39.0 SOLUTE AND PRECIPIATE EFFECTS ON MAGNESIUM RECRYSTALLIZATION

Gillian Storey (Mines)
Faculty: Amy Clarke (Mines) and Kester Clarke (Mines)
Industrial Mentor: Scott Sutton (Mag Specialties Inc.) and Dan Hartman (Mag Specialties Inc.)

This project initiated in Fall 2019. The research performed during this project will serve as the basis for a Master's thesis program for Gillian Storey.

39.1 Project Overview and Industrial Relevance

This project is a comparative study on the effects of varying precipitate and solute content on recrystallization kinetics in Mg alloys. ZK60-based alloys have compositions that are nominally Mg-5.8 Zn-0.65 Zr (wt.%) with some other possible additions [39.1]. These alloys are ideally suited for this study because they are commercial alloys with insoluble zirconium particles that influence grain size and recrystallization [39.2]. ZK60 is a typical extrusion alloy that experiences age (precipitation) hardening [39.3]. During wrought processing followed by extrusion, recrystallization initiates at grain boundaries of the specimen. Relative to alloys such as Mg-6.2 Zn (Z6), ZK60 exhibits a finer microstructure after solidification, hot work, or annealing processes due to Mg(Zn) precipitates that inhibit grain growth [39.2]. The determination of classical Avrami parameters and Zener pinning parameters for static recrystallization will be adapted to dynamic recrystallization and hot working. This will determine the effect of microstructural development kinetics on hot working parameters and material properties.

Microstructural characterization and texture evaluation through electron backscatter diffraction (EBSD) is essential to develop a kinetics model based on percent recrystallization at each time and temperature of heat treatment. An anticipated experimental outcome is that there should be a significant effect of precipitates on recrystallization behavior due to Zener pinning, yet only a minor effect from Zn solute content. Uniaxial compression tests at common extrusion temperatures (300 °C/573K, 350 °C/623K, 400 °C/673K), using a Gleeble 3500 thermomechanical simulator, allow for the simulation of different dynamic recrystallization (DRX) conditions. The occurrence of DRX can be identified from the presence of stress peaks in flow curves, and in some situations, inflection points of $\ln\varepsilon$-$\ln\sigma$ [39.4]. These observations can then be confirmed through microstructural characterization. Understanding the initiation of dynamic recrystallization for constant strain rate hot deformation processes further defines industry processing parameters for ZK60.

39.2 Previous Work

ZK60 does not have a standard composition beyond the nominal Mg-5.8 Zn-0.65 Zr (wt.%), and various rare earth elements can be added. Rare earth elements, such as zirconium, cerium, and lanthanum, can be added to improve high temperature strength and creep resistance [39.4]. Although the specific compositions of ZK60 being examined for this research program have not been previously evaluated, there are publications that study the effects of alloying, temperature, extrusion parameters on ZK60 with various other compositions. The driving force for recrystallization in magnesium alloys is caused by progressive lattice rotation at grain boundaries [39.5]. Local shearing near grain boundaries, included in **Figure 39.1**, occurs in magnesium alloys due to a lack of five independent slip systems required for homogenous plasticity. Dynamic recovery of dislocations results in new subgrains/grains. This process is progressive, with no division between nucleation and growth stages. At higher deformation temperatures, nonbasal slip occurs and deformation is more homogenous [39.5].

Research into microstructural changes of ZK60 throughout the DRX process lends an improved understanding of the process on the phenomenological level, however industry is lacking an understanding of the underlying processing parameters that control DRX. During hot deformation of materials with low to moderate stacking fault energy (SFE) at medium (500K-523K) and high temperatures (>523K), the formation of new grains occurs by conventional DRX—i.e., twinning [39.6], nucleation by bulging of dislocation tangles [39.7], and subgrain rotation [39.7]. Recently, newer mechanisms of DRX have been found to operate at lower temperatures (473-500K) [39.8]. DRX mechanisms are directly related to deformation conditions and therefore are affected by operating parameters of deformation processes, such as strain rate and temperature. Despite this information, not enough quantitative data is published to elucidate an interdependence of deformation and DRX mechanisms in ZK60 magnesium alloys.

The standards followed for extrusion of magnesium alloys in industry follow the ASTM B107/B107M-13 standard [37.9]. This standard is the general guideline for magnesium-alloy extrusion of bars, rods, profiles, tubes, and wires. The B107/B107M-13 standard is used in industry to guide the mechanical properties of ZK60. The minimum requirements for tensile strength, yield strength, and elongation for ZK60 outlined in this standard differ depending on the geometry and cross section of the extrudate. For bars, rods, and wire forms of ZK60 the minimum tensile strength and yield strength are 296 MPa (43.0 ksi) and 213 MPa (31.0 ksi), respectively [37.9]. Additionally, there are dimensional tolerances included in this standard for straightness, length, angles, roughness, radius, and flatness for products. The experimental ZK60 material used for this project conforms to the B107/B107M-13 standard.

The flow curves for a ZK60 alloy with the specific composition of Mg-5.8% Zn-0.65%Zr (wt%), processed through chill casting and homogenization heat treatment at varying deformation temperatures are included in **Figure 39.2**. It is characteristic for flow stress to increase to a maximum, and then decrease to a steady state under circumstances of hot working accompanied by DRX [39.8]. At low temperatures, the flow curve exhibits high peak stress then negligible work softening after the peak. At moderate temperatures, both peak stress and peak strain are high, but work softening is very pronounced after the peak. At the highest temperatures, steady state is attained after small peak stress and strain, with very minimal work softening. These correlations lead to further evaluation of peak stress and activation parameters, as well as activation energy required for DRX.

Metallography after compression testing at a variety of temperatures and strain rates can lend insight into active deformation mechanisms. These observations revealed features of nucleation of DRX during plastic deformation at moderate and high temperatures. At lower temperatures, 200-227 °C (473-500K), ZK60 samples exhibited twinning and dislocation glide [39.8]. These lower temperatures also revealed progressive lattice rotations in areas of high dislocation density near twin boundaries, resulting in formation of finer grains with non-equilibrium grain boundaries. Basal slip is dominant, yet there are also short thin slip lines at an acute angle to the basal slip lines. Micrographs of deformation at various temperatures are included as **Figure 39.3** [39.8]. For ZK60 (Mg-5.8% Zn-0.65% Zr (wt%)), lower temperatures 200-227 °C (473-500K), exhibited basal slip and mechanical twinning to accommodate plastic deformation. Moderate temperature 227-250 °C (500-523K) deformation is associated with cross-slip-assisted dislocation glide. At higher temperatures > 250°C (>523K), deformation is diffusion controlled and accompanied by dislocation climb [39.8].

39.3 Recent Progress

39.3.1 Sample Preparation

Initial sectioning, mounting, and polishing is a primary step required to perform metallography on future tested specimens. ZK60 and all magnesium alloys are relatively soft and introducing deformation regions is especially easy and must be avoided to observe the as-processed microstructure. These deformation regions can skew results and impede analysis through electron backscatter diffraction (EBSD). Test samples of an initial trial ZK60 alloy were sectioned with a high-speed abrasive wheel, ground with 600 grit grinding paper, then mounted in cold epoxy. This cold epoxy has a maximum curing temperature of 40°C and allowed to cure for 24 hours. These samples were then further ground to 1200 grit and then polished sequentially using 6μm, 3μm, and 1 μm diamond suspension. The specimens were cleaned between every polishing step by rinsing with water, washing with a soapy cotton ball, rinsing in water again, removing water with ethanol, and then hot air blow drying. Optical microscopy was performed between every diamond abrasive step to ensure adequate polishing. This procedure for a low deformation polish has not yet been perfected due to unintentional etching of the sample, possibly due to the pH of the diamond suspension, yet once perfected the samples will be further polished with colloidal silica or through electropolishing. When etching to reveal grain boundaries is necessary, an etchant of 4.2g picric acid, 10mL acetic acid, 70mL ethanol, and 10mL of distilled water will be used for approximately 3-5 seconds.

39.3.2 Cold Rolling Trials

To allow recrystallization to take place, samples will be prestrained by cold rolling up to 80% reduction [39.11], with the assumption that cold rolling will increase hardness uniformly due to an increase in stored strain energy. The grain size should decrease after recrystallization of these cold rolled samples. A plan to machine the initial trial ZK60 into flats plates for rolling has been detailed and proposed to a machine shop. The proposed geometry of various samples is an initial thickness of 2, 3, and 4 mm to test rolling parameters. Rolling will be done on each one of these thicknesses to determine the optimal geometry for the future experimental samples.

39.3.3 Justification of Proposed Material and Heat Treatments

The proposed experimental material is nominal ZK60 composition, with the substitution of various percentages of Zr for Ce. The compositions of this experimental material are included as **Table 39.1**. The material is varied into three different categories: Low solute (~1% Zn), medium solute (~2.5% Zn), and high solute, (~4% Zn), content. For each of these categories, there is material that is either complete solid solution, ~1% pinning phases, or ~3% pinning phases. These categories of nominally ZK60 composition allow variation of both total solute and precipitation phase percentages. The experimental matrix will be determined by the layout of compositions.

Proposed heat treatments for these experimental samples are included as **Table 39.2** and will be performed after all cold rolling trials. Microstructural analysis will be completed after each of the time-temperature combinations in order to calculate percent recrystallization. These ongoing experiments will inform future time-temperature combinations in order to ensure a static recrystallization model is completed with enough temperature and time intervals.

39.4 Plans for Next Reporting Period

Upcoming plans include determining a low deformation metallographic preparation procedure for ZK60 samples and experiments to optimize rolling, heat treatment, Gleeble testing, and microstructural analysis. Additional steps will be taken to in the upcoming months to further this project, including:

- Continued literature review on effects of alloying with rare earth elements in magnesium alloy ZK60.
- Cold rolling trials of initial ZK60 trial material and eventual cold rolling of received experimental material.
- Heat treatment at various temperatures (300, 350, and 400 °C) and times (6 - 48 hours) to determine a static recrystallization kinetics model.
- EBSD imaging of ZK60 heat treated specimens to determine percent recrystallization and overall microstructural evolution.

39.5 References

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39.6 Figures and Tables

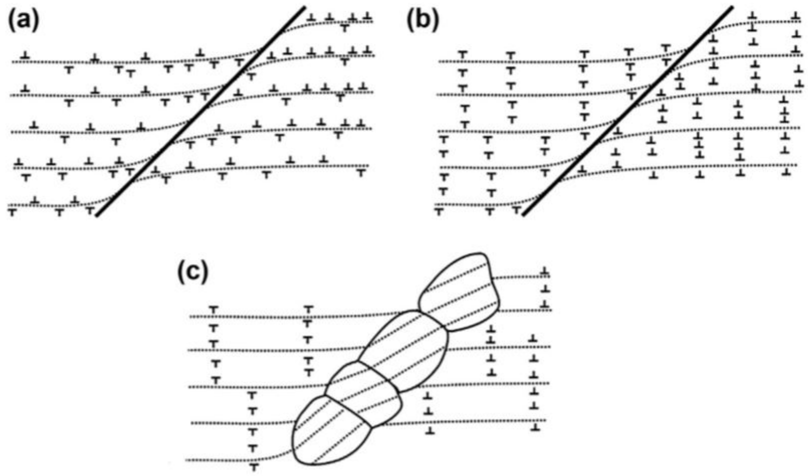

Figure 39.1: Schematic diagram showing proposed mechanism of DRX by progressive lattice rotation and dynamic recovery at grain boundaries in magnesium alloys. (a), (b), and (c) show the progression through initial shear band formation, dynamic recovery of the geometrically necessary dislocations, and subgrain/grain formation [39.5].

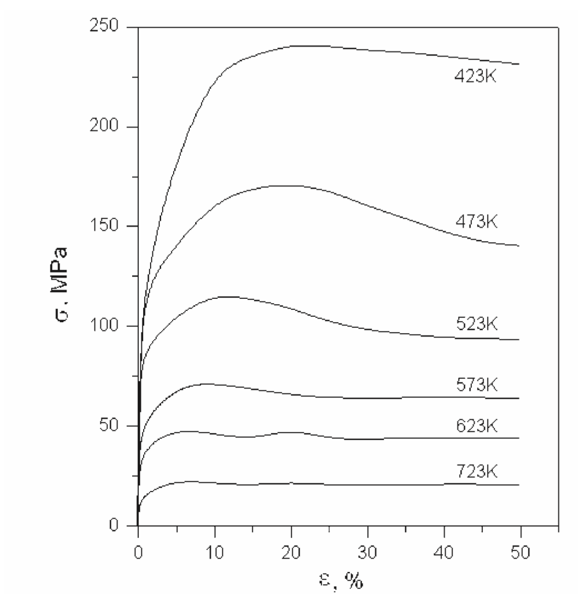

Figure 39.2: Flow curves at various temperatures for ZK60 at constant strain rate (2.8 x $10^{-3}s^{-1}$) uniaxial compression tests [39.8].

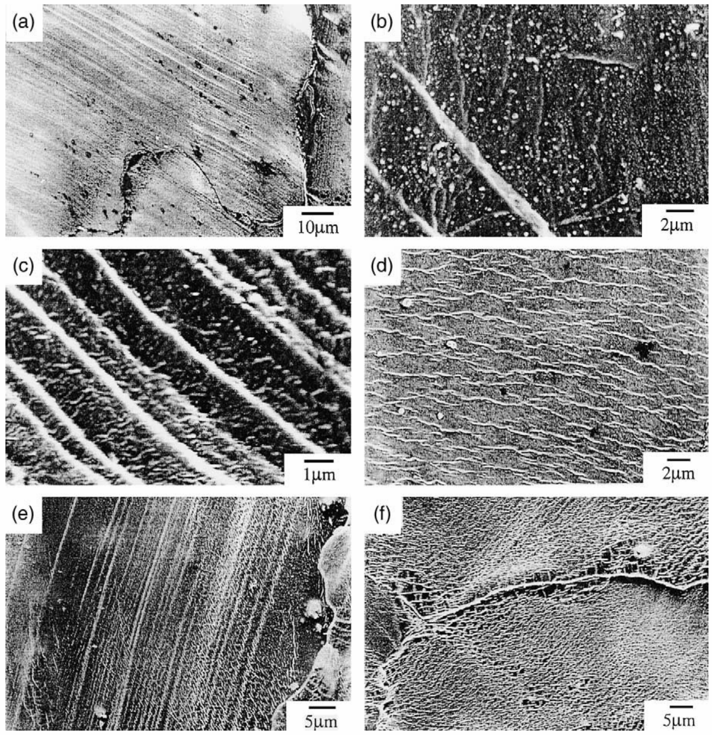

Figure 39.3: SEM secondary electron micrographs of ZK60 post-compression testing. (a) T=423 K, long straight lines of basal slip; (b) T=423 K, short thin lines of $\{11\bar{2}2\}<\bar{1}\bar{1}23>$ slip; (c) T=523 K, lines of basal slip and non-basal slip within body of original grains; (d) T=523K, short wavy lines of a dislocation cross-slip; (e), (f) T=623K, extensive multiple slip [39.8].

Table 39.1: Experimental material compositions based on ZK60 alloys (wt.%).

	Complete Solid Solution	**~ 1% pinning phases**	**~ 3% pinning phases**
Low solute (~ 1%Zn)	-	Mg-1.5Zn-0.4Ce	-
Med solute (~ 2.5%Zn)	-	Mg-3.2Zn-0.4Ce	-
High solute (~ 4%Zn)	Mg-4Zn	Mg-5Zn-0.1Ce	Mg-7.2Zn-0.33Ce

Table 39.2: Heat treatment matrix for experimental samples. HT=heat treat, Q=quench.

-	**6 hours**	**8 hours**	**12 hours**	**24 hours**	**48 hours**
300 °C/573K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
350 °C/623K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
400 °C/673K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q