Project 39: Solute and Precipitate Effects on Magnesium Recrystallization

Fall Meeting

October 13th – 15th 2020

Student: Gillian Storey (Mines)

Faculty: Kester Clarke and Amy Clarke (Mines)

Industrial Mentors: Scott Sutton and Dan Hartman (Mag Specialties Inc.)

Project 39: Solute and Precipitate Effects on Magnesium Recrystallization

- Student: Gillian Storey (Mines)
- Advisor(s): Kester Clarke and Amy Clarke (Mines)

Project Duration

MS: August 2019-August 2021

- Problem: Current recrystallization studies focus on texture modification and grain size reduction mechanisms that are not industrially viable
- Objective: Study the effects of varying precipitate and solute content on recrystallization kinetics. Determine effects of kinetics on hot working parameters and material properties. (Proposed alloy: modified ZK60)
- Benefit: Common alloys may be studied using standard processing parameters modified for industrial benefit.

Recent Progress

- Completed experimental matrix formulation
- Initial rolling and heat treatment of modified ZK60 experimental material
- Literature review

Metrics

Description	% Complete	Status
1. Literature review	90%	●
2. Determine classical Avrami parameters and Zener pinning parameters in static recrystallization	5%	●
3. Adaptation to dynamic recrystallization and hot working	0%	●
4. Characterization of recrystallization mechanisms that are enhanced (or retarded)	0%	●
5. Investigate mechanical and microstructural properties effected by recrystallization kinetics	0%	●

Outline

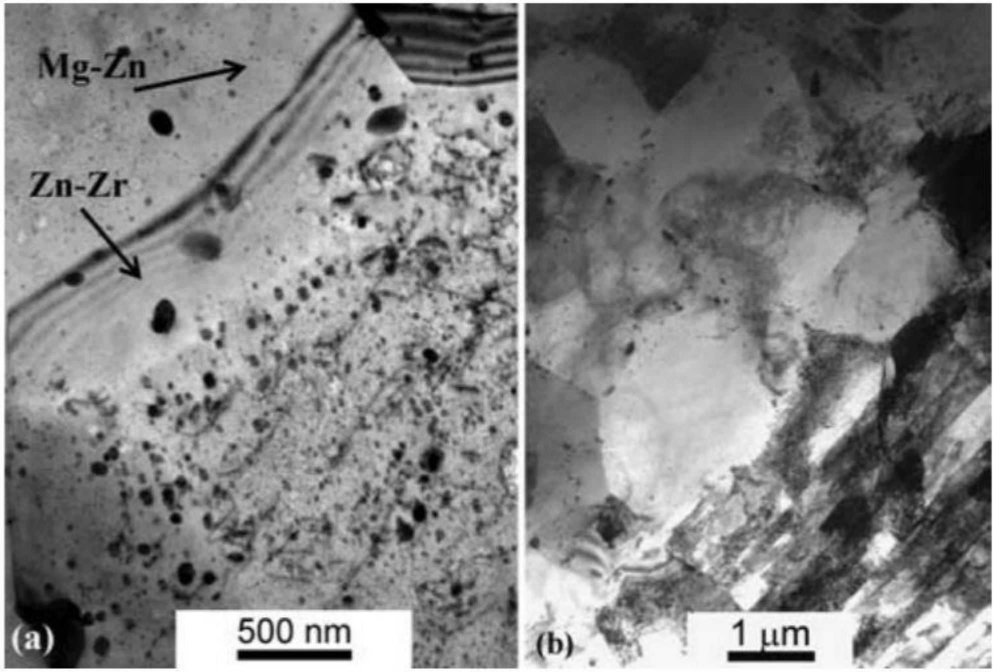
- Project Overview / Industrial Relevance
- Literature Review Highlights
- Sample Preparation
- Cold Rolling Trials
- Material and Heat Treatments
- X-ray Diffraction
- FESEM Images and EDS Results
- Grain Size Calculation
- Future Work

Project Overview

- Comparative study on effects of varying precipitate and solute content on recrystallization kinetics in Mg alloys
- ZK60: nominally Mg-5.8 Zn-0.65 Zr (wt%) [1]
  - Commercial alloy with insoluble Zn-Zr particles and Mg-Zn precipitates that influence grain size and recrystallization [2]
- Determine classical Avrami and Zener pinning parameters for static recrystallization. Then, adapt to dynamic recrystallization and hot working
- Determine effects of microstructural development kinetics on hot working parameters and material properties
  - Microstructural characterization and texture evaluation through electron backscatter diffraction (EBSD)
  - Static recrystallization studies using conventional furnaces
  - Uniaxial compression tests for dynamic recrystallization using a Gleeble 3500 thermomechanical simulator

Industrial Relevance

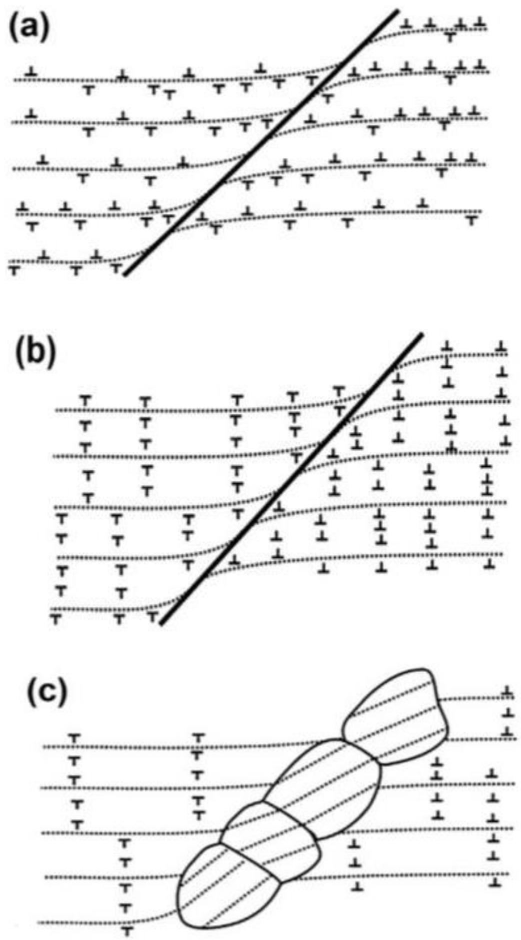
- Understanding the initiation of dynamic recrystallization for constant strain rate hot deformation processes further defines industry processing parameters for ZK60



[3] Shahzad, M., Janecek, M., Wagner, L., International Journal of Materials Research, 2009

Previous Work

- ZK60: commercial alloy with insoluble Zr particles that influence grain size and recrystallization [2]
  - Age (precipitation) hardening [4]
- Replace Zr with rare earth elements, such as Ce or La. Improves high temperature strength and creep resistance [5]
- Recrystallization driving force (T, ε)



[5]

Extrusion of Mg Alloys

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- ASTM B107/B107M-13 [6]
  - Guideline for Mg-alloy extrusion of bars, rods, profiles, tubes, and wires
  - Bars and wires: Minimum tensile strength and yield strength for ZK60 are 296 MPa (43.0 ksi) and 213 MPa (31.0 ksi)
  - Additional product dimensional tolerances
  - Experimental material conforms to this standard

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

ASTM INTERNATIONAL

Designation: B107/B107M – 13

Standard Specification for Magnesium-Alloy Extruded Bars, Rods, Profiles, Tubes, and Wire[1]

This standard is issued under the fixed designation B107/B107M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This specification covers magnesium-alloy extruded bars, rods, profiles, tubes, and wire of the composition given in Table 1.

1.2 The values stated in either inch-pound or SI units are to be regarded separately as standards. The SI units are shown in brackets or in separate tables or columns. The values stated in each system are not exact equivalents; therefore, each system must be used independent of the other. Combining values from the two systems may result in nonconformance with the specification.

1.3 Unless the order specifies the "M" specification designation, the material shall be furnished to the inch-pound units.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 The following documents of the issue in effect on date of order acceptance form a part of this specification to the extent referenced herein.

2.2 *ASTM Standards:*[2]

B117 Practice for Operating Salt Spray (Fog) Apparatus
B296 Practice for Temper Designations of Magnesium Alloys, Cast and Wrought
B557 Test Methods for Tension Testing Wrought and Cast Aluminum- and Magnesium-Alloy Products
B557M Test Methods for Tension Testing Wrought and Cast Aluminum- and Magnesium-Alloy Products (Metric)
B660 Practices for Packaging/Packing of Aluminum and Magnesium Products
B951 Practice for Codification of Unalloyed Magnesium and Magnesium-Alloys, Cast and Wrought
B954 Test Method for Analysis of Magnesium and Magnesium Alloys by Atomic Emission Spectrometry
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
E527 Practice for Numbering Metals and Alloys in the Unified Numbering System (UNS)

3. Terminology

3.1 *Definitions:*

3.1.1 *extruded bar, n*—a solid extrusion, long in relation to its cross-sectional dimensions, having a symmetrical cross section that is square or rectangular with sharp or rounded corners or edges, or is a regular hexagon or octagon, and whose width or greatest distance between parallel faces is over 0.375 in. [10 mm].

3.1.2 *extruded profile, n*—a hollow or solid extrusion, long in relation to its cross-sectional dimensions, whose cross section is other than that of wire, rod, bar, or tube.

3.1.3 *extruded rod, n*—a solid round extrusion, long in relation to its diameter, whose diameter is over 0.375 in. [10 mm].

3.1.4 *extruded tube, n*—a hollow extrusion, long in relation to its cross-sectional dimensions, which is symmetrical and is round, square, rectangular, hexagonal, octagonal, or elliptical with sharp or rounded corners, and has a uniform wall thickness except as affected by corner radii.

3.1.5 *producer, n*—the primary manufacturer of a material.

3.1.6 *supplier, n*—includes only the category of jobbers and distributors as distinct from producer.

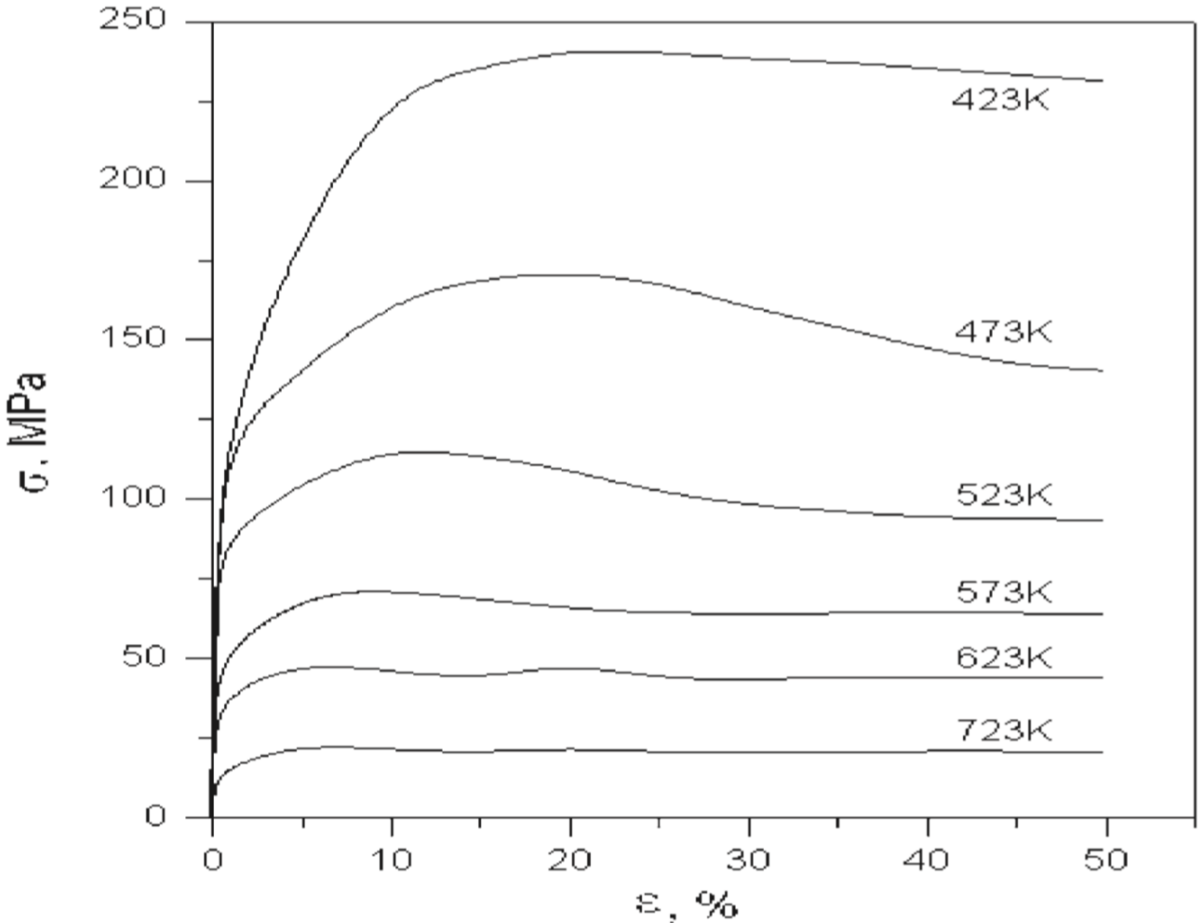
3.1.7 *wire, n*—a solid section long in relation to its cross-sectional dimensions, having a cross section that is round,

[1] This specification is under the jurisdiction of ASTM Committee B07 on Light Metals and Alloys and is the direct responsibility of Subcommittee B07.04 on Magnesium Alloy Cast and Wrought Products.
Current edition approved Nov. 1, 2013. Published December 2013. Originally approved in 1936. Last previous edition approved in 2012 as B107/B107M – 12. DOI: 10.1520/B0107_B0107M-13.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

Flow Curves for ZK60



150 °C, 302 °F

200 °C, 392 °F

250 °C, 482 °F

300 °C, 572 °F

350 °C, 662 °F

450 °C, 842 °F

[7] A. Galiyev, R. Kaibysev, G. Gottstei, Acta Materialia, 2001

Flow Curves for ZK60

(a) T: 150 °C, 302 °F
basal slip

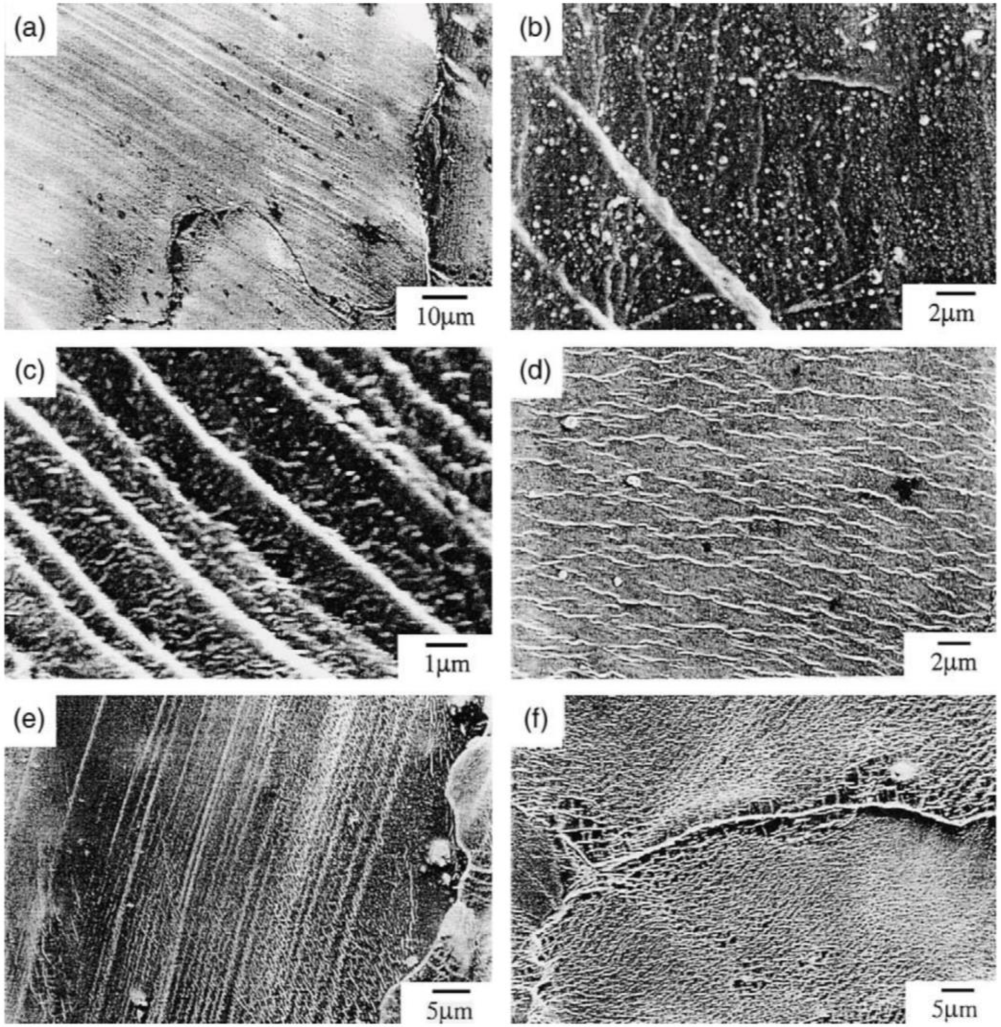
(b) T: 150 °C, 302 °F
short slip lines of
$\{11\bar{2}2\}<\bar{1}\bar{1}23>$

(c) T: 250 °C, 482 °F
basal, non-basal

(d) T: 250 °C, 482 °F
short wavy lines
of cross-slip

(e, f) T: 350 °C, 662 °F
extensive multiple slip

(ε= 12% and $\dot{\varepsilon}$=$2.8\text{x}10^{-3}s^{-1}$)



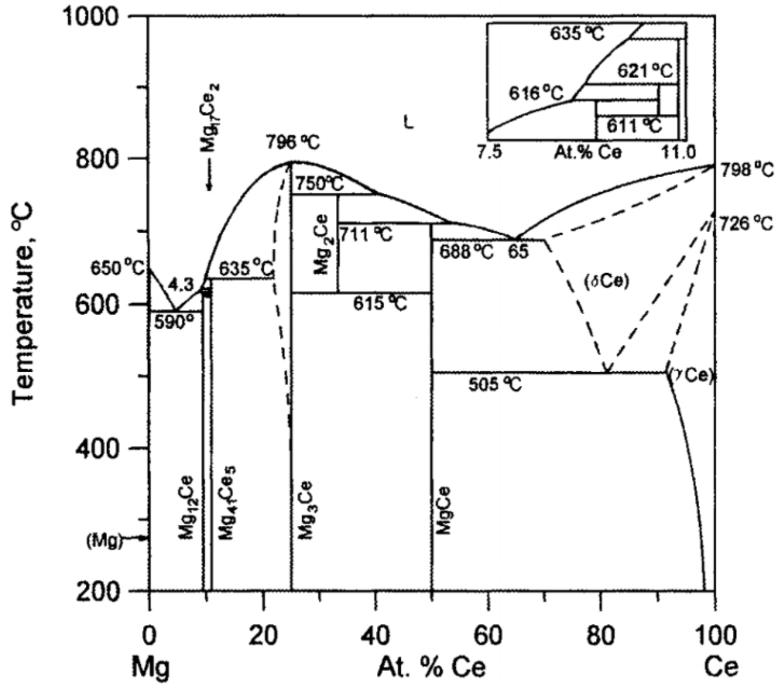
[7] A. Galiyev, R. Kaibysev, G. Gottstei, Acta Materialia, 2001

Influence of Ce additions

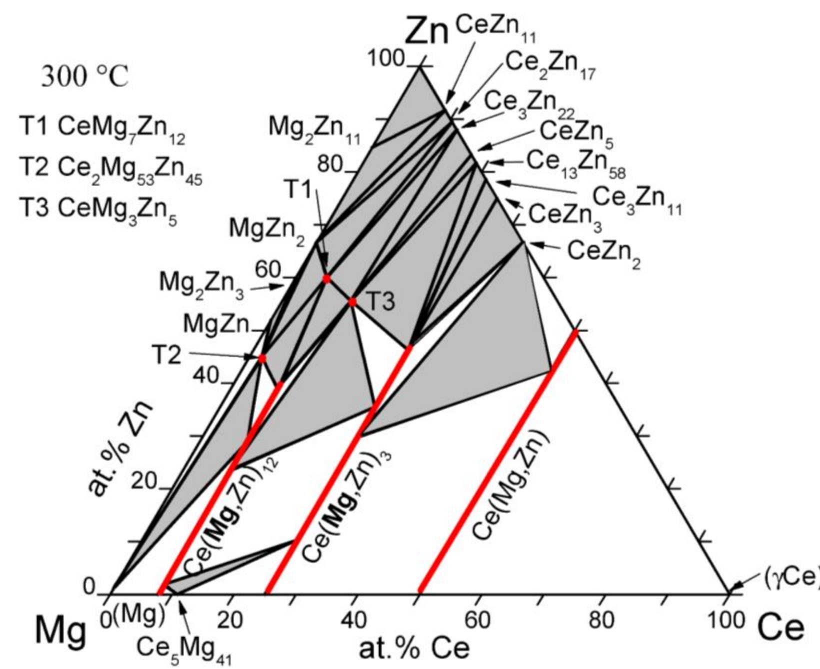
- Rare earth elements: atomic numbers 57 to 71
  - Cerium; atomic number: 58; atomic mass: 140.12; FCC; CN=1
- Attractive properties of RE additions connected to respective phase diagram [8]
- Potentially increase hardness and strength [9]
  - Increase in precipitate formation
    - $Mg_{12}Ce$ [8] and/or $Mg_{53}Zn_{45}Ce_2$ [9]

Influence of Ce additions

CANFSA CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS



[8] Rokhlin, L., Magnesium Alloys Containing Rare Earth Metals, Taylor & Francis, 2003.



[10] Schmid-Fetzer, R., and Grobner, J. Thermodynamic Database for Mg Alloys--Process in Multicomponent Modeling, Institute of Metallurgy, Clausthal University of Technology, 2012.

Recent Progress

Sample Preparation

- Initial sectioning
  - High-speed abrasive wheel, grinding with 600 grit grinding paper
- Cold epoxy mount
  - Max curing temperature of 40°C for 24 hours
- Polishing
  - Grinding to 1200 grit. Polished sequentially to 6μm, 3μm, and 1 μm diamond on a LECO PX500 Automatic Polisher. Final polishing with 0.05 μm colloidal silica
  - Cleaning with DI water, soap and heat gun. When polishing is completed, samples are cleaned with 2% micro-organic soap and sonicated in isopropanol for 10-15 minutes [11]
  - Optical microscopy to ensure adequate polishing
- Etching
  - Acetic-Picral solution: 3 g picric acid, 10 mL acetic acid, 10 mL DI water, 70 mL ethanol
  - 15-20 seconds

Cold Rolling Trial Plan

Goal: Determine elongation necessary before heat treating

- Allow for max recrystallization at a given temperature and time combination
- Determine max strain per pass to ensure necessary reduction consistently
- Determine appropriate sample size

Rolling mill in Hill Hall at the Colorado School of Mines

Rolling Trials Progress

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

Billet ID	Initial thickness (in)	Final thickness (in)	Passes	Reduction in thickness (%)	Strain per pass	Hours	Temperature (°C)
Low solute/ ~ 1% pinning phases	0.338	0.296	11	12%	N/A	24	350
Low solute/ ~ 1% pinning phases	0.321	0.281	11	12%	N/A	6	350
Med solute/ ~ 1% pinning phases	0.324	0.275	12	15%	N/A	24	350
Med solute/ ~ 1% pinning phases	0.351	0.316	8	10%	N/A	6	350
High solute/ Complete S.S	0.365	0.275	8	25%	3.08%	24	350
High solute/ Complete S.S	0.348	0.274	9	21%	2.36%	6	350
High solute/ ~ 1% pinning phases	0.286	0.233	8	19%	2.32%	24	350
High solute/ ~ 1% pinning phases	0.347	0.291	9	16%	1.79%	6	350
High solute/ ~ 3% pinning phases	0.251	0.201	8	20%	2.49%	24	350
High solute/ ~ 3% pinning phases	0.249	0.205	8	18%	2.21%	6	350

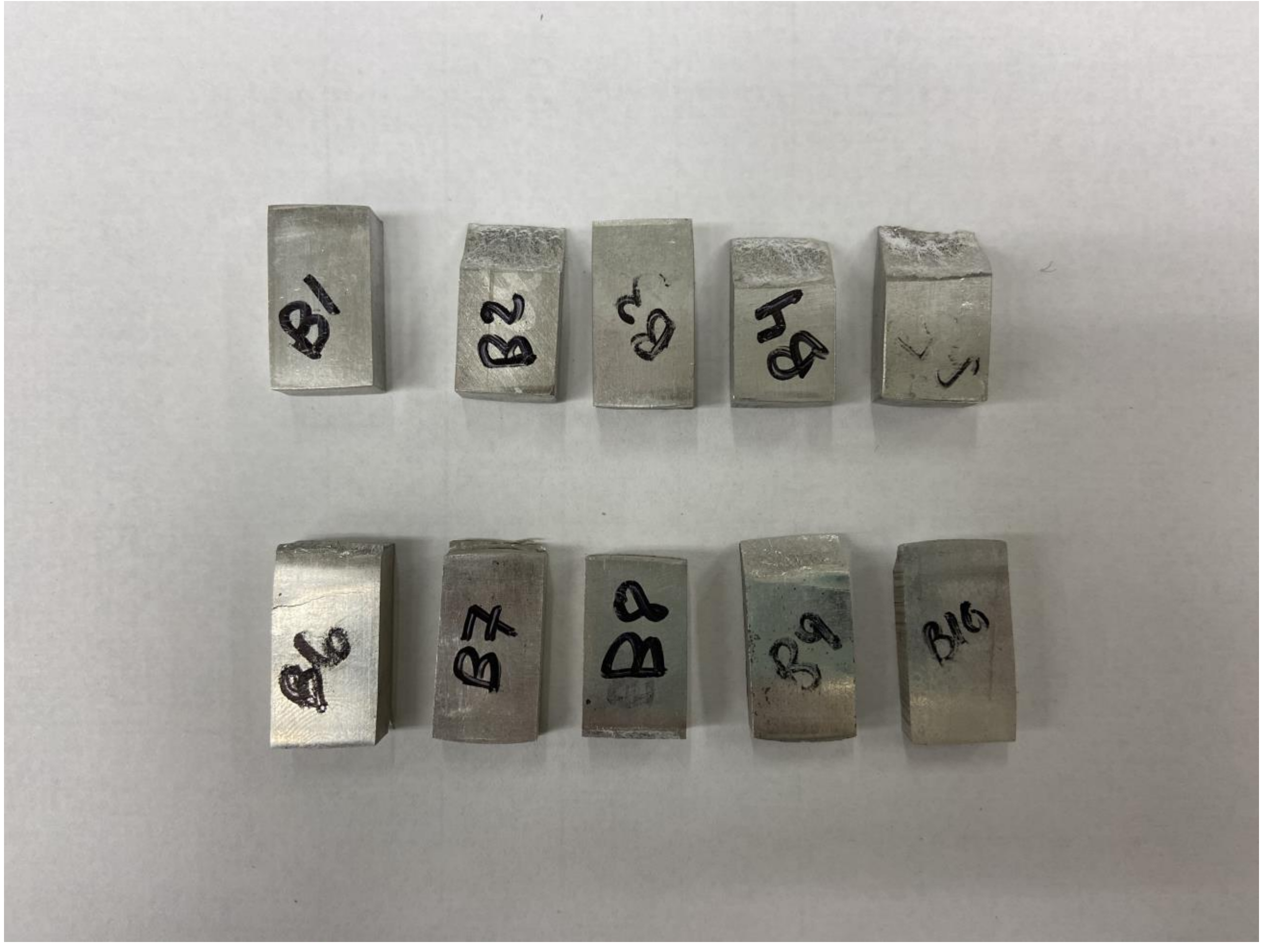
All low/1% pinning phase and med/1% pinning phase samples: 4 initial passes at 0.01” reduction and the remaining passes at 0.005” reduction

The rest: all passes at 0.01” reduction

Results:

- **Cracking and surface defects exhibited around 20% elongation and strain above 2.32% per pass**

Rolling Trials Progress



Rolled experimental ZK60 samples. Initial dimensions: 1/2 ” x 7/8 ” x 1/4”

Experimental Material

- Nominal ZK60 composition (Mg-5.8 Zn-0.65 Zr, wt%) with substitution of various percentages of Ce for Zr and varying levels of Zn
  - The nominal ZK60 composition is stated in ASTM B91-17 [1]

Composition Matrix

Billet ID	Measured Zn	Measured Ce	Target Zn	Target Ce
Low solute/ ~ 1% pinning phases	1.398	0.377	1.5	0.4
Low solute/ ~ 1% pinning phases	1.398	0.377	1.5	0.4
Med solute/ ~ 1% pinning phases	3.515	0.384	3.2	0.4
Med solute/ ~ 1% pinning phases	3.515	0.384	3.2	0.4
High solute/ Complete solid solution	4.206	0.004	4	0
High solute/ Complete solid solution	4.206	0.004	4	0
High solute/ ~ 1% pinning phases	5.26	0.118	5	0.1
High solute/ ~ 1% pinning phases	5.26	0.118	5	0.1
High solute/ ~ 3% pinning phases	6.777	0.311	7.2	0.33
High solute/ ~ 3% pinning phases	6.777	0.311	7.2	0.33

	Complete Solid Solution	~ 1% pinning phases	~ 3% pinning phases
Low solute	-	Mg-1.40Zn-0.38Ce	-
Med solute	-	Mg-3.52Zn-0.38Ce	-
High solute	Mg-4.21Zn	Mg-5.26Zn-0.12Ce	Mg-6.78Zn-0.31Ce

10 billets of experimental material, 2 of each alloy composition, with the cross-section geometry of 1/2 ” x 7/8 ”

Proposed Heat Treatments

CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Performed after all cold rolling trials
- Microstructural analysis will be completed after each time-temperature combination in order to calculate percent recrystallization
- Create static recrystallization model

-	6 hours	8 hours	12 hours	20 hours	48 hours	60 hours	72 hours
300 °C/573K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
350 °C/623K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
400 °C/673K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q

HT=heat treat
Q=quench

Heat Treatment Justification

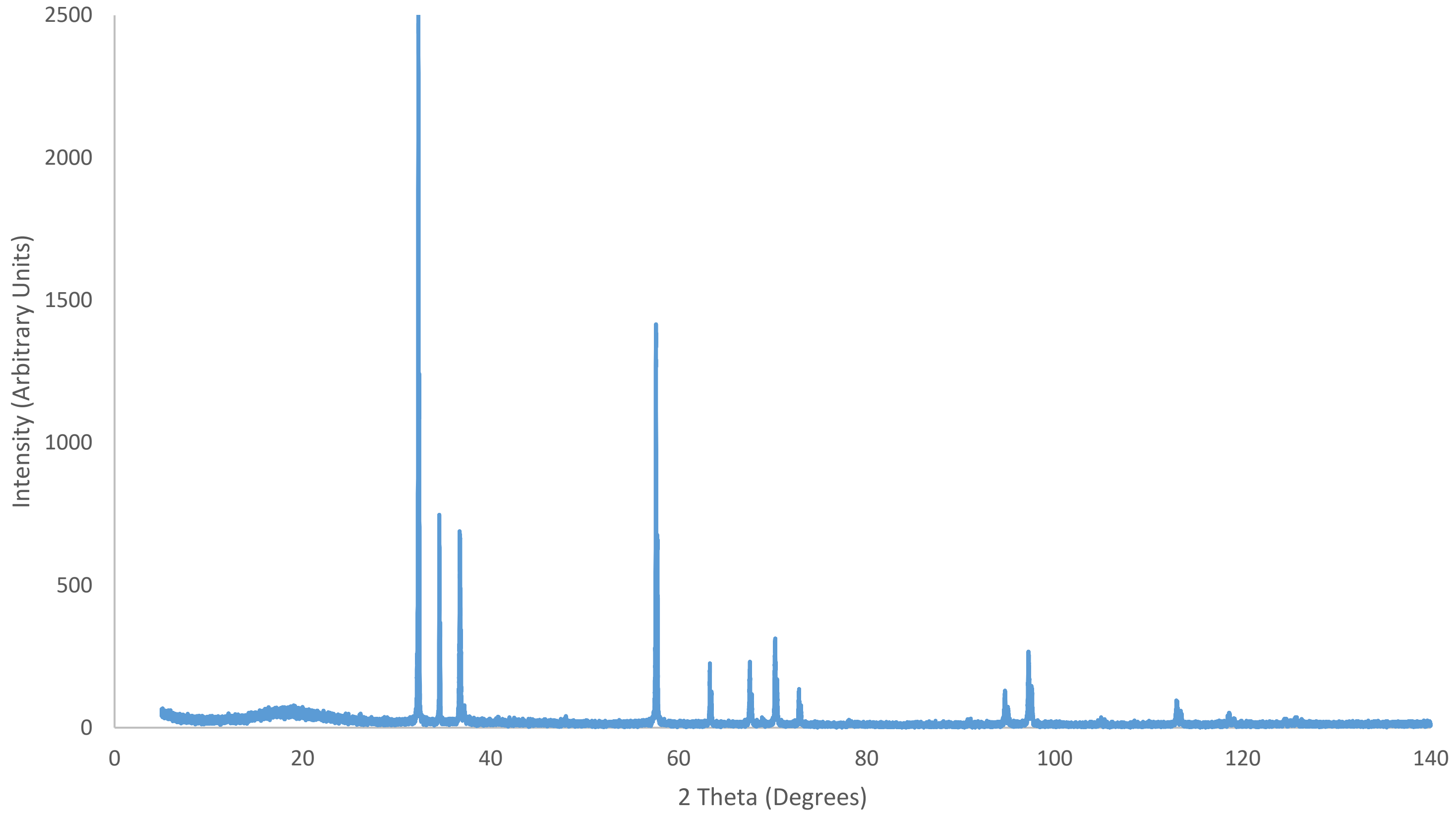
CANFSA
CENTER FOR ADVANCED NON-FERROUS STRUCTURAL ALLOYS

- Rectangular plates of commercial ZK60 ingot cut to 100 x 50 x 3 mm^3, homogenized at 340°C for 6 h and rolled at room temperature. Recrystallized (unknown percentage) after 10 h at 390°C [10]
- In a DRX study [7], uniaxial compression tests were carried out between 150 and 450°C for time intervals of 10 to 30 hours at strain rates between 10^{-5} and 10^{-1} s^{-1}

-	6 hours	8 hours	12 hours	20 hours	48 hours	60 hours	72 hours
300 °C/573K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
350 °C/623K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q
400 °C/673K	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q	HT+Q

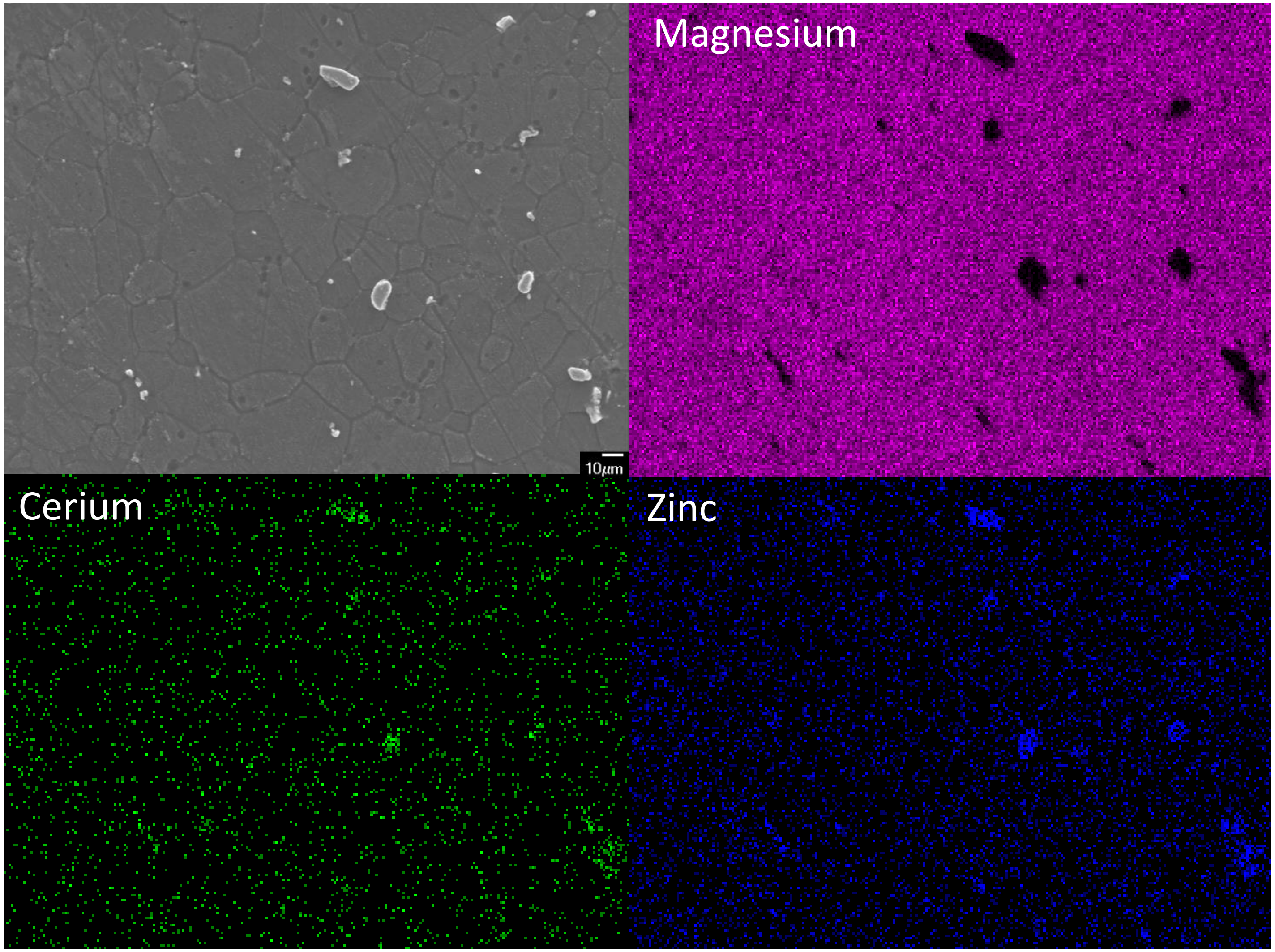
HT=heat treat
Q=quench

X-ray Diffraction



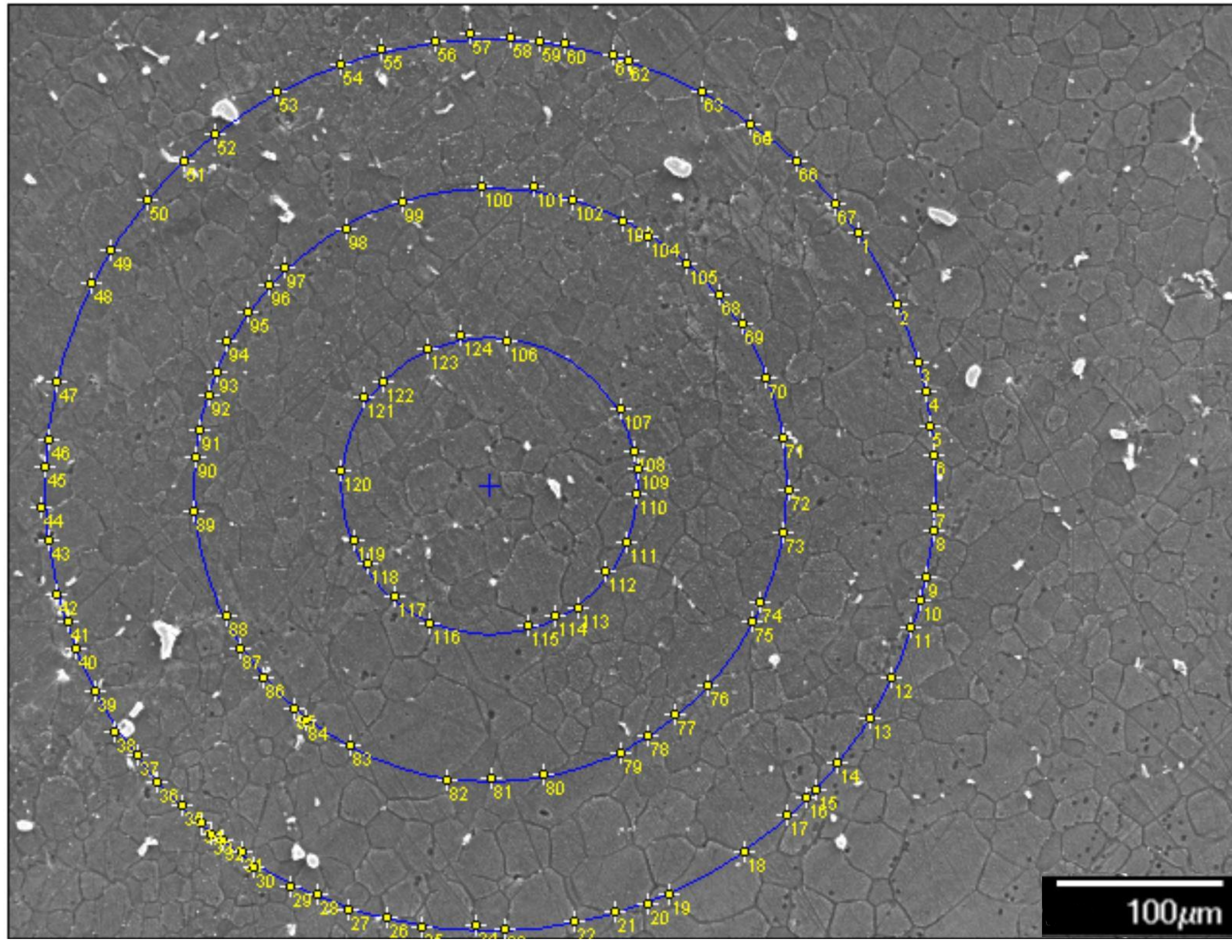
XRD scan showing a wide range of 2-Theta angles and peaks of experimental ZK60 material (High solute/~ 3% pinning phases (Mg-6.78Zn-0.31Ce))

FESEM and EDS



Grain Size Calculation

- Abrams Three-Circle Procedure
  - Exclude twins
  - ASTM E-112 [13]
- Average: 28 µm
  - Result of 5 micrographs



Progress

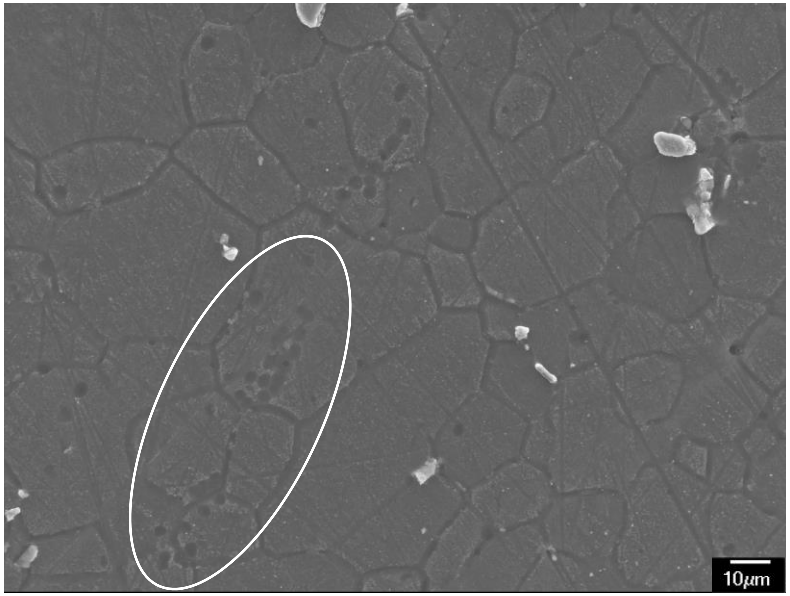
- Established polishing and etching procedure
- Cold rolling trials complete
- Start of heat treating on cold rolled samples
- FESEM imaging and EDS analysis
- Start of XRD analysis
- Grain size calculations

Future Work

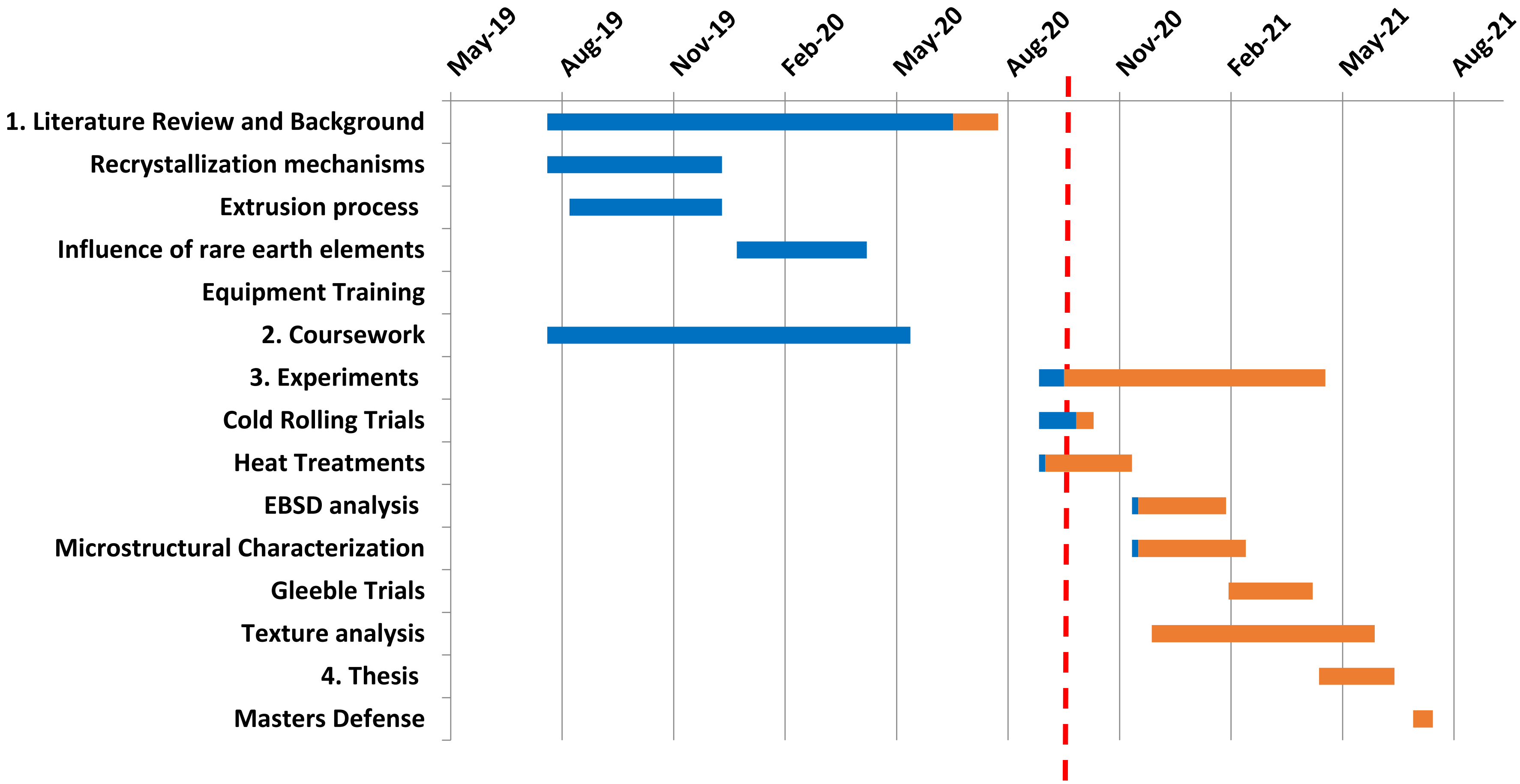
- Cold rolling of experimental material
- Continued microscopy of as-received, rolled, and rolled and heat-treated microstructures
- Heat treatment at various temperatures (300, 350, and 400 °C) and times (6 - 48 hours) to determine a static recrystallization kinetics model
- EBSD imaging of heat-treated specimens to determine percent recrystallization and overall microstructural evolution
- Dynamic recrystallization study using the Gleeble 3500 thermomechanical simulator

Challenges and Questions

- Pitting issues and regulation of proper pressure during polishing
- Further indexing of XRD scan(s) and comparing to future Thermo-Calc results
  - Identifying composition of precipitates



Progress


May-19
Aug-19
Nov-19
Feb-20
May-20
Aug-20
Nov-20
Feb-21
May-21
Aug-21
1. Literature Review and Background
Recrystallization mechanisms
Extrusion process
Influence of rare earth elements
Equipment Training
2. Coursework
3. Experiments
Cold Rolling Trials
Heat Treatments
EBSD analysis
Microstructural Characterization
Gleeble Trials
Texture analysis
4. Thesis
Masters Defense

Works Cited

1. ASTM Standard: B91-17, Standard Specification for Magnesium-Alloy Forgings, ASTM International.
2. T. Bhattacharjee, T. Sasaki, B. Suh, Role of Zr in the Microstructure Evolution in Mg-Zn-Zr Based Wrought Alloys, Magnesium Technology, (2015) 1-16.
3. Shahmad, M., Janecek, M., Wagner, L., Effects of prior homogenization heat treatments on microstructure development and mechanical properties of the extruded wrought magnesium alloy ZK60, International Journal of Materials Research, 2009.
4. J. Cho, S. B. Kang, Deformation and Recrystallization Behaviors in Magnesium Alloys, InTech-Open Science, (2013) 1-4.
5. E. I. Poliak, J.J.Jonas, Initiation of Dynamic Recrystallization in Constant Strain Rate Hot Deformation, ISIJ International. 43 (2003) 684-691.
6. ASTM Standard: B107/B107M-13, Standard Specification for Magnesium-Alloy Extruded Bars, Rods, Profiles, Tubes, and Wires, ASTM International.
7. A.Galiyev, R. Kaibysev, G. Gottstei, Correlation of Plastic Deformation and Dynamic Recrystallization in Magnesium Alloy ZK60, Acta Materialia. 49 (2001) 1199-1207.
8. Rokhlin, L, Magnesium Alloys Containing Rare Earth Metals, Taylor & Francis, 2003.
9. Sheikhani, A, Palizdar, Y, The effect of Ce addition (up to 3%) and extrusion ratio on the microstructure and tensile properties of ZK60 Mg alloy, IOP Publishing Ltd, 2019.
10. Schmid-Fetzer, R., and Grobner, J. Thermodynamic Database for Mg Alloys--Process in Multicomponent Modeling, Institute of Metallurgy, Clausthal University of Technology, 2012.
11. Jin, W., Fan, J., Zhang, H., Microstructure, mechanical properties and static recrystallization behavior of the rolled ZK60 magnesium alloy sheets processed by electropulsing treatment, Journal of Alloys and Compounds, Elsevier, 2015.
12. Davis, Casey, Effects of high shear deformation from equal channel angular pressing-conform on the microstructural and mechanical properties of magnesium alloys, Colorado School of Mines, 2019.
13. ASTM Standard: E-112, Standard Test Methods for Determining Average Grain Size, ASTM International.

Thank you!

Any comments, questions, or feedback?

Gillian Storey

gkstorey@mines.edu