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Investigating Microalloying Elements to Accelerate Zirconium Trialuminide Precipitation in Aluminum Alloys

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INVESTIGATING MICROALLOYING ELEMENTS TO ACCELERATE
ZIRCONIUM TRIALUMINIDE PRECIPITATION IN ALUMINUM ALLOYS

By
Philip D. Staublin

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Materials Science and Engineering

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This thesis has been approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE in Materials Science and Engineering.

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To Leah, Erik, Jack, and Adam

Thank you for being my family away from home.

Part of this degree belongs to each of you.

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Abstract

Precipitation of the $L1_2$ -structured coherent Al_3Zr trialuminide phase in aluminum-zirconium alloys increases the alloy strength. Precipitation of a more refined dispersion of Al_3Zr can further increase the strength of these alloys. The addition of microalloying elements which bind to zirconium may accelerate the precipitation kinetics, allowing for nucleation of a greater number of precipitates and faster precipitate growth. Zirconium binding energies are computed for a wide range of elements, based on which the elements tin, antimony, and tellurium were selected for investigation. Ternary Al-Zr-X alloys ($X = \text{Sn}, \text{Sb}, \text{Te}$) were cast and heat treated isochronally. All three additions resulted in a reduced mean precipitate radius in the peak aged condition, with tin demonstrating the most potent effect. Possible mechanisms for acceleration of Al_3Zr precipitation include nucleation on solute clusters and a reduced zirconium diffusion barrier in the presence of microalloying elements.

Chapter 1

Introduction

1.1 The Aluminum-Zirconium System

Zirconium is a useful alloying addition to aluminum for enhancing mechanical properties through both grain refinement [1, 2] and precipitation hardening [3, 4, 5, 6]. Zirconium forms a trialuminide phase (Al_3Zr) when added to aluminum. This phase forms a peritectic equilibrium with the liquid and face-centered cubic (FCC) aluminum solution phases (Figure 1.1). The stable crystal structure of Al_3Zr is the tetragonal $D0_{23}$ structure [7]; but Al_3Zr with a metastable ordered $L1_2$ structure can form easily from supersaturated liquid and solid solutions of aluminum [8]. Grain refinement in wrought alloys can be achieved by formation of Al_3Zr particles in the liquid phase during solidification. These particles nucleate face-centered cubic α -Al grains, promoting a smaller, more equiaxed grain structure [1].

Zirconium added to aluminum in small quantities (0.04 to 0.2 at%) can enable precipitation hardening to enhance alloy strength. When artificially aged by exposure to elevated temperatures, a supersaturated solid solution of zirconium in aluminum will form coherent precipitates with the metastable ordered $L1_2$ structure [4, 8]. These precipitates provide strengthening by causing dislocations to bow via the Orowan mechanism [9]. Strength gained from dislocation looping increases with decreasing

precipitate radius R and spacing λ (Equation 1.1) [4, 9, 10]. The volume fraction of precipitates formed is fairly constant for a given amount of added zirconium; for instance, at 0.1 at%Zr, the equilibrium volume fraction of Al_3Zr after heat treatment at 400°C is 0.0036 [11]. Since volume fraction is effectively fixed, the number of precipitates increases with decreasing precipitate radius, and vis-versa. Therefore, formation of a more refined precipitate dispersion is beneficial to provide additional strengthening.

$$\Delta\sigma_{\text{Orowan}} \propto \frac{\ln R}{\lambda} \quad (1.1)$$

Figure 1.1: Al-rich corner of the aluminum-zirconium phase diagram, calculated in Thermo-Calc 2018b with the TCAL5 database [11]. The metastable L_{12} solvus curve (dotted line) is calculated using first-principles thermodynamic data computed by Liu et al. [12, 13].

If the precipitates are sufficiently small, dislocation motion through the precipitates can occur, resulting in shearing and formation of an anti-phase boundary due to

disruption of the $L1_2$ ordering [9]. For the similar $L1_2$ Al_3Sc phase, the critical radius below which shearing becomes dominant is reported as around 2 nm [8].

Use of the Al_3Zr phase for precipitation hardening requires formation of a supersaturated solid solution. In traditional age-hardening alloys, such as the Al-Cu alloys, a solutionization heat treatment at an elevated temperature is used where the alloying elements can dissolve into the FCC matrix [3]. The equilibrium solubility limit of zirconium in FCC aluminum occurs at the peritectic invariant point, at approximately 0.08 at%Zr (Figure 1.1). To solutionize an aluminum-zirconium alloy would thus require heat treatment upwards of 600°C to achieve a solid solution phase which could be artificially aged at lower temperatures. However, solutionization treatments can only achieve a zirconium concentration of at most 0.08 at%Zr, and are not often effective [7].

Instead of solutionization, a supersaturated FCC solid solution can be achieved by solidification from a supersaturated liquid, with sufficient cooling rate to avoid peritectic formation of Al_3Zr . Previous work has demonstrated critical cooling rates for complete solute trapping of zirconium in the aluminum matrix at a range of compositions [6, 14]. For a zirconium concentration of 0.1 at%, the critical cooling rate is on the order of 10 K/s—achievable by conventional casting processes. As zirconium concentration increases, the critical cooling rate increases substantially, as does the superheat required to form a single-phase liquid. Because of these factors, supersaturation of zirconium by rapid solidification from the melt is limited.

Precipitation hardening in binary aluminum-zirconium alloys has been previously investigated by several authors. Knipling et al. [2] observed a peak Vickers hardness of approximately 600 MPa in an Al-0.19at%Zr alloy after isothermal ageing at 425°C for 25 hours. Transmission electron micrographs of that alloy show a fine dispersion of coherent Al_3Zr particles with reported average diameter of 13.4 ± 3.4 nm. Also

visible are large (1-2 micron) precipitate free zones at the grain boundaries, due to the known peritectic segregation of zirconium to the grain interiors [6]. Souza et al. [4] observed precipitation hardening in isothermally aged Al-0.065at%Zr and Al-0.095at%Zr alloys at 377°C, reaching peak aged Vickers hardness of approximately 525 and 375 MPa after 100 hours.

1.2 Alloying to Alter Al_3Zr Precipitation

Additional elements can be added to aluminum alloys to alter the precipitation rate, mechanism, or phase. Qian et al. [15] added 0.05 at%Cd to an aluminum-iron-manganese-silicon alloy, which caused the $\alpha\text{-Al}(\text{Mn,Fe})\text{Si}$ phase to nucleate on solute clusters. The authors observed a drastic increase in peak aged strength corresponding to a reduction in the average particle size, which was attributed to the improved nucleation behavior [15]. Zhang et al. [16] added indium and antimony to an Al-Cu alloy and observed acceleration of Al_2Cu and Guinier-Preston (GP) zone precipitation through two different mechanisms. At low ageing temperatures, indium and antimony bound strongly to vacancies and diffused faster at the expense of slower copper diffusion, forming InSb crystals which served as nucleation sites for GP zones. At relatively higher ageing temperatures, the excess vacancies bound to indium and antimony were released and allowed faster diffusion of copper, producing a finer dispersion of Al_2Cu [16].

In the aluminum-zirconium alloys, scandium is commonly added to produce coherent $L1_2 \text{Al}_3(\text{Sc,Zr})$ precipitates [17]. Precipitation of the stable $L1_2 \text{Al}_3\text{Sc}$ phase occurs first during ageing, due to the faster diffusion of scandium compared to zirconium [17]. Then the existing $\text{Al}_3(\text{Sc,Zr})$ precipitates serve as sites for growth of metastable Al_3Zr , forming a characteristic core-shell structure [18]. Scandium is quite effective at

enhancing the precipitation of the trialuminide $\text{Al}_3(\text{Sc,Zr})$ phase: the peak hardness in a ternary Al-0.1Sc-0.1Zr alloy was observed to be twice that of a binary Al-0.1Zr alloy [8]. However, scandium is quite expensive and must be avoided in many commercial applications to maintain a reasonable alloy cost; therefore it would be advantageous to find a microalloying substitute for scandium [19].

Several alloying additions have been used to modify the precipitation behavior in Al-Sc-Zr alloys, such as erbium [20], niobium and tantalum [19], antimony [21], and germanium, indium, and tin [22]. The latter three elements were noted as ineffective at changing the precipitate radius or the hardness at the peak aged condition, but did appear to accelerate $\text{Al}_3(\text{Sc,Zr})$ precipitation, shown by an earlier increase in hardness during isochronal heat treatment. The microalloying additions were also observed to segregate to the precipitate phase. Antimony was observed to have a similar effect, segregating to the Zr-rich shell of the precipitates but also increasing the peak aged hardness [21].

In the cases of germanium, indium, tin, and antimony, a favorable binding energy between the microalloying element and zirconium is posited as a possible mechanism by which precipitation is enhanced [21, 22]. The binding energy is defined as the difference in energy between the state of having the two solute atoms far apart in the aluminum matrix and the state of having said atoms as a nearest-neighbor pair. This model was used by Wolverton [23] to compute vacancy binding energies and by Booth-Morrison et al. to compute the binding energies of silicon to scandium and zirconium [24], both authors applying first-principles quantum mechanical calculations. An attractive binding energy between a solute and zirconium could provide a greater driving force for solute clustering and subsequent nucleation of Al_3Zr , or reduce the energetic barrier for vacancy-mediated diffusion of Zr [24].

Both of the above effects are demonstrated by Booth-Morrison et al. for silicon as a

microalloying addition to enhance scandium trialuminide precipitation. Particularly, Booth-Morrison et al. computed attractive binding energies between silicon and scandium, as well as silicon and zirconium. The authors additionally used first-principles computations of transition state energies to demonstrate that the diffusion barrier for scandium in aluminum is reduced by 0.29 eV/atom in the presence of a silicon solute impurity [24]. Therefore, the effect of microalloying additions on precipitation could be two-fold: solute binding between microalloying elements and zirconium may serve to provide nucleation sites for precipitate formation, and the diffusion activation energy may be reduced by the presence of the microalloying elements.

1.3 Hypothesis

If an element with a favorable nearest-neighbor zirconium binding energy is added to a binary aluminum-zirconium alloy, then the average precipitate diameter in the peak age hardened condition will be smaller, because the binding of solutes to zirconium reduces the diffusion barrier and clustering of the solutes with Zr provide additional heterogeneous nucleation sites.

To test this hypothesis first requires computation of the zirconium-solute binding energies, and selection of candidate elements which exhibit favorable binding (Chapter 2). Next, alloys must be fabricated, heat treated, and the precipitate dispersions characterized (Chapter 3 and Chapter 4). Finally, differences in average precipitate size must be modeled to ascertain the mechanism by which precipitation behavior is altered (Chapter 5). A summary of the key results is given in Chapter 6.

Chapter 2

Computational Study

2.1 Density Functional Theory - Vienna Ab-Initio Simulation Package (VASP)

Density functional theory (DFT) refers to a type of first-principles quantum mechanical calculation in which the ground-state energy of a system of electrons and nuclei can accurately be approximated [25]. This is accomplished by transforming the many-body Schrodinger equation into a set of Kohn-Sham equations representing the exact many-body problem. This allows numerical solution of the equations; however, the Kohn-Sham equations rely on a term of unknown functional form labelled the exchange-correlation energy. While the existence of an exact functional for exchange-correlation energy is guaranteed by the Hohenberg-Kohn theorem of DFT [25], the form is not known and is approximated. Therefore, the notable limitations of DFT are the uncertainty due to the unknown exchange-correlation functional, and the assumption of absolute zero temperature (as the ground-state energy has, by definition, no thermal excitation).

DFT can be used to describe a variety of materials properties, such as formation enthalpy, mixing energies, interfacial energies, solute volumes, and binding energies

[25]. Of interest to this study is the computation of solute-solute binding energies, and the volume change upon addition of solutes and solute pairs.

The Vienna Ab-Initio Simulation Package (VASP) [26, 27, 28, 29, 30, 31] is a computer code which solves the equations of DFT numerically. VASP uses a periodic boundary condition and plane waves to represent the electron configurations and charge density of a “supercell.” A supercell is analogous to a crystallographic unit cell but does not necessarily have to encompass a single crystallographic unit. The supercell geometry and atomic positions are one of four primary inputs to a VASP simulation, the others being the simulation parameters, atom pseudopotentials, and k-point mesh parameters.

The simulation parameters, supplied via a plaintext file named INCAR, specify details such as the type of geometric relaxation, number of allowed relaxation steps, precision, etc. The supercell is supplied in a file named POSCAR, wherein the elements and atomic positions are listed. For each element in the POSCAR file, a pseudopotential must be supplied in a POTCAR file. Pseudopotentials contain data for the inner non-valence electrons of a given element, which change little during minimization of the ground-state energy. To save computation time, the core electrons described by the pseudopotential are effectively fixed, and only the valence electron wavefunctions are calculated. The pseudopotentials also define the exchange-correlation functional to be used during the calculation. Finally, the k-point mesh size must be specified in the KPOINTS file. Numerical integrations of the charge density are calculated frequently by VASP in reciprocal space, and the k-point mesh defines the points at which these numerical integrals are evaluated.

The critical input values in a VASP simulation with a given supercell and set of pseudopotentials are the energy cutoff and k-point mesh size. The energy cutoff defines the number of terms used in the Fourier series representations of the electron

wavefunctions. The total energy of a supercell decreases towards the ground-state energy as the energy cutoff increases; however, the computation time increases drastically with higher values of the energy cutoff. Increasing the k-point mesh size also causes the total energy to approach the ground-state energy; however, the k-point convergence is not monotonic [25]. Convergence of the total energy with respect to energy cutoff and k-point spacing must be carefully considered. In addition, the same energy cutoff and k-point spacing must be used in all calculations which are to be compared, as differences in these parameters alter the level of convergence towards the true ground-state energy. Convergence errors are often similar between similar calculations, and thus the computation of energy differences is expected to cancel some of this systematic error.

2.2 Computational Model

Binding energies between zirconium and other elements within the face-centered cubic aluminum matrix are calculated by taking the difference between the solute energies in isolation and the solute pair (Equation 2.1). In Equation 2.1, $E^{Al_{N-2}Zr_1X_1}$ refers to the energy of a supercell with N aluminum atoms and a Zr-X solute pair. Similarly, $E^{Al_{N-1}X_1}$ refers to a supercell of N aluminum atoms and one atom of element X, while E^{Al_N} refers to an N -atom supercell of pure aluminum. The binding energy E_{bind} is negated such that a positive binding energy represents favorable binding or a tendency for the solutes to attract one another. This model is based on the model for solute-vacancy binding of Wolverton [23].

$$-E_{bind} = E^{Al_{N-2}Zr_1X_1} + E^{Al_N} - E^{Al_{N-1}Zr_1} - E^{Al_{N-1}X_1} \quad (2.1)$$

The impurity volume of single solutes V_{imp}^X in the aluminum matrix can be determined

by finding the difference in relaxed cell volume between the pure aluminum supercell V^{Al_N} and the single solute supercell $V^{Al_{N-1}X_1}$ (Equation 2.2).

$$V_{imp}^X = V^{Al_{N-1}X_1} - V^{Al_N} \quad (2.2)$$

To obtain the energetic quantities in Equation 2.1, 108 atom supercells were used consisting of $3 \times 3 \times 3$ face-centered cubic unit cells. In supercells with a single solute atom, the solute atom was placed on the origin lattice site; where a solute pair was present, the zirconium atom was placed on the origin and the second solute was placed at the first or second nearest neighbor distance (Figure 2.1). The 108 atom supercell was selected based on the convergence of total energy per atom of a single solute supercell. The 108-atom cell for $E^{Al_{107}Fe_1}$ had total energy per atom 26 meV less than the 64-atom cell; however, the cell size could not be feasibly increased due to computational limitations inherent to large systems in DFT.

Figure 2.1: VASP periodic supercells used in computing the Zr-X solute binding energies. (a) The pure aluminum supercell, used to obtain the reference bulk energy of Al. (b) A single-solute cell, Fe in this example. (c) A solute-pair supercell, at nearest-neighbor distance, Zr-Fe in this case.

All supercells were fully relaxed, adjusting both the ion positions and the supercell volume to bring the system to an energy minimum via a conjugate-gradient algorithm.

A maximum of 50 ionic relaxation steps were allowed; however, no calculation required more than 20 such steps to reach an energy minimum. A small finite temperature smearing was applied using the Methfessel-Paxton method [28] to simulate partially occupied states. The projector augmented wave pseudopotentials of Perdew, Burke, and Ernzerhof [32], provided through a database distributed with VASP, were used for all calculations. Sample VASP input and output files can be found in Appendix A.

Convergence of the total energy with respect to energy cutoff and k-point mesh size was verified on two solute pair supercells: Zr-Si and Zr-Ge. First, the energy convergence was evaluated by performing relaxations with varying energy cutoff values and a constant Γ -centered k-point mesh with $11 \times 11 \times 11$ points. An energy cutoff of 500 eV was selected to achieve a total energy converged within 1 meV (Figure 2.2). Then, the k-point convergence was verified by calculating the Zr-Fe binding energy with a reduced k-point mesh size of $9 \times 9 \times 9$. As the resulting binding energy with less k-points (-0.212 eV) was within 1 meV of the binding energy with $11 \times 11 \times 11$ k-points (-0.213 eV), the latter k-point set was considered sufficient and used for all further calculations.

Following convergence testing, single solute and solute pair cells were constructed, relaxed, and their total energies calculated. Using Equation 2.1, the binding energies between zirconium and various solutes across the transition metals and metalloids were calculated. Based on the results of convergence testing, the uncertainty in binding energy is estimated to be on the order of 10 meV; however, physical accuracy of the binding energies cannot be quantified due to the nature of the unknown exchange-correlation functional and zero-Kelvin assumptions of DFT.

Figure 2.2: Convergence of the total energy of two solute pair supercells with respect to energy cutoff, demonstrating convergence within 1 meV at an energy cutoff of 500 eV.

2.3 Zr-X Binding Energies

Nearest-neighbor zirconium binding energies increased monotonically across the third, fourth, and fifth periods (Figure 2.3). Because the elements in groups 3 through 5 (Sc, Ti, V groups) tend to form stable or metastable $L1_2$ trialuminide phases in aluminum, the highly unfavorable nearest-neighbor energy is expected. Elements exhibiting the most favorable binding energy with zirconium belong to the metalloids. Particularly, arsenic, selenium, tin, antimony, and tellurium are observed to have the highest driving force for binding to zirconium. All post-transition-metal elements were observed to have favorable binding energies with zirconium, while all of the transition metals had at least slightly unfavorable binding energies.

At the second nearest neighbor distance, the group 3, 4, and 5 elements demonstrated favorable binding energies with zirconium (Figure 2.4). Second nearest neighbor

(a) Summary of NN Zr-X binding energies for periods 3, 4, and 5

(b) Visualization of NN Zr-X binding energies on the periodic table

Figure 2.3: Summary of nearest-neighbor (NN) Zr-X binding energies within the aluminum matrix for various elements X, as computed by density functional theory.

bonding of zirconium to itself and other group 3, 4, and 5 elements such as Sc is characteristic of the $L1_2$ structure, thus the favorable binding energies are expected. Notably, the metalloid elements maintain favorable binding energies with zirconium at both the first and second nearest neighbor distance. Second-nearest neighbor binding energies for the elements in the fourth and fifth periods were not calculated; however,

based on the first nearest-neighbor binding energies, the fourth and fifth periods are expected to follow the decreasing-then-increasing trend observed for the third period elements.

Figure 2.4: Summary of Zr-X binding energies at the second nearest-neighbor distance in the aluminum matrix, as computed by density functional theory. The fourth and fifth periods are expected to follow the trend observed in the third period.

The solute binding energies with zirconium correlate loosely with the impurity volume calculated by Equation 2.2 (Figure 2.5). The transition metals generally tend to be smaller in atomic radius than aluminum [33], which is reflected in the consistently negative impurity volumes for transition metals in aluminum. However, the metalloids demonstrate both high impurity volume (i.e. larger atomic radius than an aluminum atom) and favorable zirconium binding energy. Given the modest positive impurity volume of zirconium itself, the favorable binding energy with zirconium is not likely to be due to reduction of strain and instead must relate to chemical or electronic interactions between zirconium and the metalloid elements. The shape of the curve formed by following the transition metals through Figure 2.5 is similar to the trend observed for vacancy binding energies versus impurity volumes, shown by Wolverton [23].

Figure 2.5: Variation in impurity volume for various elements within the aluminum matrix, compared to their nearest-neighbor solute binding energy with zirconium. The impurity volume is relative to pure aluminum; see Equation 2.2

2.4 Summary

Based on their favorable first and second nearest-neighbor binding energies with zirconium, antimony, tin, and tellurium are the most promising candidates for microalloying to accelerate Al_3Zr precipitation. Other possibilities such as selenium and arsenic could be effective; however, these elements were not investigated in this study due to their high volatility and toxicity [34]. The zirconium binding energies for bismuth were not computed; but as bismuth is isoelectronic with antimony, it is also expected to bind favorably to zirconium. Therefore, bismuth was also considered as a candidate element for microalloying.

Chapter 3

Experimental Methods

3.1 Casting Process

Five alloys for study were produced by conventional casting into a copper billet mold (Table 3.1). The charges were formulated from 99.99% pure aluminum, 99.9% pure zirconium foil, and $\geq 99.9\%$ pure microalloying elements—refer to Table 3.2 for raw material specifications. All compositions in this study are given in atomic percent, unless otherwise noted. Each charge has a total mass of 600 ± 2 grams, which allowed for excess material in event of a spill.

Table 3.1

Nominal compositions of alloys fabricated for studying the effect of microalloying element additions on the precipitation of Al_3Zr .

Alloy	Composition (at%)				
	Zr	Sb	Sn	Te	Bi
Al-Zr	0.1	-	-	-	-
Al-Zr-Sb	0.1	0.05	-	-	-
Al-Zr-Sn	0.1	-	0.05	-	-
Al-Zr-Te	0.1	-	-	0.05	-
Al-Zr-Bi	0.1	-	-	-	0.05

Table 3.2

Purity and source of elements used as charge materials for casting of the studied alloys.

Material	Purity (wt%)	Manufacturer
Aluminum Ingot	99.99	Belmont Metals, Brooklyn, NY
Aluminum Clips, 500 mg	99.99	Kurt J. Lesker, Jefferson Hills, PA
Aluminum Foil, 0.1 mm	99.99	Alfa Aesar, Ward Hill, MA
Zirconium Foil	99.9	Elemental Metals, New York, NY
Antimony chunks	99.9	J. T. Baker, Phillipsburg, NJ
Tin shot	99.9	Mallinckrodt, St. Louis, MO
Tellurium shot	99.999	Sigma Aldrich, St. Louis, MO
Bismuth chunks	99.9	J. T. Baker, Phillipsburg, NJ

Zirconium was incorporated in the form of a master alloy produced by arc melting with part of the pure aluminum charge material. Pieces of zirconium foil were mixed with 500 mg clips of 99.99% pure aluminum in water cooled copper wells at the bottom of the arc melter vacuum chamber. One button was fabricated for each alloy, containing all of the zirconium for that alloy combined with enough aluminum to produce a button of approximately 25 grams. Each button was melted and flipped over at least three times to ensure complete incorporation of the zirconium.

Due to their low melting points and relative volatility, tellurium, tin, and bismuth were encapsulated in packets of 0.1 mm thick aluminum foil, 99.99% purity (Alfa Aesar, Ward Hill, MA). The packets were made by rolling a strip of foil around a clean steel rod, then crimping one end of the rolled foil shut with pliers. The alloying element was then loaded into the packet, and the other end of the packet crimped shut. In the case of tellurium, the packet was filled in a glove box under argon atmosphere to prevent oxidation. For Te, a 75% recovery rate was assumed, and extra mass added to account for the assumed loss. Tin, antimony, and bismuth were added in precise amounts, i.e. assuming a 100% recovery. All materials were weighed on a balance with ± 0.01 g precision.

Charges were loaded into a graphite crucible, with the aluminum-zirconium master alloy and packet of alloying element at the bottom and pieces of aluminum ingot above. The aluminum ingot was cut into pieces of approximately 30 cubic centimeters using a Baleigh horizontal bandsaw; and the pieces were then rinsed in water and dried thoroughly before loading into the crucible. The graphite crucible was placed within the larger zirconia crucible of an induction melter within a vacuum chamber. The chamber was evacuated by mechanical and then diffusion pump to a pressure of 2.0×10^{-4} torr.

The charge was melted and superheated to 850°C and held for 10 minutes to allow mixing and ensure complete dissolution of any remaining zirconium intermetallic phases. Argon was backfilled into the chamber during melting to reach a pressure of approximately 500 torr, to mitigate loss of volatile elements to evaporation. Following the hold time, the alloy was poured into a cylindrical copper billet mold resting atop a 10 cm tall copper block (Figure 3.1). The mold comprised essentially of a copper tube with inner diameter of 38 mm and outer diameter of 89 mm, producing billets of 38 mm in diameter and 128 mm in height. The cast billets were allowed to cool to room temperature before removal from the mold.

3.2 Casting Simulation

Billet casting and solidification was simulated using Altair Inspire Cast 2019.2 [35]. The model was a simple cylinder with 38 mm diameter and 128 mm height, encased in a rectangular prism of copper mold material, 71 mm along the edges and 162 in height, the top being level with the top surface of the cylindrical billet. It was assumed that this model geometry would produce qualitatively accurate cooling curves. The mesh was automatically generated using an element size of 1.5 mm.

Figure 3.1: Mold arrangement for induction melting and casting within vacuum chamber. The charge material is loaded in the crucible, which is tilted by an external control lever. Melt temperature is monitored via optical pyrometer at the top of the chamber.

The cast material data was for aluminum 7075. A circular opening of 20 mm in diameter was placed level with the top of the mold opening, and metal set to enter at a fill velocity of $0.077 \text{ m}\cdot\text{s}^{-1}$. The initial pouring temperature was set to 991 K. Sites at the center of the billet and 5 mm from the outer edge of the billet were marked for measurement of cooling curves. Duplicate points at different distances from the billet bottom to were marked, to correspond to the locations at which samples would be taken (see Section 3.4).

3.3 Compositional Analysis

Compositional analysis of the as-cast billets was conducted by Lehigh Testing Laboratories (308 West Basin Rd, New Castle, DE 19720 USA). Inductively-coupled plasma

mass spectrometry was used to obtain the compositions. Compositions of the Al-Zr-Bi alloy were measured at Michigan Technological University via inductively-coupled plasma optical emission spectroscopy (ICP-OES). The spectrometer was standardized using three NIST standard specimens prior to testing the experimental alloys. The range of compositions, both nominal and measured, were within the calibration range of the test method used.

3.4 Specimen Preparation

The top of each cast billet was removed using a Baleigh horizontal bandsaw with water-based coolant. A 5 mm thick slice was then removed from the top of the billet via the same bandsaw method and reserved for compositional analysis. Next, the cast billets were turned to a diameter of 31.75 mm using a carbide cutting tool on a lathe. Slices of approximately 10 mm thickness were taken sequentially from the bottom of the billet, and numbered started at one (Figure 3.2). Five or six slices were obtained from each billet, cut using a water-cooled abrasive saw. Each slice was stamped on the bottom side with a number and two-letter designation to note the alloy.

Slices numbered one through five were polished through 0.04 micron silica. Refer to Appendix B for details regarding the polishing process. Slice one was reserved for metallographic analysis of the as-cast condition, while slices two through five of each alloy were cut into quarters using a wire electric discharge mill to prevent introduction of additional strain. Moist cotton was placed between the polished surface of the slice and the clamp of the mill to prevent marring of the polished surface. The quarters of slices two through five were used for isochronal heat treatment (see Section 3.5).

(a) Initial machining process

(b) Billet slicing schematic

Figure 3.2: Processing steps for preparation of slices from cast billets. (a) Initial processing shown left-to-right: first the billet top is removed, then the diameter turned to 31.75 cm. (b) Billets are cut into 10 mm thick slices and numbered starting at the bottom. The upper surfaces of each slice are polished (red arrow).

3.5 Heat Treatment

Quarter slices of the cast billets were heat treated isochronally, starting at 150°C and increasing every three hours. The temperature was increased from 150°C to 200°C in the first step, and then increased in 25°C increments up to 550°C. After each step, one piece of each alloy was removed from the furnace and water quenched to room temperature. After increasing the temperature, the furnace was allowed 15 minutes to heat up before beginning the three hour timer.

The pieces were situated within the furnace atop an aluminum 7075 plate, to which a K-type thermocouple was affixed to monitor the temperature. Temperature was recorded every ten seconds throughout the heat treatment. The arrangement of the pieces was such that the number two billet slice (bottommost) of each alloy was at the front of the furnace, with numbers three through five arranged in order towards the rear. Thus, the order in which pieces were removed was such that the pieces from

lower in the billet were removed at the earlier heat treatment steps.

3.6 Hardness and Conductivity

Vickers macrohardness measurements were made on the polished surface of each isochronally heat treated piece, using a LECO V-100-C2 hardness tester. A load of 5 kg and dwell time of 10 seconds were used, and the resulting indentations measured manually under a 10x objective lens optical microscope. Ten indentations were made on each sample, and the standard deviations reported. The indentations were spread across each sample in the same manner (Figure 3.3) with the position of each indentation being assigned a number between 1 and 10. These positions were then assigned an approximate distance from the billet center, such that the interaction between hardness and distance away from the billet center could be assessed.

Figure 3.3: Pattern of Vickers macrohardness indentations on the heat treated samples, representative. Indentations were arranged in a similar manner on each isochronally heat treated sample, placed relative to the billet center by eye.

Conductivity of each isochronal sample piece was measured by the eddy-current

method using a Fischer Sigmascope SMP10 with ES40 probe at 60 kHz frequency. Each sample was measured ten times, five of which were on the polished surface and five of which were on the reverse face. Standard deviations are reported, and the interaction between measurement location and conductivity was assessed.

3.7 Microstructural Analysis

3.7.1 Scanning Electron Microscopy

Scanning electron microscopy was used for imaging and microprobe analysis of microstructural features in the as-cast specimens and selected samples from the isochronal heat treatment. A Phillips/FEI XL-40 Environmental scanning electron microscope was used in the high vacuum mode, with 15 kV accelerating voltage. Specimens were not coated, and were affixed directly to the microscope stage using carbon tape. Pieces of pure copper tape were adhered to the sample surface to enable calibration of the beam current. Quantitative energy dispersive spectroscopy was conducted to measure composition locally at various microstructural features such as second phases.

3.7.2 Thin Film Sample Preparation

Thin foils for transmission electron microscopy were prepared from selected isochronal samples. First, wire electric discharge milling was used to cut vertical slices from the isochronal heat treatment samples, of approximately $150\mu\text{m}$ thickness. These slices were manually ground to $100\mu\text{m}$ thickness on dry 800 grit silicon carbide paper; thickness was verified by micrometer. 3 mm discs were punched from the ground slices, and

electropolished in 15% HNO_3 in methanol at -35°C and 20 V. The electropolishing device is a SouthBay Technology MS501B MetalThin Twin Jet electropolisher; the jet speed was set to 5 and the sensitivity was set at 6.5. Foils were plasma-cleaned for 10 minutes immediately prior to insertion to the transmission electron microscope (TEM).

3.7.3 Transmission Electron Microscopy

Imaging and energy dispersive spectroscopy of thin foils was conducted in an aberration-corrected FEI Titan Themis scanning transmission electron microscope (S-TEM) at 200 kV. Images were obtained in both high-resolution conventional TEM mode using a Gatan CCD camera and in S-TEM mode using a high-angle annular dark field (HAADF) detector array. Plasma-cleaned specimens were loaded onto a double-tilt holder, to enable tilting of the specimen to find a zone axis. Either a (100) or (110) zone axis was located for high-resolution imaging, within a maximum tilt of 20° in either direction.

Energy dispersive spectroscopy was performed in S-TEM mode to map the local composition of the specimens. The dead time was approximately 20%. Electron energy loss spectrometry (EELS) was used to measure the local foil thickness, for calculation of the precipitate number density. The EELS spectrum was acquired in S-TEM mode across the regions where images were obtained, and the foil thickness quantified assuming an average atomic number of 25. The error of the EELS thickness measurement is approximately $\pm 20\%$.

3.7.4 Image Analysis

Precipitate diameter, circularity, and number density was measured using the ImageJ software. The scale was set first for all analyzed images. In the case of second phase size analysis on backscatter scanning electron microscopy images, a threshold was applied to the image to isolate the bright second phase particles. Then the automated particle analyzer tool was used to produce the average Feret's diameter, area, and circularity of each particle. At least 80 particles were measured for each alloy condition.

In the case of S-TEM HAADF images, the particles were analyzed by manually encircling each particle with the ellipse selection tool, and obtaining the measurements individually. The brightness and contrast was adjusted periodically to allow measurement of as many particles as possible in each image. However, variation in foil thickness across the image in the HAADF images creates a gradient in the background, which renders measurement of every particle difficult. As many particles were measured as could be visually identified with reasonable accuracy. For calculation of number density, particles which could be observed but not accurately measured were counted and added to the number of particles per image.

Chapter 4

Results

4.1 Compositional Analysis

Composition measurements at Lehigh labs by inductively-coupled plasma mass spectrometry (ICP-MS) show a zirconium level consistently within ± 0.005 at% of the target composition of 0.1 at% (Table 4.1). The silicon and iron content of each alloy was below 0.01 at%, consistent with the use of 99.99% pure aluminum charge material. Magnesium content was not assessed by ICP-MS, but read below 0.01 at% when measured by optical emission spectroscopy (OES) at Michigan Technological University. The microalloying content of the ternary alloys was below the target of 0.05 at% in all cases except the case of the Al-Zr-Sn alloy, which contains precisely 0.05 at% Sn according to ICP-MS measurement. Measurement of bismuth content by ICP-MS read lower by almost 0.035 at% compared to the OES measurements at the center and bottom of the as-cast billet. Note that the ICP-MS measurements were taken at the top of the billet; therefore it is reasonable to assume that downward segregation of bismuth occurred due to its higher density.

Table 4.1

Compositions of alloys produced for studying the effect of microalloying element additions on the precipitation of Al_3Zr , measured by inductively-coupled plasma mass spectrometry (ICP-MS). The bottom two rows indicate optical emission spectroscopy measurements conducted at Michigan Technological University.

Alloy	Composition (at%)						
	Zr	Sb	Sn	Te	Bi	Fe	Si
Al-Zr Top	0.098	-	-	-	-	0.005	0.005
Al-Zr-Sb Top	0.101	0.033	-	-	-	<0.001	0.004
Al-Zr-Sn Top	0.098	-	0.050	-	-	0.003	<0.001
Al-Zr-Te Top	0.098	-	-	0.042	-	<0.001	0.004
Al-Zr-Bi Top	0.095	-	-	-	0.005	<0.001	0.010
Al-Zr-Bi Slice 5	0.095	-	-	-	0.040	<0.001	0.005
Al-Zr-Bi Slice 1	0.094	-	-	-	0.039	0.001	0.002

4.2 Billet Cooling Rates

The cooling curves from casting simulation at various points along the billet demonstrates cooling rates in the range from 10–40 K/s (Figure 4.1). The center of the billet had the slowest cooling rates at the beginning of the solidification simulation. At both the center and outer edge, the cooling rates were initially slower for positions further from the bottom of the billet. 20 seconds following pouring, the simulated cooling rates at all tested positions converged to approximately 10 K/s as the temperatures reached 600 K.

4.3 As-cast Microstructure

No primary Al_3Zr particles were identified in any of the as-cast alloys, including the binary Al-0.1Zr alloy (Figure 4.2). Primary phases containing the microalloying

Figure 4.1: Simulated cooling curves for a cast billet of A7075 with initial temperature of 991 K. The “inner” readings were taken at the billet center, and the “outer” readings were taken 5 mm from the outer edge.

elements were observed in all alloys except the binary Al-0.1Zr alloy which had no more than trace contaminant elements. These phases are identified as AlSb, β -Sn, Al_3Te_2 , and pure Bi in the case of the Al-Zr-Sb, Al-Zr-Sn, Al-Zr-Te, and Al-Zr-Bi alloys, respectively. In particular, the presence of primary Bi was concerning in the bismuth-bearing alloy due to the low melting temperature of bismuth [36]. (271.5°C). Due to concerns regarding the melting of primary Bi during heat treatment and doubt that sufficient bismuth entered solid solution in the aluminum matrix, the Al-0.1Zr-0.05Bi alloy was not subjected to isochronal heat treatment or analyzed further.

4.4 Hardness and Conductivity

Hardness and conductivity both increase initially as the temperature increases during isochronal heat treatment (Figures 4.3 and 4.4), due to the formation of Al_3Zr precipitates and concurrent reduction of matrix solute content. All alloys except the

tin-bearing alloy reach peak hardness at 450°C; the tin-bearing alloy reaches peak hardness at 425°C, one heat treatment step prior to the others. The point of peak hardness also corresponds to the peak conductivity for each alloy. Following the peak hardness, the hardness decreases at a similar rate for all alloys due to coarsening and dissolution of the precipitate phases, and possibly transformation of the metastable $L1_2$ structure to the equilibrium $D0_{23}$ structure. The hardness was not observed to vary with the location of the indentation on the sample—i.e. the radial distance from the billet center did not have a significant effect on the measured hardness (??).

The Al-0.1Zr-0.05Sn alloy was observed to have a fine dispersion of primary β -Sn particles initially and at the 200°C isochronal step. At the 300°C step, the dispersion of Sn particles coarsened to an average diameter approximately twice that of the initial dispersion (Table 4.2). As in the as-cast alloy, β -Sn particles were observed as bright spots in backscatter electron images and their composition verified by energy dispersive spectroscopy (EDS, see Figure 4.5c).

Table 4.2

Average size of β -Sn particles in Al-0.1Zr-0.05Sn alloy at two different stages of isochronal heat treatment, as measured by image analysis. N is the number of measured particles; standard error is reported.

Temperature Step (°C)	N	Average Diameter (μm)
200	225	1.03 ± 0.06
300	128	2.8 ± 0.2

4.5 Precipitate Size and Distribution

The Al-0.1Zr-0.05Sn alloy contained a greater number density of precipitates than the binary Al-0.1Zr alloy (Table 4.3), as measured from scanning transmission electron microscopy (S-TEM) high angle annular dark field (HAADF) images. The number

density relies on the foil thickness, which was measured by electron energy loss spectrometry and has an assumed error of $\pm 20\%$:

$$NumberDensity = \frac{N}{A \times t} \quad (4.1)$$

In Equation 4.1, N is the number of particles contained in the analyzed images, A is the total area of the analyzed images, and t is the foil thickness. Of these variables, only the foil thickness has an associated error; therefore, the percent error in number density is equal to the percent error in foil thickness. However, the accuracy of number density measurements is expected to increase as the analyzed image area increases. Thus, the precipitate number density calculated for the Sb-bearing alloy is likely the least accurate of the reported values.

Table 4.3

Average size and number density of Al_3Zr precipitates measured by scanning transmission electron microscopy. N is the number of measured particles for each alloy condition; standard errors are reported. In the lower table, Area indicates the total area of the images analyzed, as used in computing number density.

Alloy	Temperature Step ($^{\circ}\text{C}$)	N	Average Diameter (nm)
Al-Zr	425	84	9.1 ± 0.2
Al-Zr	450	93	10.4 ± 0.2
Al-Zr-Sb	450	164	6.7 ± 0.1
Al-Zr-Sn	425	88	5.8 ± 0.2
Al-Zr-Te	450	126	8.8 ± 0.2
Alloy	Area (μm^2)	Foil Thickness (nm)	Number Density (m^{-3})
Al-Zr 425 $^{\circ}\text{C}$	0.54	120 ± 20	$1.6 \pm 0.3(\times 10^{21})$
Al-Zr 450 $^{\circ}\text{C}$	0.27	260 ± 50	$2.4 \pm 0.5(\times 10^{21})$
Al-Zr-Sb 450 $^{\circ}\text{C}$	0.40	50 ± 10	$30 \pm 6(\times 10^{21})$
Al-Zr-Sn 425 $^{\circ}\text{C}$	0.13	40 ± 10	$8 \pm 2(\times 10^{21})$
Al-Zr-Te 450 $^{\circ}\text{C}$	0.27	130 ± 30	$6 \pm 1(\times 10^{21})$

Visual comparison of the alloy S-TEM images can show the distinction in precipitate size, but not necessarily in number density due to the variable thickness of the thin film TEM specimens (Figure 4.6). In addition to these areas of high precipitate density, many areas near grain boundaries were located which contained few or no precipitates. Images of precipitate free zones were not captured or analyzed and therefore the reported precipitate number density only reflects the grain interior regions where precipitates are plentiful due to peritectic zirconium segregation. Based on the measured radius and estimated number density, the volume fraction of Al_3Zr can be estimated by Equation 4.2. The estimated volume fractions (Table 4.4) are reasonably close to the predicted equilibrium volume fraction in a binary Al-0.1Zr alloy at 450°C of 0.00356 [11]. Errors are attributed to the limited area inspected and measured in the TEM, which are not necessarily representative of the entire bulk alloy.

$$\text{VolumeFraction} = \frac{4}{3}\pi r^3 \cdot (\text{NumberDensity}) \quad (4.2)$$

Table 4.4

Estimated volume fractions of Al_3Zr based on measured precipitate diameter and number density.

Alloy	Temperature Step (°C)	Volume Fraction
Al-Zr	425	0.0006 ± 0.0001
Al-Zr	450	0.0014 ± 0.0003
Al-Zr-Sb	450	0.0008 ± 0.0002
Al-Zr-Sn	425	0.005 ± 0.001
Al-Zr-Te	450	0.0023 ± 0.0005

The crystal structure of the precipitates was determined to be $L1_2$ by selected area electron diffraction in the TEM (Figure 4.6). In addition, high resolution S-TEM images on (100) and (110) zone axes show direct evidence of $L1_2$ ordering (Figure 4.7). Fourier transforms of the high magnification S-TEM lattice images are analog to selected area electron diffraction patterns, and show superlattice spots from S-TEM

image regions which contain precipitates.

In high-resolution S-TEM energy dispersive spectroscopic analysis, the microalloying elements were not observed to occur within the precipitate phases at concentrations significantly greater than the surrounding matrix (Figure 4.8). The precipitates were additionally confirmed to be comprised of zirconium by EDS mapping in the S-TEM.

(a) Al-0.1Zr

(b) Al-0.1Zr-0.05Sb

(c) Al-0.1Zr-0.05Sn

(d) Al-0.1Zr-0.05Te

(e) Al-0.1Zr-0.05Bi

Figure 4.2: Backscatter electron micrographs of the ternary Al-Zr-X alloys investigated. No primary Al_3Zr was identified. The bright phases are intermetallics containing the ternary microalloying additions; the dark spots are pits or holes left from the polishing process.

Figure 4.3: Evolution of Vickers macro hardness with respect to temperature during isochronal heat treatment of Al-0.1Zr-0.05X (at%) alloys. Each temperature step represents 3 hours at that temperature. Standard deviations reported.

Figure 4.4: Evolution of electrical conductivity with respect to temperature during isochronal heat treatment of Al-0.1Zr-0.05X (at%) alloys. Each temperature step represents 3 hours at that temperature. Standard deviations reported.

Figure 4.5: Dispersion of β -Sn particles in Al-0.1Zr-0.05Sn alloy observed to coarsen between the 200°C and 300°C isochronal heat treatment steps. The composition of the particles were measured by energy dispersive spectroscopy (EDS), but the interaction volume overlapped with the matrix resulting in a visible aluminum peak (c).

(a) Al-0.1Zr 425°C

(b) Al-0.1Zr-0.05Sn 425°C

(c) Al-0.1Zr 450°C

(d) Al-0.1Zr-0.05Sb 450°C

(e) Al-0.1Zr-0.05Te 450°C

(f) Al-0.1Zr-0.05Sb 450°C SAED

Figure 4.6: Scanning transmission electron micrographs of Al-Zr-X alloys, showing Al_3Zr precipitates as bright spots. (f) is a representative selected area electron diffraction (SAED) pattern for a (110) zone axis, showing smaller superlattice spots between the larger FCC diffraction spots.

(a) Al-0.1Zr-0.05Sb (110) zone axis

(b) Al-0.1Zr-0.05Te (100) zone axis

Figure 4.7: High-resolution scanning transmission electron micrographs showing direct evidence of $L1_2$ ordering in Al₃Zr precipitates. (a) HAADF image of three Al₃Zr precipitates in the Al-0.1Zr-0.05Sb alloy at the 450°C isochronal heat treatment step, along a (110) zone axis. (b) HAADF image of three Al₃Zr precipitates in Al-0.1Zr-0.05Te alloy at 450°C, along a (100) zone axis.

(a) HAADF Image of scanned area

(b) Al map

(c) Zr map

(d) Te map

Figure 4.8: Energy dispersive spectroscopy maps of local composition in the Al-0.1Zr-0.05Te alloy, demonstrating no measurable segregation of Te into the Al_3Zr precipitate phase.

Chapter 5

Discussion

5.1 Microstructure Evolution

The lack of primary Al_3Zr particles in the as-cast alloys indicates the cooling rates were sufficient to achieve solute trapping during solidification. The lower billet slice has a simulated cooling rate greater by about 20 K/s than the billet slices used in isochronal treatment; thus the isochronally heat treated pieces have a higher likelihood of containing primary Al_3Zr . However, this difference in cooling rate is not large in magnitude, and no primary Al_3Zr was observed in the pieces of the Al-0.1Zr-0.05Sn alloy which were heat treated to 200°C and 300°C. Furthermore, the electrical conductivity measured on the as-cast bottom billet slice matches the conductivity of the first isochronally heat treated pieces, indicating no measurable difference in matrix zirconium concentration between the first and second billet slices. Based on data summarized by Knipling [6], and the cooling rates from the casting simulation of 10–40 K/s, no primary Al_3Zr would be expected in the studied alloys. Therefore, it is assumed that all the zirconium was kept in solid solution during solidification.

Energy dispersive spectroscopy during scanning electron microscopy was unable to determine the concentration of microalloying elements kept in solution in the as-cast state. However, based on the slightly lower conductivity of the ternary alloys (except

Al-0.1Zr-0.05Sn) compared to the binary Al-Zr alloy (Figure 4.4), some amount of microalloying element is likely held in solid solution. This is also reflected in the slightly higher hardness in the ternary alloys compared to the binary alloy at low temperature isochronal heat treatment steps. In the case of the Sn-bearing alloy, the conductivity is equal to or higher than the conductivity of the binary Al-Zr alloy at low temperature isochronal heat treatment steps. This same phenomenon was observed in an Al-0.06Sc-0.06Zr-0.01Sn alloy which was verified to have some tin kept in solution [22]; therefore some tin can be assumed to be in solution in the Al-0.1Zr-0.05Sn alloy in this study. However, the extent of tin in solution is clearly limited based on the visible β -Sn particles in the as-cast state as well as in the isochronal samples aged to 200°C and 300°C (Figure 4.5). The lack of sufficient microalloying additions kept in solution may be a limiting factor on the effectiveness of these elements on Al_3Zr precipitation.

In the case of the Al-0.1Zr-0.05Sn alloy, the fine primary dispersion of β -Sn appears to be responsible for elevated as-cast hardness and higher hardness at the initial four isochronal heat treatment steps as compared to the other alloys (Figures 4.3 and 4.5). The increased strength could also be due to greater solid solution strengthening from greater tin concentrations kept in the matrix phase. At the 300°C step, the primary dispersion of β -Sn appears to have coarsened sufficiently to no longer provide a significant contribution to the alloy strength, either by limiting dispersion strengthening or by having siphoned tin out of solid solution. Because the primary tin particles would have melted during heat treatment, grain boundary diffusion of tin to reduce the solid-liquid interfacial area may be responsible for the rapid coarsening. This coarsening could also be due to the 5 K/s lower simulated cooling rate in billet slice 2 (where the first 4 isochronal samples were taken) compared to billet slice 3. Slower cooling rates could lead to longer growth time and therefore larger primary phases

during solidification. However, at the 250°C step, the slightly lower hardness indicates either a reduction in solid solution strength or coarsening of the β -Sn dispersion; since that measurement is taken from slice 2, the data suggest coarsening rather than a difference in as-cast structure as the cause of the hardness drop. Primary phases of other microalloying elements did not appear to provide any dispersion strengthening.

From the conductivity data, the precipitation of Al_3Zr appears to have been accelerated in the Sn- and Sb-bearing alloys compared to the binary alloy. In the case of the Al-0.1Zr-0.05Sn alloy, the conductivity begins markedly increasing at 375°C, while the other alloys increase in conductivity at the following isochronal step, 400°C. The Sn-bearing alloy additionally reached peak aged condition one 25°C isochronal step earlier than the other three alloys (Figure 4.4). The only acceleration observed in the hardness and conductivity data for the Sb-bearing alloy is higher hardness and conductivity in the three heat treatment steps leading up to the peak aged condition at 450°C. Acceleration in either the nucleation or growth of the precipitates could result in the precipitation behavior observed in the Al-0.1Zr-0.05Sn alloy, and both effects could be caused by an increase in the effective diffusion coefficient of zirconium in the presence of tin solute atoms. Nucleation could additionally be enhanced if tin solute clusters or β -Sn could serve as heterogeneous nucleation sites.

The measured precipitate number densities are lower by two orders of magnitude compared to those observed in Al-0.1Sc-0.1Zr alloys isochronally aged to 400°C by Knipling et al. [8]. Additionally, the average $\text{Al}_3(\text{Sc},\text{Zr})$ precipitate diameter observed by Knipling et al. after isochronal treatment to 400°C was 3.4 ± 1.4 nm, smaller than observed in the Al-0.1Zr and Al-0.1Zr-0.05Sn alloys treated to 425°C in this study [8]. The lower diameter is likely due to the lower heat treatment temperature, and the enhanced number density in the Sc-containing alloy is likely due to the greater overall concentration of Sc+Zr along with the faster diffusion of scandium serving to promote faster nucleation.

To differentiate between possible mechanisms for accelerated precipitation, the S-TEM data can be combined with thermodynamic modelling. Firstly, the S-TEM compositional mapping data indicate a lack of microalloying elements contained within the Al_3Zr precipitates. Based on the favorable first and second nearest-neighbor binding energies of the metalloids, the possibility is considered that the microalloying elements could substitute favorably on either the Al or Zr lattice sites of the $L1_2$ Al_3Zr structure. Substitution of the microalloying elements within the precipitates, or their presence as a core-shell structure, would be expected if pre-existing solute clusters of microalloying elements served as precipitate nucleation sites. While the mixing energies of microalloying elements in the Al_3Zr lattice were not computed, the experimental evidence suggests that mixing does not occur despite the favorable binding energies. This could indicate an increased enthalpy for a microalloying solute to bind with multiple zirconium atoms simultaneously. However, heterogeneous nucleation of Al_3Zr on microalloying element clusters cannot be entirely ruled out, as the microalloying elements could be present in quantities too small to be detected by energy dispersive x-ray spectroscopy.

5.2 Precipitation Model

Precipitation via the nucleation and growth process can be modeled using the numerical Kampmann and Wagner model (KWN model) [10, 37]. Recently, Deane et al. have made available a modified KWN model with accompanying MATLAB code for simulation of precipitation in the Al-Sc system during multi-step heat treatment [10]. The KWN model uses classical nucleation theory to model formation of nuclei during

finite sequential time steps (Equations 5.1 through 5.4), and models growth, coarsening, and dissolution of precipitates from each prior step by Equation 5.5 [10, 37].

$$r^* = \frac{-2\gamma_{Al_3Zr}}{\Delta G_v} \quad (5.1)$$

$$Z = \frac{V_a \Delta G_v^2}{8\pi \sqrt{kT \gamma_{Al_3Zr}^3}} \quad (5.2)$$

$$\beta^* = \frac{16\pi X_{Zr} D \gamma_{Al_3Zr}^2}{\Delta G_v^2 a_0^4} \quad (5.3)$$

$$I = N_v Z \beta^* \exp\left(\frac{-4\pi \gamma r^{*2}}{3kT}\right) \exp\left(\frac{8kT a_0^4}{V_a^2 \Delta G_v^2 D X_{Zr} t}\right) \quad (5.4)$$

$$\frac{dR}{dt} = \frac{D}{R} \frac{X - X_r}{X_e - X_r} \quad (5.5)$$

The KWN code of Deane et al. [10] can be adapted to simulate Al_3Zr precipitation by substituting thermodynamic data for the Al-Zr system. The symbols in the above equations and values of thermodynamic properties are listed in Table 5.1; data from several sources were used in the model. Notably, first-principles thermodynamic data for the Gibbs energy and solvus curve of the metastable $L1_2$ Al_3Zr phase was computed by Liu et al. [12, 13]. From the Gibbs energy data, the energy for formation of a critical nucleus ΔG_v was calculated. If the corresponding critical radius r^* was less than two unit cells of Al_3Zr , the critical radius was fixed at two unit cells.

To evaluate possible effects of microalloying elements on various input properties, a full factorial design-of-experiments construction was simulated. The factors were Al_3Zr interfacial energy, initial solute concentration, zirconium diffusion activation energy, and the contribution of solute binding to the critical nucleation energy. For the latter, the energy for formation of a critical nucleus, ΔG_v , was reduced by

Table 5.1

Thermodynamic and kinetic data used in modeling metastable Al₃Zr precipitation during isochronal heat treatment, using the KWN model.

Property	Value	Reference
Diffusion pre-exponential D_0	0.0728 m ² s ⁻¹	[38]
Diffusion activation energy Q	242 kJ·mol ⁻¹	[38]
Gibbs energy of Al ₃ Zr $\Delta G_f^{Al_3Zr}$	$-46500 - 6.385T$ J·mol ⁻¹ K ⁻¹	[12]
Mixing energy parameter L_0^{FCC}	$-152947 - 21.3T$ J·mol ⁻¹ K ⁻¹	[7]
Energy of pure FCC Zr ΔG_0^{Zr}	$7600 - 0.9T$ J·mol ⁻¹ K ⁻¹	[36]
Lattice parameter of Al ₃ Zr a_0	0.408 nm	[6]
Al ₃ Zr Shear Modulus $G_{Al_3Zr}^{shear}$	57 GPa	[39]
Anti-phase boundary energy γ_{APB}	0.445 J·m ⁻²	[39]
Al ₃ Zr interfacial energy γ_{Al_3Zr}	0.1 J·m ⁻²	[40]
Average atomic volume V_a	1×10^{-5} m ⁻⁵	-
Nucleation site density N_v	6×10^{25} m ⁻³	-
Initial matrix Zr concentration X_{Zr}	0.1 at%Zr	-

0.2 eV/atom, approximately the magnitude of the binding energy for two nearest-neighbor Zr-Sn solute pairs assumed to be included in the critical nucleus. The diffusion activation energy ranged between 222 and 242 kJ·mol⁻¹; the higher value was previously measured experimentally and the lower value represents a reduction on the order of the 0.29 eV/atom observed by Booth-Morrison et al. in the Al-Sc-Si system [24]. The interfacial energy was varied between 0.03 and 0.1 J·m⁻², to cover the range between the previously reported value of 0.1 J·m⁻² and a lowest expected interfacial energy. Initial solute content was varied between the nominal 0.1 at%Zr and 0.2 at%Zr, the latter case assuming peritectic segregation to the grain interiors.

The simulated heat treatment matched the experimental isochronal heat treatment, with 3 hours being spent at each temperature step from 150 to 450°C in 25°C increments, skipping 175°C. Responses included the average precipitate diameter and precipitate number density after heat treatment to 450°C. Only the main effects and two-way interaction terms were included in the model analysis.

Figure 5.1: Main effects plot for factors included in the KWN model design-of-experiments study. The upper panels show the effect of factors on average precipitate diameter, and the lower panels show the effects on precipitate number density.

The diffusion activation energy and interfacial energy had the strongest effects of the model terms (Figure 5.1). These terms are significant at 95% confidence in determining the output average precipitate diameter, along with initial zirconium matrix concentration. With increasing diffusion coefficient and decreasing interfacial energy, the average precipitate diameter after simulated heat treatment is reduced. The predicted number density is mostly controlled by the interfacial energy, consistent with the dependence of the nucleation rate I on the exponential of the interfacial energy cubed (Equation 5.3). The diffusion activation energy is not significant at 95% confidence in determining the number density. Reducing the critical nucleation energy by quantities on the order of the solute binding energy did not have a significant effect on the simulated precipitate size or number density. Of the two-way interaction terms, only interactions with interfacial energy were significant.

(a) Average Precipitate Diameter (nm)

(b) Log Precipitate Number Density (m⁻³)

(c) Combined contour plot; area highlighted which reproduces Al-0.1Zr experimental results

Figure 5.2: Effect of diffusion activation energy and interfacial energy on simulated average precipitate diameter and number density, using the KWN model.

Without solute binding contribution to nucleation, and with the initial solute concentration set at the nominal 0.1 at%Zr, the diffusion activation energy and interfacial energy required to obtain the experimentally observed 10.4 nm average diameter and $2 \times 10^{21} \text{ m}^{-3}$ number density were 226 kJ/mol and 0.05 J/m^{-2} , respectively. This interfacial energy is lower than previously reported in attempts to model Al_3Zr precipitation, which have shown an interfacial energy of 0.1 J/m^{-2} [40] (Figure 5.2).

To reduce the precipitate diameter and increase the number density predicted by the KWN model, the diffusion coefficient must be kept nearly constant and the interfacial energy reduced (Figure 5.2). Therefore, the simulation supports an argument for interfacial segregation of microalloying elements to reduce the precipitate interfacial energy. While segregation was not observed in the S-TEM, it cannot be ruled out—very small quantities of microalloying element may be segregated to the particles but below the detection limit of x-ray spectroscopy. A nano-scale characterization technique such as atom-probe tomography which can resolve such small local changes in composition may be able to confirm interfacial segregation.

5.3 Effectiveness of Microalloying Elements

The Al-0.1Zr-0.05Sb, Al-0.1Zr-0.05Sn, and Al-0.1Zr-0.05Te alloys all exhibited a smaller average precipitate diameter than the binary Al-0.1Zr alloy at the respective peak aged temperature steps (Figure 5.3). The hypothesis is therefore confirmed, despite uncertainty in the exact mechanism by which precipitation behavior is enhanced. Both tin and antimony could be used individually to achieve a slightly smaller precipitate radius and therefore greater number density and concomitant increases in strength.

Future work is recommended to determine the mechanism by which the microalloying

Figure 5.3: Interval plot demonstrating the difference in average precipitate diameter between the binary Al-0.1Zr alloy and the ternary alloys at their peak aged conditions. The error bars represent the 95% confidence intervals; where the error bars do not overlap therefore represents a significant difference ($p < 0.05$).

elements affect precipitation of Al_3Zr . In particular, an insightful experiment could test the isothermal coarsening rate of the zirconium particles in the binary and microalloyed specimens. If the coarsening rate is accelerated in microalloyed samples, an acceleration of the diffusion rate is the most likely mechanism: lower interfacial energy or an enhancement of nucleation rate would either reduce the coarsening rate or have no effect. To investigate interfacial segregation of microalloying elements, as well as solute clustering at lower temperature heat treatment steps, nano-scale characterization techniques such as atom-probe tomography would be useful. Replication of the results pertaining to the Sn-bearing alloy is recommended, to verify the drastic increase in peak-aged hardness can be reproduced. Finally, experiments are recommended to assess whether adding antimony and tin simultaneously to an Al-Zr alloy produces an additive effect in improving Al_3Zr precipitation strengthening.

Chapter 6

Conclusions

Precipitation of Al_3Zr was shown to be accelerated by addition of microalloying elements tin, antimony, and tellurium to binary Al-0.1Zr (at%) alloys. These elements were shown to have attractive binding energies to zirconium within the aluminum matrix by first-principles density functional theory calculations. In the case of tin and antimony, Vickers microhardness increased during isochronal heat treatment one 25°C step earlier compared to a binary Al-0.1Zr alloy. All Al-Zr-X alloys ($\text{X} = \text{Sn}, \text{Sb}, \text{Te}$) demonstrated a smaller average Al_3Zr precipitate radius in the peak aged condition as compared to the Al_3Zr after the same heat treatment.

In particular, the Sn-bearing alloy was observed to significantly increase Vickers microhardness in the peak aged condition (500 ± 16 vs. 410 ± 10 MPa), and also reach the peak aged condition earlier than the binary alloy. Because no segregation of Sn into the Al_3Zr precipitates was observed, nucleation of Al_3Zr on existing tin clusters may not be the dominant mechanism. The effect of tin on reducing the activation energy for diffusion of zirconium was considered as an alternative mechanism, and modeled using the numerical Kampmann and Wagner precipitation model. The model demonstrated an increased number density after isochronal heat treatment to 425°C when the diffusion activation energy of zirconium was lowered.

Integrated computational materials engineering (ICME) proved useful in this study,

reducing the time and expenditure on experimental verification of the wide range of possible microalloying elements. The binding energy computations in this study consumed a total of 894 hours of wall-clock time; however, up to four simulations were run simultaneously, resulting in slightly less than two weeks of time spent on computation. Including approximately one week of preparing simulation inputs and analyzing the resulting data, computing binding energies consumed less than one month of research time. In comparison, fabrication, preparation, characterization, heat treatment, testing, and analysis of the four alloys studied herein required over three months of research time. To analyze experimentally the entire suite of possible microalloying elements, even only including the 12 most “reasonable” elements, would require roughly six times more time spent. In time saved alone, the application of ICME is highly beneficial.

Tin, antimony, and to a lesser extent, tellurium are promising microalloying additions for the formation of a more refined dispersion of Al_3Zr precipitates. Further work will be required to ascertain the precise mechanism by which precipitation is accelerated through additions of these elements.

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Appendix A

VASP Input and Output Files

A.1 Sample INCAR File

The INCAR file contains the input settings and control options for the VASP program. Each line in the file below is commented to show its function.

```
SYSTEM = Al-1Zr-1Mg FCC

ISIF = 3          #Allow the cell and ions to fully relax
ISMEAR = 1        #Use the Methfessel-Paxton method for ↵
                  partial occupancies
SIGMA = 0.2       #Smearing width in eV
NPAR = 4          #Balance orbital calculations across 4 ↵
                  sets of cores
PREC = Normal     #Use normal precision
LREAL = Auto      #Automatically select projection ↵
                  operators
NSW = 50          #Allow 50 ionic steps
IBRION = 2        #Use the conjugate gradient algorithm ↵
                  for relaxation
ENCUT = 500       #Energy cut-off (eV)
```

A.2 Sample KPOINTS File

The KPOINTS file defines the mesh size for automatically generated k-point grids, with the number of k-points along each reduced lattice vector given in the fourth line.

```
11x11x11
0
Gamma
11 11 11
0 0 0
```

A.3 Sample POSCAR File

The POSCAR file defines the atom types and initial positions. The top part of the file describes the initial cell geometry in the form of three real-space lattice vectors, and then the atomic positions are given in fractional components of these vectors.

```
FCC 108-atom NN defect pair
1.0
    12.0000000000      0.0000000000      ↵
      0.0000000000
    0.0000000000      12.0000000000      ↵
      0.0000000000
    0.0000000000      0.0000000000      ↵
      12.0000000000
  Al    Zr    Mg
  106    1    1
Direct
    0.0000000000      0.166666667      0.166666667
    0.166666667      0.000000000      0.166666667
    0.000000000      0.000000000      0.333333333
    0.000000000      0.000000000      0.666666667
    0.333333333      0.000000000      0.000000000
    0.666666667      0.000000000      0.000000000
```

0.000000000	0.333333333	0.000000000
0.000000000	0.666666667	0.000000000
0.000000000	0.166666667	0.500000000
-0.000000000	0.166666667	0.833333333
0.333333333	0.166666667	0.166666667
0.666666667	0.166666667	0.166666667
0.000000000	0.500000000	0.166666667
-0.000000000	0.833333333	0.166666667
0.166666667	-0.000000000	0.500000000
0.166666667	-0.000000000	0.833333333
0.500000000	0.000000000	0.166666667
0.833333333	0.000000000	0.166666667
0.166666667	0.333333333	0.166666667
0.166666667	0.666666667	0.166666667
0.166666667	0.166666667	0.333333333
0.166666667	0.166666667	0.666666667
0.500000000	0.166666667	0.000000000
0.833333333	0.166666667	0.000000000
0.166666667	0.500000000	0.000000000
0.166666667	0.833333333	0.000000000
0.000000000	0.333333333	0.333333333
0.000000000	0.666666667	0.333333333
0.000000000	0.333333333	0.666666667
0.000000000	0.666666667	0.666666667
0.333333333	0.000000000	0.333333333
0.333333333	0.000000000	0.666666667
0.666666667	0.000000000	0.333333333
0.666666667	0.000000000	0.666666667
0.333333333	0.333333333	0.000000000
0.666666667	0.333333333	0.000000000
0.333333333	0.666666667	0.000000000
0.666666667	0.666666667	0.000000000
-0.000000000	0.500000000	0.500000000
-0.000000000	0.833333333	0.500000000
-0.000000000	0.500000000	0.833333333
-0.000000000	0.833333333	0.833333333
0.333333333	0.166666667	0.500000000
0.333333333	0.166666667	0.833333333
0.666666667	0.166666667	0.500000000
0.666666667	0.166666667	0.833333333
0.333333333	0.500000000	0.166666667
0.666666667	0.500000000	0.166666667

0.33333333	0.83333333	0.16666667
0.66666667	0.83333333	0.16666667
0.16666667	0.33333333	0.50000000
0.16666667	0.66666667	0.50000000
0.16666667	0.33333333	0.83333333
0.16666667	0.66666667	0.83333333
0.50000000	-0.00000000	0.50000000
0.50000000	-0.00000000	0.83333333
0.83333333	-0.00000000	0.50000000
0.83333333	-0.00000000	0.83333333
0.50000000	0.33333333	0.16666667
0.83333333	0.33333333	0.16666667
0.50000000	0.66666667	0.16666667
0.83333333	0.66666667	0.16666667
0.16666667	0.50000000	0.33333333
0.16666667	0.83333333	0.33333333
0.16666667	0.50000000	0.66666667
0.16666667	0.83333333	0.66666667
0.50000000	0.16666667	0.33333333
0.50000000	0.16666667	0.66666667
0.83333333	0.16666667	0.33333333
0.83333333	0.16666667	0.66666667
0.50000000	0.50000000	0.00000000
0.83333333	0.50000000	0.00000000
0.50000000	0.83333333	0.00000000
0.83333333	0.83333333	0.00000000
0.33333333	0.33333333	0.33333333
0.66666667	0.66666667	0.33333333
0.66666667	0.33333333	0.66666667
0.33333333	0.66666667	0.66666667
0.33333333	0.50000000	0.50000000
0.66666667	0.83333333	0.50000000
0.66666667	0.50000000	0.83333333
0.33333333	0.83333333	0.83333333
0.50000000	0.33333333	0.50000000
0.83333333	0.66666667	0.50000000
0.83333333	0.33333333	0.83333333
0.50000000	0.66666667	0.83333333
0.50000000	0.50000000	0.33333333
0.83333333	0.83333333	0.33333333
0.83333333	0.50000000	0.66666667
0.50000000	0.83333333	0.66666667

0.33333333	0.33333333	0.66666667
0.66666667	0.66666667	0.66666667
0.66666667	0.33333333	0.33333333
0.33333333	0.66666667	0.33333333
0.33333333	0.50000000	0.83333333
0.66666667	0.83333333	0.83333333
0.66666667	0.50000000	0.50000000
0.33333333	0.83333333	0.50000000
0.50000000	0.33333333	0.83333333
0.83333333	0.66666667	0.83333333
0.83333333	0.33333333	0.50000000
0.50000000	0.66666667	0.50000000
0.50000000	0.50000000	0.66666667
0.83333333	0.83333333	0.66666667
0.83333333	0.50000000	0.33333333
0.50000000	0.83333333	0.33333333
0.00000000	0.00000000	0.00000000
0.16666667	0.16666667	0.00000000

A.4 Sample OUTCAR File

The OUTCAR file contains the output and results of each calculation step performed by the VASP program. Due to its large length, only the relevant information regarding the converged total energy is displayed below.

```

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
-----
free  energy    TOTEN  =          -407.95212217  eV

energy  without entropy=          -407.95635520  energy(↔
sigma->0) =          -407.95353318

d Force = 0.7240405E-04[ 0.467E-04, 0.981E-04]  d ↔
Energy = 0.7186581E-04 0.538E-06
d Force = 0.2834432E-01[ 0.279E-01, 0.288E-01]  d Ewald↔
          =-0.2736250E-03 0.286E-01

```

```

-----

POTL0K:  cpu time      0.1320: real time      0.1321

-----

reached required accuracy - stopping structural energy ↵
  minimisation
writing wavefunctions
  LOOP+:  cpu time 1465.6302: real time 1491.1548
  4ORBIT:  cpu time   0.0000: real time   0.0000

total amount of memory used by VASP MPI-rank0 2235704.↵
  kBytes
=====

base      :      30000. kBytes
nonlr-proj:      7086. kBytes
fftplans  :      8671. kBytes
grid      :     14958. kBytes
one-center:       419. kBytes
wavefun   :    2174570. kBytes

General timing and accounting informations for this job↵
:
=====↵

Total CPU time used (sec):  ↵
    49189.789
      User time (sec):    ↵
        47692.102
      System time (sec):  ↵
        1497.687
    Elapsed time (sec):  ↵
        54668.235

Maximum memory used (kb):  ↵
    2384816.
Average memory used (kb):  ↵
    0.

```

Minor page faults:	↔
114430	
Major page faults:	↔
0	
Voluntary context switches:	↔
4681	

Appendix B

Metallographic Preparation

Metallographic preparation for all aluminum specimens in this study was conducted according to the process outlined below. Specimens smaller than 31.75 mm (1.25 inches) in diameter were mounted in EpoxySet resin (Allied High Tech Products, Rancho Dominguez, CA). The epoxy was allowed to cure for at least 12 hours. The as-cast billet slices were not mounted, as they were already 31.75 mm in diameter (see Section 3.3).

Plane grinding was conducted on each sample manually on 320 grit SiC paper with water wash, for at least 15 seconds or longer as required to produce a planar surface. After this step and between each subsequent step, the samples were washed with soap, cotton, and warm water, then ultrasonically cleaned in a 50% solution of ethanol in water. Coarse and fine grinding steps were conducted on a Struers Labo-Pol three-sample autopolisher, following the steps outlined in Table B.1. When polishing the as-cast billet slices, only one sample at a time was polished in the Struers autopolisher.

Following the 3 micron diamond fine grinding step (Step 3 in Table B.1), the samples were viewed under an optical microscope to inspect for evidence of diamond embedding. Due to the softness of the samples in the as-cast condition and the large surface area of the as-cast billet slices, diamonds were occasionally observed to

embedded into the surface of the sample. Embedded diamonds were removed during ultrasonic cleaning, but left visible indentations in the sample surface of approximately 2 micron diameter and similar depth (Figure B.1). If indentations were visible during optical microscopy inspection following the 3 micron diamond step, the sample was polished on a Buehler vibratory polisher with 3 micron alumina suspension on a felt pad for 6 to 8 hours. The long and gentle vibratory polishing process enabled removal of the diamond indentations without further embedding of polishing media.

Table B.1

Polishing procedure for aluminum samples investigated in this study. The vibratory polishing step (Step 4) was only conducted on samples where diamond embedding was observed following the diamond grinding steps.

Step	Pad	Abrasive	Time	Pressure
1	Allied SiC paper	320 grit SiC, water wash	Until Plane	Manual
2	Struers MD-Largo	Allied 15 micron diamond, glycol suspension	5-6 minutes	30 N
3	Struers MD-Mol	Allied 3 micron mono- crystalline diamond paste, Allied RedLube	5-8 minutes	25 N
4	Buehler felt cloth	Buehler 3 micron alumina, suspension in water	6-8 hours	Vibratory polish
5	Allied Final P	Allied 0.04 micron silica suspension	2 minutes	15 N

Figure B.1: Evidence of indentations left due to diamond polishing media embedding in the sample surface following the coarse and fine grinding steps. (a) Dark spots in optical image, used as evidence to suggest the need for vibratory polishing. (b) Scanning electron microscopy image demonstrating the morphology of the indentations.