3} or crystalline^{4,5} alloys prepared by mechanical alloying (MA), as well as both amorphous^{6,7,8} and crystalline^{9,10} Mg alloys by rapid solidification. Due to the density advantages of Mg alloys for structural applications it was deemed worthwhile to see if mechanical alloying could produce amorphous alloys with enhanced mechanical and high temperature properties, and improved corrosion resistance if possible. An amorphous phase has been reported near Mg₃₈Al₅₇Ca₅¹ and now has been found with other elements in place of Ca.

II. EXPERIMENTAL PROCEDURES AND ANALYSIS

Many of the experimental details have been described previously. Three 5/8" steel balls were normally used for milling, though initially three 1/2" balls and two 1/4" balls were used. Larger vials were also made from the same heat treated S5 tool steel to permit use of three 13/16" balls for more intense processing. Powders were loaded into the vial in an argon glovebox, usually at around 10 - 20 ppm O₂. Run times ranged from 0.25 to 100 h. Early Mg-Al-Ca runs were done at -100 °C or -150 °C. The vial was cooled by a liquid nitrogen stream

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while shaking, using a temperature controller with 36 gauge thermocouples mounted on the vial. The exterior vial temperature was controlled to within 2 °C at the thermocouple and 10 °C over the vial's exterior. The temperature inside the vial was found to be within 3-5 °C of the control temperature. O-ring seals leaked at low temperature and were replaced by copper-sealed vacuum flanges. For runs at ambient the vial temperature was around 40 - 60 °C.

The total amount of powder milled ranged from 0.5 to 2.5 g in standard vials, and 5 to 7.5 g in the large vials. Powder masses larger than these resulted in inhomogeneous processing. A thin adherent layer was always present on the walls and media, in addition to some free powder. The powder thickness on the balls and vial was found to be about equal. The ratio of free to total mass was constant at 36 ± 1 % for 0.5 to 2.5 g powder mass. The structure was determined by x-ray diffraction, using Cu K_{α} radiation from a Phillips PW1729 generator with a Norelco diffractometer equipped with a graphite exit beam monochromator and a Nicolet L11 powder diffraction system. X-ray diffraction patterns of free and adherent powders were identical for powder masses up to about 2.0 - 2.5 g in a standard vial using three 5/8" dia. balls, so 2 g was chosen as a maximum for further work. Powder density was measured to better than 0.1% accuracy using a Micromeritics Accupyc 1330 helium pycnometer. Vickers microhardness measurements were made using a Wilson Tukon 300 microhardness tester with a 25 g load, after embedding the powder in epoxy and polishing with 1 μ m alumina. Oxygen analysis by fast neutron activation was also performed, and levels in Mg and Ca were about 1.0 and 0.9 wt% respectively, but about 0.01 wt% in Al and 0.07 wt% in Ti powders. Overall oxygen content was typically about 0.4 wt% before milling, and about 0.7 wt% after. Oxygen in the vial atmosphere was negligible, so the extra oxygen was evidently acquired on exposure to air after milling.

The densities of amorphous alloys containing Ca, Ti, or Y were compared to theoretical densities using the volume form of Vegard's law,

$$v = x\Omega_{\text{Mg}} + y\Omega_{\text{Al}} + z\Omega_{\text{M}} \quad (1)$$

where v is the molar volume, x , y , and z are in at%, Ω_i is the molar volume of pure element i , and M is the glass-forming element. The ratio of the experimental density to the theoretical

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density was 0.994 for a $\text{Mg}_{39}\text{Al}_{58}\text{Ti}_3$ alloy, 1.000 for a $\text{Mg}_{39}\text{Al}_{58}\text{Y}_3$ alloy, and 1.019 for a $\text{Mg}_{38}\text{Al}_{57}\text{Ca}_5$ alloy.

When $\text{Mg}_{54}\text{Al}_{36}\text{Ca}_{10}$ was milled at $-100\text{ }^\circ\text{C}$ for 4 h from either prealloyed $\text{Mg}_{17}\text{Al}_{12}$ and Ca or from elemental powders, the x-ray diffraction patterns were almost identical. This shows that MA leads to a unique steady-state result after sufficient time (under 4 hours in this case), regardless of initial state, as others have found¹¹. X-ray intensities were measured by least squares fitting of each diffraction scan to a sum of Pearson VII functions¹², which can vary between a Cauchy and Gaussian shape according to the shape parameter. This parameter was fixed at a best value for each phase where possible to allow comparison across alloying conditions. The asymmetric main amorphous peak was fitted using a sum of two Pearson functions.

III. RESULTS AND DISCUSSION

A. Effects of Processing Variables on Structure

1. Milling Time

The effect of milling time, temperature, powder mass, and ball size was studied in $\text{Mg}_{38}\text{Al}_{57}\text{Ca}_5$. Considering milling time first, Figure 1 (a) to (d) shows that crystalline peak intensities decrease as amorphous peaks grow in intensity. The amorphous phase is already present at 0.25 h; the pattern cannot be fit well without it.

Figure 2(a) shows the integral width of the Al (200) peak, corrected for instrumental and K_{α} broadening. It increased rapidly during the first hour, then approached a plateau. Without higher order lines the linewidths cannot be used to determine the relative contributions from strain and size broadening. However in the data of Hong et al¹³ on Ni_3Fe at $23\text{ }^\circ\text{C}$ the strain width W_e and width from crystallite size W_s are highly correlated, and the geometric mean of the ratio W_e/W_s is 0.9. In the results of Schulz et al¹⁴ on Ni-Zr alloys the geometric mean ratio in the early stages of processing is 1.8 (with larger scatter), and for Oehring et al¹⁵ on Ti-Al alloys (closer to the present alloy) the ratio is 2.5 (with much larger scatter). Assuming an approximate ratio of 2, with Cauchy size and Gaussian strain broadening¹⁶, the calculated crystallite size is shown in Figure 2(b). A few TEM observations of the $\text{Mg}_{38}\text{Al}_{59}\text{Ca}_5$ alloy after 1/2 h of milling,¹⁷ when

Figure 3 shows the amorphization reaction is more than half complete, show a few largely unreacted Al layers with grains flattened in the plane of the layer to a thickness/width aspect

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ratio of about 0.4 and grain sizes averaging 80 nm, layer remnants with an average spacing of 125 nm composed of only 1 or 2 grains with grain sizes ranging from 40 to 100 nm, and small thin isolated Al crystallites with aspect ratios of about 0.3 and grain sizes of 7 to 70 nm which are also spaced 100 - 150 nm apart. These observations are in reasonable agreement with the fitted grain size of 65 nm at ½ h in Figure 2(b). We will take the mean layer spacing at ½ h as 125 nm.

Figure 3 shows the summed intensity of the Al peaks, falling rapidly before 1 h then decreasing very slowly. The Al phase is almost dominant at compositions as close as $Mg_{29}Al_{68}Ca_3$ (see Figure 9, where the amorphous and Al phases coexist to the left of the amorphous region). Therefore the lingering Al intensity after 1 h may result from residual Al-rich regions persisting until the concentration profile becomes nearly uniform, exacerbated by slowdown in the rate of size decrease as seen in Figure 2(b).

Figure 3 also shows the growth of the amorphous peak intensity, virtually complete after the first hour, which is very rapid compared to many transition metal alloys.¹⁸

In Mg-Al-Ca alloys the three elements reacted at different rates. In Figure 3 the Ca lines disappeared before 0.25 h, and Mg lines at about 0.8 h, vs. about 1 h for the majority of the Al. The reaction times for Ti, Y, V, Zr, or rare earths substituted for Ca ranged up to 8 hours. Cr and Mo never fully reacted even after milling for as long as 100 h. Several reasons for the differences in reaction time are possible. Assuming the elemental particles take on a lamellar topology over time, one significant factor should be the elemental diffusion rate. The analysis is complicated by several factors, however. First, a bulk diffusion coefficient measured at elevated temperature can underestimate by several orders of magnitude the diffusion rate near room temperature where diffusion in grain boundaries and dislocations dominates. Moreover diffusion rates depend on concentration, which varies throughout a particle. In addition reported diffusion coefficients have uncertainties sometimes approaching an order of magnitude.

In order to compare actual and theoretical diffusion distances we need to know the lamellar repeat distance or spacing λ as a function of time, or equivalently the strain $\varepsilon = \ln(\lambda/\lambda_0)$ where λ_0 is the initial value. For two element layers of equal thickness $\lambda/2$, the layer half thickness required to mix from each interface is $d = \lambda/4$. Now for a given strain rate $\frac{1}{2} \frac{d\varepsilon}{dt}$,

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the lamellar spacing decreases exponentially (with a time constant $\mathbf{t} = -1/\dot{\epsilon}^{1/2}$ for a fixed strain rate), carrying the atoms inward in opposition to their outward motion by diffusion, and resulting in a steady state diffusion profile with constant half-thickness w . This width w will be of the order of the diffusion distance $(D\mathbf{t})^{1/2} = (-D/\dot{\epsilon})^{1/2} = (-Dd/\dot{d})^{1/2}$ that occurs during the time \mathbf{t} needed for the layer thickness to shrink by $1/e$, where D is the diffusion constant and $\dot{d} = dd/dt$.

When d shrinks to about $(-Dd/\dot{d})^{1/2}$ the mixing will begin to approach completion. Full data on λ is unavailable, so we will make use of the crystallite size to very roughly approximate the distance $\lambda/2$ between original elemental interfaces (though crystallite size should decrease more rapidly with time than $\lambda/2$ does). Thus the curve in Figure 2(b) was used to approximate $2d$, after correction by a multiplicative factor of 0.96 to the observed value at $1/2$ h. The approximate distances d and w are compared in Figure 4. Setting them equal results in

$$D \approx -d \dot{d} \quad (2)$$

to give the diffusion rate required. No more than an order of magnitude agreement could be expected at best, due to the uncertainties in diffusion rate in addition to the approximations above. There is also a large experimental uncertainty in the actual Cu reaction time. Thus Figure 4 shows a surprisingly good correlation, except that the actual diffusion distances exceed the calculated diffusion distances by a factor of about 1500, an indication of enhanced diffusion due to excess vacancies,¹⁹ or possibly mechanical mixing,²⁰ though the latter should not correlate with diffusivity. The diffusion coefficients used were primarily those for tracer impurity diffusion of the elements in Al.²¹ Not shown is Ti because of lack of data for diffusion of Ti in Al, diffusion rates of Al in Ti that increase strongly if Fe impurity levels exceed more than about 1 ppm²², and reported chemical diffusion rates at 50°C that vary by as much as 35 orders of magnitude for Al in α -Ti^{22,23} and 36 orders of magnitude in Ti₃Al.^{22,24} Note that Y may be a slow diffuser in Al²⁵ and may not fit this correlation, but its diffusion rate data are unavailable.

A second factor affecting reaction rates is that the softest elements may deform most rapidly at first, becoming thinner so the diffusion distance decreases more rapidly. In the cases where the reaction time is known it correlates fairly well with hardness as seen in

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Figure 5. The hardness values²⁶ are for the fully work-hardened condition. A third factor that could affect the reaction rate is the free energy of mixing between the elements. However no correlation was found, except that hard elements such as Cr and Mo with a positive free energy of mixing never alloyed completely, as discussed below. The overall conclusion is that milling time for most elements appears to correlate with diffusion rate and also with hardness.

As seen in

Figure 3, $Mg_{17}Al_{12}$ appeared at an early stage of processing, then disappeared. This is expected even in binary alloys, where interdiffusion at an A-B interface results in a range of compositions that may temporarily produce various possible compounds. As compositional fluctuations diminish these give way to the final phases. In a ternary alloy transient phases from all three binary diagrams may appear²⁷. The formation, then disappearance, of $Mg_{17}Al_{12}$ accounts for the rapid early rate of elemental consumption and later slowdown seen in Figure 3, while the amorphous phase grows more steadily. Unlike $Mg_{17}Al_{12}$,

Figure 3 shows that Mg_2Al_3 starts to appear when the elements have mostly disappeared, so it evidently crystallizes from the amorphous phase, in agreement with the fact that these two phases subsequently coexist in dynamic equilibrium.

2. Milling Temperature

A variable of significant interest is the milling temperature. Although the welding and reduction in thickness of elemental layers during MA may be relatively insensitive to temperature, alloying requires mixing of some kind. The rate of thermal diffusion would change by many orders of magnitude between 50 °C and -150 °C; a rough estimate of the expected change can be made using diffusion coefficients for related equilibrium alloys. Reported activation energies for diffusion of Mg in Al are 1.19 to 1.45 eV in Al primary solid solutions, 1.22 eV in $Mg_{17}Al_{12}$, and a low value of 0.59 eV in Mg_2Al_3 .²¹ Excluding Mg_2Al_3 , between 50 °C and -150 °C these would give a drop in diffusion rate by a factor of 10^{30} to 10^{37} . For Mg_2Al_3 it would drop by 10^{15} . However the actual results are almost independent of temperature. As seen in Figure 3, amorphous alloy formation is complete after one hour of milling at 50 °C. All low temperature milling of this alloy was done for 4 h, and showed that the reaction is complete by 4 h. In addition, in Figure 6(a) the low temperature relative Al peak intensity after 4 h is similar to the 50 °C intensity after about 3 h, suggesting a milling time increase at low temperature by only

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33%, and at most a factor of 4. Because of the rapid refining of lamellar thicknesses with time at very early times a large change in diffusion rate will lead to only a small change in milling time, but according to Equation (2) and

Figure 2(b) an increase in milling time from 3 to 4 h requires a change in diffusion rate by only a factor of 1.1, and for 1 to 4 h a factor of 17, either of which is small compared to 10^{30} or 10^{37} .

Put in other terms, these results represent activation energies of only about 0.003 and 0.04 eV respectively. The rate of reaction therefore appears to be almost independent of temperature, much as others have found fairly minor dependence,²⁸ another indicator of mechanical mixing or enhanced diffusion. A further comparison is provided by $Mg_{69}Al_{27}Ca_4$ (which forms a crystalline alloy) where Mg reacted fully in less than 2 h and Al in less than 0.5 h at -100 °C. In addition, recall that the reaction rate is high not only at low temperature but at 50 °C as well. From Figure 4, the effective diffusion rate at 50 °C is larger than expected for thermal diffusion by a factor of 2×10^6 . Finally,

Figure 2(a) shows that the Al linewidth increases at low temperature, as if there is some decrease in atomic diffusion at low temperatures resulting in decreased grain size.

It should be noted that comparison of Figure 1(d) and (e) show decreased Mg_2Al_3 content at low temperature, as expected for the same reason. Figure 6(b) shows a decrease of 65% at -100 °C and 75% at -150 °C. On the other hand, milling at -100 °C yields about twice as much Mg_2Al_3 at 8 h as at 4 h. Thus the question of whether there is a lower steady state value at low temperature or just a much slower reaction rate for Mg_2Al_3 formation (unlike the Al phase) requires further data.

3. Local Energy Density

Note in Figure 6(a) that milling with 5/8" balls cuts the milling time by at least a factor of 2, since the intensity fell to near zero before 1/2 h. Increasing ball size or reducing the mass of powder milled also had a significant effect on the steady-state structure of mechanically alloyed powder, as others have reported.^{29,30,31} More energetic processing with 5/8" balls also produced broader linewidths, as seen in Figure 2(a).

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Alloy formation in MA involves diffusion over a distance of well under 1 μm , and is therefore controlled by local conditions. The physically meaningful impact energy parameter is thus the local energy density (LED), i.e. the energy per unit volume per impact deposited locally by deformation at each point in the impact zone, rather than the total energy per impact as suggested previously.²⁹ The energy density varies with radial distance from the center of the impact. The impact energy is deposited into a thin, small volume of material, so the LED should vary in an inverse fashion with powder thickness and thus with total powder mass. Figure 1(d) and (f) shows the x-ray diffraction patterns for 0.55 g and 2.5 g powder masses in $\text{Mg}_{38}\text{Al}_{57}\text{Ca}_5$ alloys. Note the existence of Mg_2Al_3 phase in Figure 1(d) and its near absence in Figure 1(f) where the LED is much lower. It was also nearly absent in a 10 g run with 5/8" balls. Figure 6(b) shows that Mg_2Al_3 intensity trends toward a steady state value that depends on milling conditions and again is lower for 1/2" balls, where the LED is lower. (Not shown in the figure is the value at 28 h with 1/2" balls, where the intensity has leveled out at 23.5%.) The dependence on milling intensity is revealed in Figure 7(a), which shows the total Mg_2Al_3 x-ray peak intensity I vs. the inverse of the powder mass m for three different ball sizes. It increases nearly linearly with inverse powder mass for 5/8" balls (and, we assume, for other ball sizes), and therefore increases with LED (while the energy per impact stays constant). From Figure 7(a) there appears to be a threshold for the appearance of the Mg_2Al_3 phase, so if I is a function only of the local energy density \hat{u} then $I(\hat{u}) = 0$ at some threshold value \hat{u}_0 . Although I cannot be negative, if its dependence on \hat{u} has a given mathematical form which increases with \hat{u} the evaluation of that function at $\hat{u} = 0$ will yield a fixed negative intensity value $I_0 = I(0)$. Now \hat{u} in turn depends on D and m , $\hat{u} = \hat{u}(D, m^{-1})$, and it seems reasonable to assume that \hat{u} goes to zero at $D = 0$ and at $m^{-1} = 0$. (The latter assumption (namely $\hat{u}(D, 0) = 0$) would not actually be correct at very large powder masses because a ball's energy deposition would not penetrate to unlimited depth due to powder inertial effects, but we can ignore that here.) Then $I(\hat{u}(D, 0)) = I_0$, and all fit lines versus m^{-1} in Figure 7(a) should have the same intercept I_0 . Accordingly, taking I as linear in m^{-1} , all points were fitted to a single function $I = I_0 + I_m(D)/m$, where $I_m(D)$ is the slope dI/dm^{-1} . Neither exponential nor power law functions for $I_m(D)$ gave completely optimal fits, and

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multiplication of these functions by polynomials in D did not improve the fit very rapidly with increasing polynomial order, but a product of these two functions gave a good empirical fit. The result is $I = I_0 + Ae^{bD}D^p/m$, where $I_0 = -.027$, $A = 0.041$, $b = 3.9$, $p = 1.4$, and A is expected to be a function of the ball velocity (which is invariant for a Spex mill). The fits, shown in Figure 7(a), are quite good and thus support the common intercept I_0 and the idea that the Mg_2Al_3 intensity depends only on \hat{u} the LED. The slope function $I_m(D)$, displayed in Figure 7(b), shows the strong increase in Mg_2Al_3 intensity with ball diameter (the exponent of the similar but slightly inferior power law fit was $p = 3.9$, somewhat higher than the value 3 expected if it were proportional only to the ball mass).

B. Phase Diagrams Under Mechanical Alloying

1. Amorphous Phase Region

Alloys from 60 Mg, Al, and Mg-Al based binary and higher alloy systems were investigated. Amorphous phases were found in alloys containing a few percent of Ti, Y, Ca, Zr, V, Er, and Pr in compositions near $Mg_{40}Al_{60}$. Of these, Ti, Y, Zr, and Er were slightly superior at promoting the amorphous phase. The x-ray diffraction patterns are shown in Figure 8. DSC measurements later showed Ti, V, and Y amorphous alloys to be the most stable, crystallizing only at very high reduced temperatures T_x/T_1 , the crystallization temperature to liquidus temperature ratio. The systems with Ca, Ti, and Y were investigated over a broad range of compositions, the former most thoroughly, and their MA phase diagrams are shown in Figure 9 to Figure 11. Most of the information in Figure 9 has been published previously. Compared to the equilibrium diagram, the new features are that 1) the Mg_2Al_3 phase is largely replaced by an amorphous phase and 2) certain crystalline phases display large solid solubility extensions, as will be discussed below.

Most amorphous alloys contained 5-20% Mg_2Al_3 , as labeled in Figure 1(c), though it is not too obvious due to peak broadening. Only under the lowest LED conditions was Mg_2Al_3 nearly absent, as seen in Figure 1(f). The strong suppression of Mg_2Al_3 by MA may be a result

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of its complex crystal structure. It responded almost indistinguishably to addition of each of the ternary elements. Either Mg_2Al_3 or $Mg_{17}Al_{12}$ could adversely affect ductility, since both were extremely brittle when conventionally alloyed. Thus Mg_2Al_3 in milled powders would be undesirable since it could immediately start growing without nucleation, when heated to consolidate or extrude the powder.

The Al phase began to appear in ternary amorphous alloys with > 65% Al, and in the Mg-Al binary at 60% Al. Like other crystalline phases its presence increased with LED. For 0.5 g runs (at -100 °C, which should cause it to decrease slightly) its level in $Mg_{40}Al_{60}$ was about 50%, vs. a few percent for 2 g runs (at 50 °C). However in contrast to Mg_2Al_3 it was readily disrupted. Three percent of any of the glass-forming elements suppressed it completely, and for Ti, V, and Zr only 1% was needed.

2. Crystalline Phases

In the equilibrium Mg-Al-Ca phase diagram there are five compounds. Al-Ca compounds have by far the largest negative heats of formation in this system,³² but despite this they were rarely found. Moderate-sized single phase regions of $Mg_{17}Al_{12}$ and Mg were found, while Mg_2Al_3 was highly suppressed. In contrast, the single-phase Mg_2Ca region covered a large portion of the phase diagram (see Figure 9). At equilibrium Mg_2Ca is a line compound in the Mg-Ca binary system,³³ with maximum Al solubility of 1% at 370 °C³⁴, and much lower solubility expected at 50 °C. This phase showed large changes in its lattice parameters. The molar volumes calculated from them were fitted to the volume form of Vegard's law, equation (1), by adjusting the effective molar volumes in the alloy Ω_i^{alloy} , where i represents Mg, Al, or Ca. The fit was good ($R^2 = 0.92$). The results are given in Table I, along with the molar volumes Ω_i^0 for the pure elements.³⁵

The reason for the high stability of Mg_2Ca , and low for Al-Ca compounds, may be partly explained by the growth rates of these compounds. The phase composition in MA alloys results from opposing processes of growth vs. destabilization due to high defect densities. If we temporarily assume their destruction rates are similar, those with the highest growth rate (at the

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off-stoichiometric as-milled composition) should dominate. Information on growth rates was obtained from DSC studies. In $\text{Mg}_{38}\text{Al}_{57}\text{Ca}_5$ three exotherms occurred prior to melting. X-ray diffraction on samples heated to just above each of these peaks established that they represented nucleation of $\text{Mg}_{17}\text{Al}_{12}$ and Al_2Ca and growth of Mg_2Al_3 respectively as peak temperature increases³⁶. The Mg_2Al_3 was present initially and had already grown to about 30% of its final level prior to its peak. A Kissinger analysis on DSC scans performed at different heating rates yielded activation energies of 2.56, 2.80, and 2.35 eV with peak temperatures of 285, 356, and 425 °C respectively at 10 °C/min heating rate. Using these data the growth rates calculated for Mg_2Al_3 and Al_2Ca at 50 °C are lower than for $\text{Mg}_{17}\text{Al}_{12}$ by a factor of 10^3 and 10^4 respectively, agreeing with the lack of dominance of Mg_2Al_3 and Al_2Ca . The Mg_2Ca phase was not seen in milled alloys until the Ca level reached 10%. There a new DSC peak appeared below the other peaks at 234 °C, probably due to Mg_2Ca growth, though x-ray analysis was not performed to confirm this. If this is correct, Mg_2Ca would grow more rapidly than the other phases at 50 °C (unless its activation energy is extremely high), explaining its high stability. These results must be applied with caution, for two reasons. First, the composition of crystalline phases formed during MA is frequently far from that at equilibrium, unlike those grown in the DSC, and this could affect growth rates. Second, in the DSC the Mg_2Al_3 phase grows in an alloy compositionally altered by the previous growth of $\text{Mg}_{17}\text{Al}_{12}$ and Al_2Ca , which could affect its growth rate. Nonetheless these results do seem to predict the relative stability of the phases, and thus perhaps that destruction rates are less variable than growth rates.

In addition to the three alloy systems above, a number of others systems were explored to some extent. Si was tried in spite of forming the ionic compound Mg_2Si because it is one of a very few light elements having negative enthalpy of mixing with Mg as well as Al (and also Cr), but it was unsuccessful. The addition of 5% Li is tolerable and should reduce the density by 4.3%. Cr and later Mo were also added to amorphous alloys in the hope of improving corrosion resistance. Dramatic improvements in corrosion resistance with Cr and certain other elements in amorphous alloys are well known^{37,38} due to formation of a passive Cr-rich oxy-hydroxide layer at the surface. Generalized rates of attack tend to be higher in amorphous alloys, but this favors

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the passivation process.³⁹ If Cr could be added to a Mg-containing amorphous alloy a passive layer might form at fairly low Cr levels, due to more rapid dissolution of Mg. The choice of Al and Si as alloying additions to Mg was originally made partly to try to lower the free energy of solution of Cr, as described further below. However Cr reacted slowly and incompletely and destabilized the amorphous phase, as did Mo.

C. Alloying Thermodynamics

Ti, Zr, and V have a rather large positive heat of mixing with Mg, as seen in Table II. The liquid phase heats of mixing at infinite dilution were taken from Miedema's semiempirical model,⁴⁰ except for the rare earths, where values were estimated from enthalpies of formation. Column 5 of Table II shows regular solution heats of mixing at infinite dilution of a third element in a Mg₄₀Al₆₀ alloy.⁴¹ Free energies of mixing for 5 at% of each element in Mg₄₀Al₆₀ are shown in column 6. Because short range ordering and the tendency to segregate are excluded, most of the latter values are meaningless for *equilibrium* ternary alloys. Indeed, the binary equilibrium phase diagrams of Mg with Ti, Zr, and V show severe immiscibility, as expected from their heats of mixing. The tendency to immiscibility is exacerbated by the boiling point of Mg, which at 1090 °C falls well below their melting points (and of most other elements listed), so no temperature exists where both elements are liquid. Further, the Al-rich liquidus temperature in binary phase diagrams of Al with Ti, Zr, and V rises very rapidly, reaching the boiling point of Mg at about 1% Zr, 3% Ti, and 3.5% V. As a result a single phase Al-containing liquid containing appreciable amounts of both Mg and either Ti, Zr, or V is unlikely to exist, precluding formation of these alloys by rapid solidification. MA thus provides the only practical route to production of such alloys, aside possibly from evaporation or sputtering. Partial or complete mixing by MA is well known in alloys with positive enthalpies of mixing.^{42,43} Mechanical alloying in the present alloys only occurred where the overall regular solution heat of mixing is negative, but that may be due either to inadequate milling time or the high hardness of Cr and Mo, which may tend to become embedded in a softer matrix and avoid flattening out. This could explain the partial reaction observed.

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IV. CONCLUSIONS

Amorphous phases were found in ternary Mg-Al based alloys near the equilibrium Mg_2Al_3 phase. Mg_2Al_3 was suppressed to low levels by MA, but nearly eliminated only at low LED. Amorphous phase formation was rapid, being nearly complete in one hour for $Mg_{38}Al_{57}Ca_5$ alloys. Milling times of 1 to 8 hours were required for complete reaction, depending on the ternary constituent. The rates of reaction correlated with elemental hardness and with atomic diffusion rates. The rate of mixing was many orders of magnitude faster than predicted by normal diffusion rates. Low milling temperatures had little effect on reaction rates or on the final structure of the alloy. Crystallinity increased strongly with local energy density. Y, Ti, Zr, Er, Ca, V, and Pr all served as glass-formers, but amorphous alloys suffer from low ductility. Outside of the amorphous region, Mg_2Ca was by far the most dominant phase. This may be explained by the relative growth rates of the crystalline phases, as determined by DSC studies. Cr and Mo, which are hard and have a positive overall free energy of mixing, did not alloy completely with amorphous alloys within 100 h. Other elements such as Ni, Cu, and Zn, well-known as glass formers in rapidly solidified Mg alloys, did not form an amorphous phase by MA in either Mg or Mg-Al based alloys. Up to 5% Li could be added, decreasing density by over 4%, without increasing crystallinity.

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Table I. Effective elemental molar volumes Ω^{alloy} in the Mg_2Ca phase compared to the volume Ω° in the pure element.

Element	Ω° , cm^3/mole	Ω^{alloy} , cm^3/mole	Percent change
Mg	13.99	15.9	+ 13%
Al	9.999	8.1	- 19%
Ca	26.28	19.3	- 27%

Table II. Thermodynamic data for alloys of selected glass-forming elements with Mg and Al.

Element	Melting Point, ^a °C	$\Delta H^{\circ}_{\text{mix}}$ of Elements, eV			$\Delta G_{\text{mix}}^{\text{b}}$, eV
		with Mg	with Al	with $\text{Mg}_{40}\text{Al}_{60}$	
Li	181	-0.01	-0.13	-0.08	-0.008
Mg	650		-0.08		
Al	660	-0.07			
Si	1414	-0.35	-0.09	-0.20	-0.014
Ca	842	-0.27	-1.01	-0.71	-0.038
Sc	1541	-0.15	-1.68	-1.07	-0.055
Ti	1670	+0.61	-1.22	-0.49	-0.027
V	1910	+0.85	-0.63	-0.04	-0.006
Cr	1863	+0.85	-0.37	+0.12	+ 0.001
Mn ^c	1246	+0.36	-0.73	-0.29	-0.018
Ni	1455	-0.13	-0.85	-0.56	-0.031
Cu	1085	-0.16	-0.29	-0.24	-0.015

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Zn	420	-0.13	0.02	-0.04	-0.006
Y	1522	-0.28	-1.89	-1.24	-0.063
Zr	1855	+0.24	-1.96	-1.08	-0.055
Mo	2623	+1.39	-0.21	+0.43	+0.016
Er	1529	-0.19			
Pr	931	-0.35	-1.80	-1.22	-0.062

^a See reference 33.

^b At 50°C for 5% M in Mg₄₀Al₆₀

^c Mn was not alloyed but is used here to show the trend in heats of mixing across transition metals

Table III. Selected results of mechanical alloying in other systems

Composition		Phases Found ^a	Comments
Mg ₈₂ Cu ₁₈		Mg ₂ Cu, Mg	Amorphous phase (known from rapid quenching ⁴⁴) not found. High density.
Mg ₃₀ Ca ₄₀ Cu ₃₀		a(?), Mg ₂ Cu, CaCu	Possibly an amorphous phase, but high density, oxidation prone due to high Ca content.
Mg ₅₀ Ca ₂₀ Cu ₃₀		Mg ₂ Ca, MgCu ₂	Possible amorphous phase disappeared with reduced Ca.
Mg ₈₆ Ni ₁₄		Mg, Ni, Mg ₂ Ni	Incomplete reaction, sharp crystalline lines after 4 h.
Mg _{1-x} Zn _x , ≤ x ≤ 0.4	0.2	Mg, Mg ₇ Zn ₃ , Mg ₂ Zn ₃ (tr)	Mg ₇ Zn ₃ has narrow equilibrium thermal range of stability, eliminated by using lower milling intensity (½" balls).
(Mg ₂ Zn ₃) ₉₀ Ti ₁₀ , (Mg ₂ Zn ₃) ₉₅ Ca ₅		MgZn ₂ , a	Eliminated Mg ₂ Zn ₃ but replaced by MgZn ₂ . Amorphous phase not pursued because of high density.
(Mg ₂ Zn ₃) ₉₀ Y ₁₀		Mg ₃ Zn ₆ Y	Almost single phase (with traces of possible Mg-Zn compounds).
Mg ₃₉ Al ₅₈ Cu ₃		a, Mg ₂ Al ₃ , Al	Al strongly stabilized
(Mg ₂ Al ₃) _{1-x} Ni _x , ≤ x ≤ 5	1	Mg ₂ Al ₃ , Al ₃ Ni, a	Amorphous phase rapidly eliminated with increasing x, replaced by Mg ₂ Al ₃ and Al ₃ Ni.
(Mg ₂ Al ₃) ₉₇ Zn ₃		Al, Mg ₂ Al ₃ , a	Al stabilized, with increased lattice parameter.
(Mg ₂ Al ₃) ₉₇ Sc ₃		Al, a, Mg ₂ Al ₃ , Mg ₁₇ Al ₁₂ , Al ₃ Sc	Lower density. More crystalline - unlike other rare earths, Sc did not stabilize amorphous phase.

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$(\text{Mg}_2\text{Al}_3)_{95}\text{Li}_5$	Al, <i>a</i> , Mg_2Al_3 , $\text{AlLi}(\text{tr})$	Al strongly stabilized.
$(\text{Mg}_2\text{Al}_3)_{95}\text{Si}_5$	Al, Mg_2Si	No amorphous phase produced.
$(\text{Mg}_{39}\text{Al}_{58}\text{M}_3)_{1-x}\text{Li}_x$, M=Ti, Y; $2 \leq x \leq 5$	<i>a</i> , $\text{Mg}_2\text{Al}_3(\text{tr})$	Li added to lower density, almost no effect on crystallinity
$(\text{Mg}_{39}\text{Al}_{58}\text{Y}_3)_{90}\text{Li}_{10}$	<i>a</i> , Mg_2Al_3 , $\text{Al}(\text{tr})$, $\text{AlY}_2(\text{tr})$	Al and AlY_2 slightly stabilized (Al with significantly decreased lattice parameter)
$(\text{Mg}_{39}\text{Al}_{58}\text{Ti}_3)_{90}\text{Li}_{10}$	<i>a</i> , Al, $\text{Mg}_{17}\text{Al}_{12}$, $\text{Al}_3\text{Ti}(\text{tr})$	Al and $\text{Mg}_{17}\text{Al}_{12}$ strongly stabilized
$(\text{Mg}_{38}\text{Al}_{57}\text{Ca}_5)_{95}\text{Si}_5$	Mg_2Al_3 , Al_4Ca	Si added as Si or Mg_2Si , reaction slow, only complete after 28 h. Al_4Ca rarely seen elsewhere.
$(\text{Mg}_{38}\text{Al}_{57}\text{Ti}_5)_{97}\text{Cr}_3$	Al, $\text{Mg}_{17}\text{Al}_{12}$, Cr, $\text{AlTi}(\text{tr})$	Al with reduced lattice parameter, $\text{Mg}_{17}\text{Al}_{12}$ slowly increasing with time, Cr lines remaining sharp, up to 100 h milling time.
$(\text{Mg}_{39}\text{Al}_{58}\text{Y}_3)_{97}\text{Cr}_3$	Mg_2Al_3 , <i>a</i> , $\text{Cr}_2\text{Mg}_3\text{Al}_{18}$, $\text{Al}(\text{tr})$	Cr added as $\text{Cr}_2\text{Mg}_3\text{Al}_{18}$, not completely consumed after 32 h. Mg_2Al_3 stabilized.
$(\text{Mg}_{39}\text{Al}_{58}\text{Ti}_3)_{98}\text{Mo}_2$	Al, $\text{Mg}_{17}\text{Al}_{12}$, <i>a</i> , Mo	Al with reduced lattice parameter, Mo with sharp lines after 30 h.
$(\text{Mg}_{39}\text{Al}_{58}\text{Y}_3)_{98}\text{Mo}_2$	<i>a</i> , Mo, Mg_2Al_3 (tr)	Mo had no effect after 100 h.

^a In order of decreasing abundance for each composition. *a* represents the amorphous phase, (tr) means only a trace present, (?) means identification of the phase is uncertain.

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Figures

Figure 1

X-ray diffraction patterns of $Mg_{38}Al_{57}Ca_5$ powders milled using three 1/2" and two 1/4" diameter balls and 0.55 g powder at room temperature for (a) 0.25 h, (b) 0.5 h, (c) 1 h, and (d) 4.3 h. Two of the unlabeled small peaks in pattern (a), at about 67.5° and 72.7° , are Mg peaks; the remainder are mostly $Mg_{17}Al_{12}$ peaks. Bullets (\bullet) mark the largest Mg_2Al_3 peaks and clusters of peaks in pattern (c). Pattern (e), milled at $-150^\circ C$, and (f), using 2.5 g powder, both show decreased Mg_2Al_3 levels.

Figure 2

(a) The width of the Al (200) x-ray diffraction peak in $Mg_{38}Al_{57}Ca_5$ alloys vs. milling time under various milling conditions (1/2" or 5/8" balls, normal or low temperature) as labeled (there was enough uncertainty due to an overlapping Fe (110) peak that a common width value had to be used for the 5/8" ball fits) and (b) log plot of the calculated Scherrer crystallite size vs. milling time for the 1/2" ball room temperature data in (a), fitted with a curve of the form $\exp(a + bt + c \ln(\cosh(dt)))$.

Figure 3

Sum of intensities (peak areas) for all Al, Mg, Ca, $Mg_{17}Al_{12}$, Mg_2Al_3 , or amorphous x-ray peaks in $Mg_{38}Al_{57}Ca_5$ alloys over a 2θ range of $26-52^\circ$, as a fraction of total intensity, vs. milling time under constant milling conditions ($50^\circ C$, 1/2" balls, and 0.55 g powder mass). The scattering factor varies by element so that intensities are not equal to the absolute concentrations of these phases, but scattering factors for Mg and Al are very similar, so the concentration and intensity differ significantly only for Ca.

Figure 4

The estimated actual diffusion distance $\lambda/4$ at the time of complete reaction is plotted against the calculated diffusion distance of the order of $(-D/t)^{1/2}$. Here and in Figure 5 Cr and Mo are not shown because they did not fully react even after long milling times. Other elements are not shown for lack of information on either reaction time or diffusion rate in Al.

Figure 5

Elemental reaction time in mechanical alloying versus elemental hardness. Vickers hardness numbers were converted to approximate Brinell values.

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Figure 6

Normalized intensity (as in Figure 3) vs. milling time for (a) Al and (b) Mg_2Al_3 phases under various milling conditions.

Figure 7

(a) Normalized Mg_2Al_3 intensity vs. inverse powder mass in $Mg_{38}Al_{57}Ca_5$ alloys milled at room temperature using three 13/16" dia. balls, three 5/8" dia. balls, or three 1/2" and two 1/4" dia. balls, mostly for 4 hours (the largest powder masses required longer times). The effect of the 1/4" balls, with 1/8 the mass of the larger balls, can probably be neglected. Note that the 2 g point with 5/8" balls does not agree well with the fit line. Since most of the peaks in its diffraction pattern showed anomalous widths and peak intensities, a contamination problem is suspected and it was excluded from the fit. (b) The slope function $I_m(D)$ for the fit in part (a), plotted vs. ball diameter.

Figure 8

The lower six x-ray diffraction patterns are alloys with 3% of the ternary element, milled with three 5/8" balls and 2.5 g powder at room temperature. The top three patterns are 5% ternary alloys, milled the same way. The position of the main amorphous peak shifts with alloying element due to differing atomic sizes. The low peak near 20° in some scans is due to incomplete coverage of the adhesive mounting tape.

Figure 9

Phase diagram for mechanically alloyed Mg-Al-Ca alloys. The predominant phase at each composition is represented by the symbols shown. Solid symbols represent nearly single-phase results (with less than 5% of other phases present). Open symbols indicate the presence of two or more phases at significant levels (greater than 5%). Approximate boundaries are drawn around single-phase regions. In most cases where there is little data these are fairly speculative, intended only to point out their existence.

Figure 10

Phase diagram for mechanically alloyed Mg-Al-Ti alloys. Symbols as in Figure 9. AlTi, AlTi₃, and Ti exist over a range of composition as shown.

Figure 11

Phase diagram for mechanically alloyed Mg-Al-Y alloys. Symbols as in Figure 9.

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