

THERMALLY-STABILIZED NANOCRYSTALLINE MAGNESIUM ALLOYS

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Abstract

Advanced nanocrystalline alloys have shown remarkable property improvements, particularly, order-of-magnitude strength increases, when compared to their coarse-grained counterparts. However, a major obstruction to the widespread application of such materials is the degradation of properties via rapid grain growth at even ambient temperatures. Conventional methods for circumvention of this problem at low temperatures have largely steered toward kinetically pinning the boundaries with dispersoids, or through misorientation of grain boundaries, yet even these methods have limited utility at elevated temperatures needed for routine sintering and forming operations. In this work, we will present a synergistic approach to the development of thermally stable nanostructured Mg-alloys which incorporates elements of predictive modeling of suitable alloy systems, fabrication of nanostructured alloy powders by high energy ball milling and consolidation of the powders at elevated temperatures.

Introduction

Mg based alloys have many desirable mechanical properties, such as low density and high specific strength, compared to conventional structural materials such as steel and aluminum. Reports from the private sector have shown that weight reduction is the single most important factor in the reduction in fuel consumption [1]. Recently, as a consequence, the drive to use Mg based alloys has increased in commercial automotive applications, and thus, this driving force has led to the extensive evaluation of magnesium alloys. Despite the desirable mechanical properties, current Mg alloys show limited strength. This is especially true at elevated temperatures. As a result, the application of Mg based alloys in vehicles has been heavily restricted, particularly high strength applications, currently reserved for alloyed steels [2-3].

While mechanisms such as solid solution strengthening and precipitate dispersion can be used to strengthen metallic alloys, it has been shown that much larger increases can be realized by refining the grain size to the nanoscale [4]. However, as the grain size decreases, the percent microstructure constituted by grain boundaries increases and can be in excess of 50%. Thus, grain boundaries in nanocrystalline materials can account for a large increase of the total free energy of the system. The reduction of this excess free energy, via the removal of grain boundary area, represents a large driving force for grain growth. It has been demonstrated that extensive grain growth at room temperature occurs in low melting point, nanocrystalline metals, such as Mg, which results in a dramatic loss of mechanical strength [4]. Thus, the thermal stability of nanocrystalline Mg alloys must be realized if these materials are to ever be adopted for extended high-temperature structural applications.

For this work, we present a synergistic approach to the development of thermally stable nanostructured Mg-alloys which incorporates elements of predictive modeling as a guiding hand for selecting suitable alloy systems for fabrication of thermally stabilized nanostructured Mg-alloy. Using a regular solution approximation derived elsewhere [6], an estimation of the effect of various solutes on decreasing grain boundary energy can be made. The model takes into consideration the elastic enthalpy change and the change in cohesive energy for both the lattice and grain boundary area for an estimation of the enthalpy change associated with grain boundary segregating solutes. Equation 1 is used to estimate the effect of stabilizing a nanocrystalline microstructure;

$$\Delta\gamma = \gamma^* - \gamma_o = \Gamma\Delta H_{seg} \quad (1)$$

where $\Delta\gamma$ is the reduction in grain boundary energy, γ^* is the effective grain boundary energy after solute segregation, γ_o is the initial grain boundary energy for Mg, ΔH_{seg} is the change in the enthalpy of the system due to the segregation of solute to the grain boundaries, and Γ is the excess amount of segregated solute per unit grain boundary area. If the interaction of a solute with a Mg grain boundary has an effect of lowering the interfacial energy of the associated boundary, then a collection of solute at that grain boundary occurs. If the boundary energy can be lowered to zero, then the immediate effect is the existence of an equilibrium grain boundary area. Furthermore, if the effects of precipitation and can be kinetically hindered, then the system will reside in a deep metastable state. This approach has been shown to be successful in stabilizing nanocrystalline Fe-, Cu-, and Pd-alloys systems [6-9]. Herein we report how these principles, for the first time, have been applied to nanocrystalline Mg systems with the effect of drastically increasing the high temperature stability of the matrix. In the best case, we show that a Mg 4at%Fe alloy is capable of retaining an average grain size of 45 nm after annealing at 200°C for one hour (51% of the absolute melting temperature of pure Mg).

Experimental Methodology

Using Equation (1) and reference [6], four solutes were selected as candidates for stabilization of nanocrystalline Mg: Fe, V, Mn, and Y. Out of the four solutes, Y was suggested to have the least effect (25% reduction in grain boundary energy). It has been experimentally shown that the bulk or global solute content has an effect of stabilizing a high grain boundary area, and hence, a smaller grain size [7]. Therefore, eight magnesium-based materials were synthesized, which comprised of pure Mg plus 1 and 4 at% of each of the candidate solutes.

All alloying reactions were prepared in a high purity argon filled glove box (m-Braun, O₂ and humidity contents <0.1 ppm). Mg

compounds were synthesized by charging a milling vessel with Mg (99.8% Alfa Aesar) and either Fe (99.99% Sigma-Aldrich), Mn (99.99% Sigma-Aldrich), V (99.5% Alfa Aesar) or Y (99.9% ESPI) using a 10:1 mass ratio of milling balls to powder. Hexane (3.5:10 surfactant to well volumetric ratio) was added to inhibit agglomeration of the metal powder during milling. The reactions were sealed under argon and ball milled for 20 hours using a proprietary high energy milling process at Wildcat Discovery Technologies (San Diego, CA).

The materials were recovered under an inert atmosphere and dried at room temperature under vacuum for approximately 15 hours to give ~ 1g of loose powder for each composition. Each of the eight materials was separated into seven batches. One of the batches was left without heat treatment, while the remaining six were heated to 100, 200, 300, 400, and 500°C for 1hr under vacuum.

The particle size of the 4 at% samples was assessed by scanning electron microscopy (JEOL). EDAX spectroscopy was used to confirm the absence of contaminants. X-ray diffraction patterns were obtained and the crystallite size was estimated by applying the Scherrer equation [10]. The (002) and (101) reflection peaks were used to measure the grains size. A Mg-ingot standard and Gaussian peak calibration were used to correct XRD peak broadening from instrumental errors. To verify the x-ray estimated grain size measurements, Mg with 4at% Fe and Y were investigated with transmission electron microscopy. Additionally, equal channel angular extrusion [11] was performed on all powders at 200°C as a means to consolidate the powder into a bulk form.

Results and Discussion

The SEM images in Figures 1 show that the as-milled particle morphologies for all four 4at% solute containing alloys is approximately 20µm and are somewhat spherical. While not shown here, it was observed that the 1at% alloys showed similar morphology and grain size.

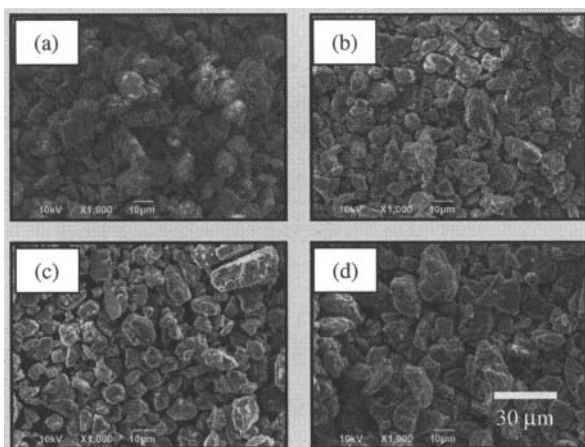


Figure 1. SEM images of as-milled particle morphologies for (a) Mg4at%Fe, (b) Mg4at%Mn, (c) Mg4at%V, and (d) Mg 4at% Y showing ~20 µm average particle size.

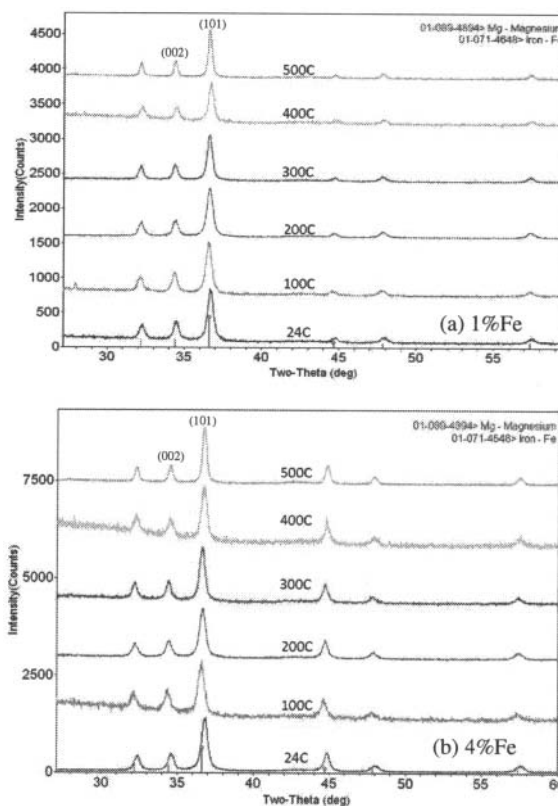


Figure 2. X-ray diffraction analysis patterns as a function of increasing annealing temperature for (a) Mg1at%Fe and (b) Mg4at%Fe.

Figure 2 shows the x-ray diffraction patterns for Mg1at%Fe and Mg4at%Fe annealed at various temperatures for one hour after the high-energy milling. The six other alloy systems (V, Mn, and Y in 1at% and 4at% concentrations) show very similar x-ray analysis trends, and are not shown for brevity. The broadening (as measured at half the maximum intensity of the peak) was observed to decrease with increasing annealing temperature for all alloys, suggesting that some grain growth has taken place. The appearance of secondary phases is not observed in the x-ray spectrum up to the highest temperatures tested (500°C), but this does not necessarily indicate that secondary phases are not present. Such phases might be in volume fractions too small to detect, or perhaps the phase itself is nanocrystalline, and therefore, cannot be distinguished above the background.

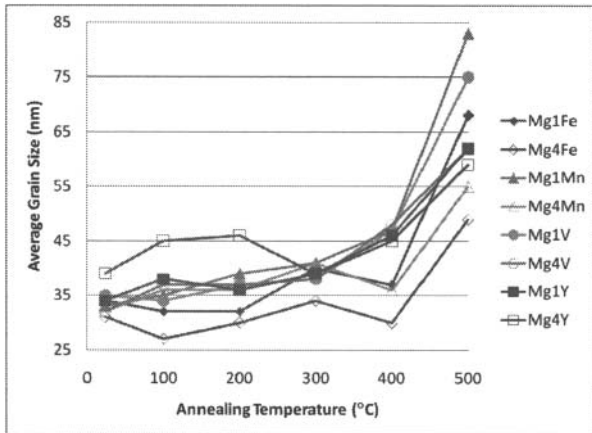


Figure 3. X-ray approximated average grain size as a function of annealing temperature for high-energy milled nanocrystalline Mg-alloys.

The average grain size approximations from the x-ray spectrum data for each alloy are given in Figure 3. The Fe-containing alloys are observed to have the greatest influence on preventing grain growth, with the 4at%Fe alloy retaining finer grain sizes than the 1at%Fe alloy. While Fe additions show the best thermal stability, Fe is known to cause severe galvanic corrosion when in contact with Mg. Metals that are higher in the electrochemical series displace metals which are lower in the sequence. This means that when connecting two metals, the metal with lowest potential will corrode. The same is true on the atomic scale, which plays importance in corrosion of solid solutions and grain boundary embrittlement. Thus, while Y was shown to induce less thermal stability, Mg and Y have the same potential (-2.37V) while Fe does not (-0.44V). Therefore, MgY nanocrystalline alloys should show superior corrosion resistance but have a larger average grain size.

TEM observation of the microstructure of Mg 4at% Fe and Mg 4at% Y, annealed at 200°C, are given in Figure 4. From these images, it can be seen that the average grain size is larger in the Y-containing alloy (~70 nm) than in the Fe-containing alloy (~45 nm) annealed at the same temperature for the same amount of time, which indicates that Fe is likely a better stabilizer.

Preliminary trial extrusions with equal channel angular extrusion (ECAE) for consolidation of milled powder resulted in complete bulk consolidate with no evidence of particle boundaries and no porosity. The samples were prepared by loading billets made of Nickel 100 alloy with the alloyed powder separated by thin metals disks. The powder was pre-compacted with a Ni steel rod, which was then welded shut. The can was then extruded at 160°C around a 90° die intersection angle for four passes via route A (no rotation about billet long axis during subsequent passes) [11]. The billet sectioned along the extrusion direction mid-plane is shown in Figure 5. ECAE resulted in full consolidation of the powder. Preliminary investigations on the effect of severe plastic deformation at high temperatures suggest that some grain growth has taken place. Future studies will be used to optimize extrusions parameters to limit excessive grain growth in these samples.

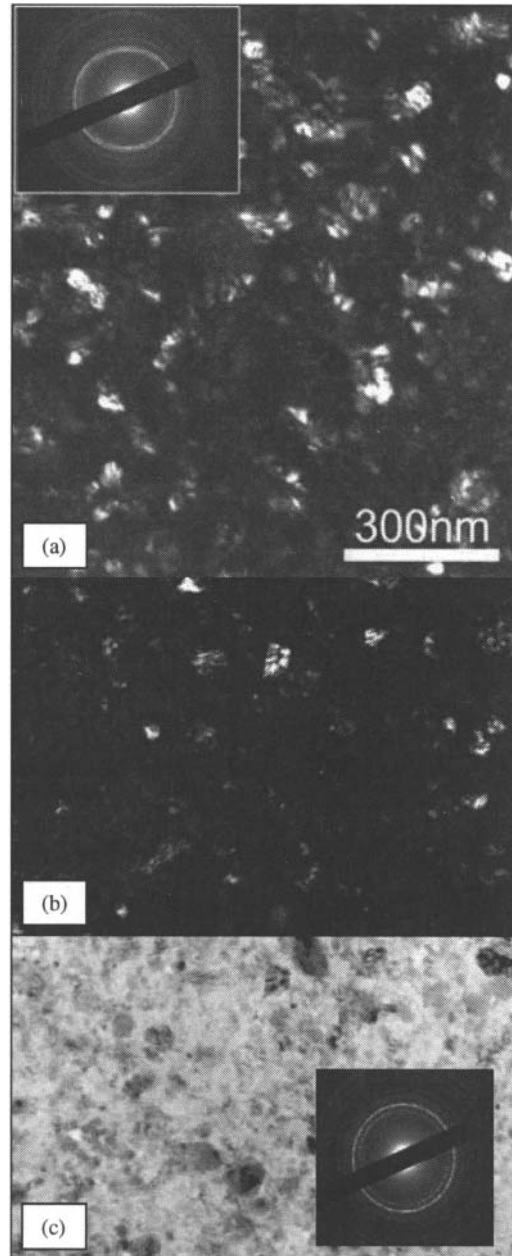


Figure 4. TEM images showing nanocrystalline grain size after 200°C for (a) Mg4at%Fe – dark field, (b) Mg 4at%Y – dark field and (c) Mg4at%Y – bright field.

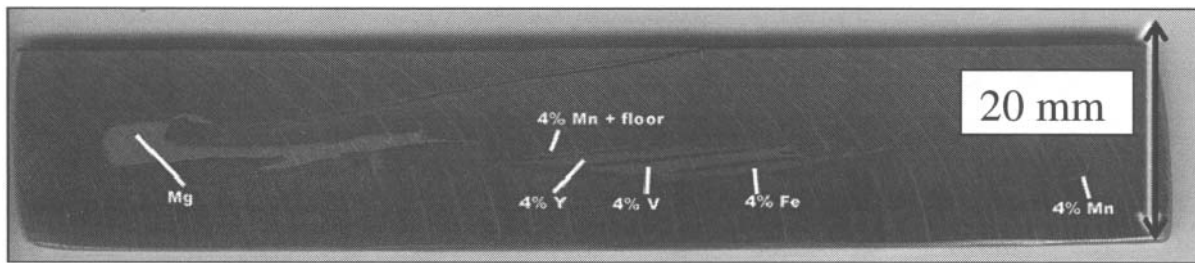


Figure 5. Cross-section of ECAE billet showing fully dense pure microcrystalline Mg, Mg4at% Fe, Mg 4at% Mn, Mg 4at% V and Mg 4at% Y alloys.

Summary

Select solutes concentrations of Fe, Mn, V and Y were successfully used to produce thermally stabilized nanocrystalline Mg with the likely mechanism of stabilization being interfacial energy reduction and/or solute drag. These results are consistent with findings and observations made in several other alloy systems [6-9]. X-ray analysis indicates that increasing the bulk solute content increases the thermal stability. The work presented shows Fe to be an excellent solute for stabilization and retention of the nanocrystalline structures (~45 nm after 200°C/1h annealing). Preliminary studies show ECAE to be an effective method of producing bulk samples from the nanocrystalline powders. Future studies will investigate this stabilizing effect in more advanced alloys, such as the AZ or WE series of alloys, as it may be possible to improve and tailor engineer properties.

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