Solute and Precipitate Effects on Ce-containing Mg Alloy Dynamic Recrystallization Kinetics

Storey, G.K.[1]; Sutton, S.[2]; McBride, B.N.L[1]; Hartman, D.[2]; Clarke, A.J.[1]; Clarke, K.D.[1]

[1]Center for Advanced Non-Ferrous Structural Alloys (CANFSA), Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, CO 80401, canfsa.org

[2]Mag Specialties Inc., Denver, CO, 80210

Abstract

Composition variations in precipitate and solute content of ZK60 Mg alloys, with Zn variations and Ce substitutions, impact dynamic recrystallization (DRX) behavior, microstructure, and mechanical properties. A constitutive model was developed based on hot compression testing at various strain rates and temperatures, quantifying the relationship between temperature, strain rate and imposed strain. Ce additions are shown to impede DRX kinetics more than Zn. Texture weakening is observed in post-DRX microstructures and varies based on composition.

MANUSCRIPT BODY

ZK60 alloys are known to have high mechanical strength relative to other Mg alloys. Low melting point precipitates, such as Mg_3Zn_7 in Mg-Zn-Zr alloys, can cause incipient melting during thermomechanical processing if temperatures are too high. The substitution of rare earth elements, such as Ce, for Zr allows for the formation of higher melting point precipitates, improving elevated temperature properties and higher temperature processing windows. Ce additions are also known to enhance corrosion resistance, improve creep resistance, and ultimately accelerate dynamic recrystallization (DRX) [1]. Conventional Mg alloys exhibit improved formability at higher temperatures when non-basal slip systems are activated, further facilitating dislocation slip. In this way, DRX during processing is a powerful way to improve grain structure and resultant mechanical properties.

Internal stored energy accumulates during slip deformation, while DRX reduces stored energy. Continuous DRX (CDRX) at rotated lattice regions in the area of grain boundaries is the dominant DRX mechanism in Mg alloys. The CDRX mechanism is known to occur via subgrain rotation during compressive deformation in the temperature range of 250-500°C [2]. There is limited knowledge about the formation of preferred crystallographic orientations in Mg alloys due to other possible deformation mechanisms, such as discontinuous DRX (DDRX) and twin DRX [3]. DDRX occurs by prior grain boundary protrusion toward surrounding, high dislocation density grains, while twin DRX occurs at twin intersections or fragments. In alloys with rare earth elements, particle-stimulated nucleation (PSN) in the vicinity of second phase particles has also been shown to occur [4]. Texture weaking in Mg alloys has been associated with PSN, as well as other phenomena including particle pinning, solute drag, and heterogeneous deformation promoting shear band formation [4]. Alloying with rare earth elements, such as Ce, can increase both strength and ductility, while reducing crystallographic texture.

Creating constitutive models of the DRX process in various Mg alloys can help guide processing to efficiently create products with desirable microstructures. Fu et al. studied DRX mechanisms in Mg-Zn-Mn alloys microalloyed with Sm, La, and/or Ca and determined that DDRX and PSN mechanisms weakened the basal texture [5]. The occurrence of CDRX was observed by Xu et al. in a Mg-13Gd-4Y-2Zn-0.5Zr (wt%) alloy during compression-torsion deformation at 450°C. It was also determined that strain rate affects dominant DRX mechanisms [6]. Mg alloy properties are highly dependent on the relationship between specific rare earth elements and the dominant DRX mechanisms.

Calculation of hot flow stress and DRX can give insight into ideal processing conditions. Flow stress is a parameter that characterizes mechanical properties during hot deformation and is dependent on deformation temperature, strain rate, and strain [7]. In modeling strain hardening and DRX during hot deformation, it is essential to investigate both process parameters and deformation mechanisms. There are multiple avenues to model flow stress for hot deformation that have been developed over the years. Hollomon developed a mechanical equation at small plastic strains [8]. Subsequently, Mecking and Kocks considered microstructural evolution and mechanical properties and determined that structural parameters such as dislocation density can describe DRX flow curves [9]. For Mg alloys, it is characteristic for flow stress to increase with strain due to work hardening, then decrease after it reaches the peak as DRX occurs at a critical strain [7]. This study focuses on analyzing DRX and strain hardening and calculating the critical stress for DRX to occur.

The alloy used for this study is a modified ZK60 (Mg-Zn-Zr) composition, with deliberate variations in Zn levels and a replacement of Ce for Zr in various amounts. It is an extrusion alloy that experiences precipitation hardening and exhibits a finer microstructures after solidification, hot working, or annealing processes. The composition matrix is separated into 3 levels of Zn, varying the hypothesized solute volume, and 3 levels of Ce, varying the hypothesized precipitate volume (electronic supplementary table S1). The variations in Zn and Ce within these alloys result in changes to second phase insoluble particle type, volume fraction, and distribution. ZK60 is ideally suited for this study, because it is a commercial alloy with insoluble Mg-Zr precipitates that influence DRX kinetics and texture. The samples for this study were machined into small cylindrical compression specimens with a diameter of 10 mm and a height of 15 mm, with the cylinder height longitudinal to the extrusion direction.

Electron backscatter diffraction (EBSD) was completed on all alloys and processing conditions. After compression testing, each sample was mounted, ground, and polished to 0.05 µm colloidal silica and etched after each polishing step in a solution of 4.2g picric acid, 70 mL ethanol, 10 mL glacier acetic acid, and 10 mL deionized water, for 10 s [12]. The polished surface for these samples was longitudinal to the compression direction. EBSD mapping analysis was performed with a 20 kV electron beam, 18 mm working distance, and 2 µm step size. Each inverse pole figure (IPF) map was processed with Neighbor Pattern Averaging & Indexing (NPAR) in the Orientation Imaging Microscopy (OIM) software.

Uniaxial compression tests on small cylindrical samples of each of the five alloys was conducted on a Gleeble 3500 thermal-mechanical simulator. All samples were compressed to a final true strain of 0.8 and were deformed at approximate engineering strain rates of 0.001, 0.01 and 0.1 s^{-1} at either 350 or 400°C. One set of thermocouples was welded on the surface at half height of each sample and used to monitor temperature throughout the test. The samples were lubricated at the surface of each anvil with layers of Ni paste and grafoil. Each sample was heated at 5°C/s under force control to the deformation temperature (350 or 400°C), held in displacement control for 30 s to ensure the temperature throughout the sample was homogenous, deformed to approximately 0.8 true strain and quenched with compressed air (electronic supplementary figure S1). Load-displacement data was obtained from the compression tests and converted to true stress-true strain using standard conversion equations. This data gives way to analysis of flow behavior and microstructural characterization.

True stress-strain curves for all five alloys tested at all processing conditions are presented in electronic supplementary figure S2. In general, the flow stress increases to a maximum, then decreases to a steady state when DRX is present. This maximum flow stress is the peak flow stress used through DRX modeling and calculations. At higher strain rates, flow stress increases to a high peak stress, then exhibits moderate work softening. At medium strain rates, flow stress increases to a moderate peak stress, with negligible work softening. At low strain rates, there is a small peak stress and strain, and negligible work softening. This is characteristic of DRX behavior for Mg alloys [7]. A flow stress curve is normally separated by a work-hardening stage, transition stage, softening stage and steady stage. A greater true stress is required for DRX in alloys processed at lower temperatures.

The onset of DRX can also be identified phenomenologically from the inflection point in the strain hardening rate versus flow curve [9]. The critical stress identified from strain hardening rate graphs identifies the onset of DRX and occurs lower than the peak stress. A third order polynomial, equation 1, is fit to each true stress-strain curve up to the peak stress. A third order polynomial effectively fits data with prolonged and multiple peaks.

$$\theta = A\sigma^3 + B\sigma^2 + C\sigma + D$$

(1)

where $\theta = \frac{d\sigma}{d\varepsilon}$ and constants A, B, C and D allow for calculations of certain DRX conditions. When this equation is differentiated,

$$\frac{\mathrm{d}\theta}{\mathrm{d}\sigma} = 3\mathrm{A}\sigma^2 + 2\mathrm{B}\sigma + \mathrm{C}$$

(2)

The minimum point of this derivative equation correlates to the critical stress.

The validity of these equations in comparison to models of expected DRX behavior is confirmed by Najafizadeh et al. in analysis of 304H stainless steel [10]. Calculation of critical stress according to the derivative goes as follows:

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}\sigma^2} = 0 \rightarrow 6\mathrm{A}\sigma_\mathrm{c} + 2\mathrm{B} = 0 \rightarrow \sigma_\mathrm{c} = \frac{-\mathrm{B}}{3\mathrm{A}}$$

(3)

Each θ/σ polynomial relation and associated σ_c are tabulated and utilized to determine the Zener-Hollomon parameter (electronic supplementary table S2). The activation energy can also be determined by equations for the Zener-Hollomon parameter, Z [11]:

$$\dot{\varepsilon} = A_1\sigma^{n_1} = A_2 \exp(\beta\sigma) = A(\sinh(\alpha\sigma))^n \exp(-\frac{Q}{RT})$$

(4)

$$\mathrm{Z} = \dot{\varepsilon} \exp\left[\frac{Q_{def}}{RT}\right] = A(\sinh(\alpha\sigma))^n$$

(5)

$$Q_{def} = \mathrm{R}\left[\frac{\partial ln\varepsilon}{\partial \ln(\sinh(\alpha\sigma))}\right]_\mathrm{T} * \left[\frac{\partial lnsinh(\alpha\sigma)}{\partial(\frac{1}{T})}\right]_{\dot{\varepsilon}}$$

(6)

where Q_{def} is the deformation activation energy, R is the gas constant (8.314 J/mol K), σ is flow stress, T is the deformation temperature, n, A_1, β, A_2, and α are material constants. A graph of peak stress (σ_p) for each alloy versus temperature displays that increases in Zn content increases σ_p that occurs before DRX (electronic supplementary figure S3). The effect of strain rate on σ_p was also analyzed and increases in strain rate require increased σ_p during DRX. This increase is relatively linear, due to the direct relationship between σ_p and strain rate. The value of n_1 is obtained from the linear regression of ln $\dot{\varepsilon}$-σ_p using equation 4 [11] (electronic supplementary figure S4). The values of β are determined by the slope of the linear regression of ln$\dot{\varepsilon}$-ln σ_p. The values of n_1, β, and α values ($\alpha = \beta/n_1$) are determined (electronic supplementary table S3). From these values, it is essential to calculate activation energy, Q, for DRX. The linear slope of lnε vs. ln[sinh($\alpha\sigma$)], varied by temperature is the left side of equation 5. The linear slope of ln[sinh($\alpha\sigma$)] vs. 1/T at different strain rates is the right side of equation 6. The Q value for each $\dot{\varepsilon}$ and T is calculated to further determine Z values, as presented in electronic supplementary table S2 and shown graphically in electronic supplementary figure S4. Q increases with Zn content, and similarly but to a lesser degree with Ce content. The average Q for the LZ-0.4Ce alloy is 81.9% less than the average Q for the HZ-0.3Ce alloy. The average Q for HZ-0Ce is 69.5% less than the average Q for HZ-0.3Ce.

Z values are calculated based on $\dot{\varepsilon}$, Q, R and T of each, as set up in equation 5, and are shown in electronic supplementary table S3. This Zener-Hollomon parameter describes the effect of both strain rate and temperature on flow stress. For Mg alloys there is a linear relationship between flow stress and the Zener-Hollomon parameter [11]. The linear relationship for each of alloy is determined (electronic supplementary figure S5) and utilized to determine a constitutive equation describing DRX kinetics. The stress exponent (n) and constant A are determined from the linear regression of each dataset (electronic supplementary table S3). The constitutive equation can be modeled using tabulated values in the format:

$$\sigma_p = \frac{1}{\alpha}(\left(\frac{Z}{A}\right)^{\frac{1}{n}} + \left(\frac{Z}{A}\right)^{\frac{2}{n}} + 1)^{\frac{1}{2}} \tag{7}$$

An additional relation between Z and σ_p based on the linear regression of the two is determined for each alloy, accounting for the stress exponent, n, and constant A (electronic supplementary table S4). Similar modeling methods has been deemed accurate for thermomechanically processed Mg alloys, specifically a T-4 treated ZK60 Mg alloy by Yu. et.al [11]. The model shows more variation for samples processed at high strain rates and lower temperatures, meaning that DRX processes are less predictable under these conditions and should be avoided in industrial processing. Samples with higher Zn content, as well as higher Ce content, have slower DRX and require more energy for the process to begin.

Texture weakening is observed after DRX (electronic supplementary figure S6). The red colored grains are basal grains, whereas the blue/green grains are non-basal grains. The basal texture weakens and the non-basal texture is preferential, with the exception of some basal areas throughout the sample. There are some long, elongated and un-recrystallized grains in certain areas where DRX did not occur. Many of these grains were near-basal oriented, potentially due to less slip in these regions. Zener pinning and solute drag have an effect on how significantly DRX occurs throughout the microstructure, and increased amounts of Zn and Ce cause less homogenous post-DRX texture, due to areas with previously inhomogeneous solute distribution. This observance is particularly prevalent in the HZ-0.3Ce and HZ-0.1 Ce alloys. An increase in strain in these compression tests, especially at lower temperatures, causes increased inhomogeneous texture.

The DRX kinetics during compression testing at elevated temperatures and resultant microstructural properties in a set of designed Mg-Zn-Ce alloys were investigated in this study to give further insight into the effect of varying solute and precipitate content. The following conclusions were determined.

1. Ce additions impede DRX kinetics to a greater extent than Zn additions, per wt.% increase. Ce additions dramatically increase precipitate fraction and Zener pinning, while Zn additions primarily increase solute drag. Zener pinning, by this reasoning, has a greater impact on retarding DRX kinetics than solute drag. The activation energy, Q, is lowest for the HZ-0Ce alloy, but is the highest for the HZ-0.3Ce alloy because of this.
2. The determined constitutive equations for the DRX process reflect the activation energy and effective Zener-pinning effect in each alloy and can be used to determine industrially relevant processing parameters, given different processing conditions.
3. The σ_p, determined via flow curves, and σ_c, determined through calculations, are an accurate representation of DRX initiation. Q and σ_p are directly correlated, and σ_p is greater for alloys with greater Ce additions and Zn content. Greater dependence on Ce additions is observed than for Zn additions.

4. Texture weakening and randomization is prevalent in the microstructure after DRX. A less homogenous basal texture is observed with increases in Zn, higher strain rates and lower temperatures.

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REFERENCES

[1] Silva, E.P. & Pinto, H.C: Effect of Ce-base mischmetal addition on the microstructure and mechanical properties of hot-rolled ZK60 alloy, Journal of Magnesium and Alloys, 2020.

[2] Roodposhti, S., Sarkar, K.L, Murty, H. Brody, R, & Scattergood: R. Grain boundary sliding mechanism during high temperature deformation of AZ31 magnesium alloy, Mater.Sci.Eng.A, pp. 171-177, 669, 2016.

[3] Fatemi, S.M & Paul, H: Characterization of continuous dynamic recrystallization in WE43 magnesium alloy, Materials Chemistry and Physics, 257, 2020.

[4] Dong, J., Sun, J., Jin, L., Zhang, Z., & Ding, W.: Texture evolution in Mg-Al and Mg-RE alloy during hot extrusion, 135h International Conference on Fracture, 2013.

[5] Fu, L., Le, Q., Hu, W., Zhang, J., & Wang, J.: Strengths and Ductility Enhanced by Micro-Alloying Sm/La/Ca to Mg-0.5Zn-0.2Mn Alloy. Journal of Materials Research and Technology, 9(3): pp6834-6849, 2020.

[6] Xu, P., Yu, J. & Zhang, Z.: Microstructure and texture Evolution of Mg-Gd-Y-Zn-Zr Alloy by Compression-Torsion Deformation. Materials, 12(17), 2019.

[7] Liu, J., Cui, Z. & Li, C.: Modelling of flow stress characterizing dynamic recrystallization for magnesium alloy AZ31B. Computational Materials Science, 41(3), pp. 375-382, 2008.

[8] HOLLOMON J H. The mechanical equation of state [J]. Trans AIME, 171: 535-545, 1947.

[9] MECKING H, KOCKS U F. Kinetics of flow and strain-hardening [J]. Acta Metallurgica, 29(11): pp.1865-1875, 1981.

[10] Najafizadeh, A. & Jonas, J.: Predicting the Critical Stress for Initiation of Dynamic Recrystallization, ISIJ International, 46(11): 1679-1684, 2006.

[11] Yu, H., Yu, H., Min, G., Park, S., You, B., & Kim, Y.; Strain-Dependent Constitutive Analysis of Hot Deformation and Hot Workability of T4-Treated ZK60 Magnesium Alloy, Met. Mater.Int, 19(4), pp651-665, 2013.

[12] Lin, T., Zhou, J.X., Jing, Y.T, Zhang, L.L, & Meng, X.B.; Improving mechanical properties of ZK60 magnesium alloy by cryogenic treatment before hot extrusion, Dr Gruyter, 2020.