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**Solid-State Production of Single-Crystal Aluminum and Aluminum-
Magnesium Alloys**

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by

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Thesis

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Abstract

Solid-State Production of Single-Crystal Aluminum and Aluminum-Magnesium Alloys

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The University of Texas at Austin, 2010

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Three sheet materials, including high purity aluminum, commercial purity aluminum, and an aluminum-magnesium alloy with 3 wt% magnesium, were produced into single-crystals in the solid-state. The method, developed in 1939 by T. Fujiwara at Hiroshima University, involves straining a fully recrystallized material then passing it into a furnace with a high temperature gradient at a specific rate. This method preserves composition and particulate distributions that melt-solidification methods do not. Large single crystals were measured for their orientation preferences and growth rates. The single-crystals were found to preferably orient their growth direction to the $\langle 120 \rangle$ to $\langle 110 \rangle$ directions, and $\langle 100 \rangle$ to $\langle 111 \rangle$ directions normal to the specimen surface. The grain boundary mobility of each material was found to be a function of impurity content. The mobility constants observed were similar to those reported in the literature, indicating that this method of crystal growth provides an estimate of grain boundary mobility. This is the first study the effect of impurities and alloying to this single-crystal production process, and to show this method's applicability in determining grain boundary mobility information.

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Chapter 1 Introduction

1.1 PURPOSE OF STUDY

The goal of this study is to grow single-crystals of aluminum and an aluminum-magnesium alloy in the solid-state and to determine the factors which affect their growth using the method developed by T. Fujiwara [1,2,3,4,5,6]. Under investigation is the applicability of the Fujiwara process to alloys with the intent to explain the results and trends observed with known fundamental behavior of grain growth, and growth of large single crystals in particular. Three materials were considered for this investigation: a high purity aluminum (Al HP), commercial purity aluminum (Al 1100), and an aluminum-magnesium alloy with 3wt% Mg (Al-3Mg).

Single crystals have unique properties and applications compared to their more common polycrystalline forms. Common methods for single crystal production include the Bridgman [7], Czochralski [8], and Chalmers [9] methods. These involve solidification from a melt, which results in a number of difficulties and limitations. This may lead to undesirable segregation, particularly in alloys, and inhomogenities in composition. Mixing of the melt to avoid these issues may introduce other defects into the growing crystal, and even the crucible material may contaminate the melt it is holding. Because of these issues, solidification processes are more suited for the growth of pure single-crystal metals, and may cause difficulty in producing single-crystal alloys.

Segregation problems increase as the alloying content is increased. These methods are also not applicable to parts already formed.

1.2 INTRODUCTION TO SINGLE-CRYSTAL GROWTH METHOD

The method used to create single crystals under investigation here was invented by Prof. Takeo Fujiwara in 1939 at Hiroshima University [2]. The method developed by T. Fujiwara, although having gone through several iterations and improvements, basically involves straining a material a specified amount then slowly entering it into a furnace so that the material is exposed to a steep temperature gradient as it gradually enters and is annealed in the furnace. A single grain at the tip of the material grows out and along the length of the specimen as it enters the furnace. This process has a number of great advantages over other single crystal production methods. Since the material is kept at a lower temperature than melt-solidification methods and is never heated to its melting temperature, all of the issues surrounding solidification can be avoided, and the material's composition and particulate distributions remain unchanged. This process can also be appended to specify the orientation that the single crystal grows and can be applied in an inert atmosphere environment to eliminate oxidation, or other unfavorable reactions, at the temperatures used. This process has been studied primarily in metals of commercial purity, and limited information has been presented on its use for producing single crystal alloys [10,11].

When studying the fundamental behavior of metals, the issue of grain size and orientation is an important consideration, as is dispersoid content. Creating single

crystals from a melt-solidification process does not preserve the dispersion of particulates and distribution of alloying elements. The Fujiwara solid-state method creates single crystals with minimal to no change in these other microstructural features. This can allow for direct comparison between single-crystal specimens and the original material from which they were produced, with the only microstructural difference being grain size. The Fujiwara method allows for single crystals to be grown in any orientation, with the same microstructural features, and is not restricted to one preferred growth orientation, as exhibited by many materials in solidification growth.

1.3 EXPERIMENTAL CONSIDERATIONS

Experiments are used to determine factors that affect the growth of single crystals by the Fujiwara method to help better understand its capabilities and limitations. Certain conditions are thought to be beneficial, and others harmful, for solid-state single crystal growth. Growth rate and crystal size obtained will be explained through known parameters, such as the activation energies for grain nucleation and grain growth, pre-strain, temperature, and composition. In the Fujiwara method, a certain amount of cold strain is applied to the specimen, referred to as pre-strain, to reach a critical amount of strain to allow for recrystallization to occur upon subsequent annealing. The amount of pre-strain required is also thought to be a function of rate and temperature, since for static annealing the critical strain is related to the rate of heating and prior strain. This is elucidated in Figure 1, which shows slow and fast heating rates for an aluminum material with varying amounts of cold work from rolling. Below this critical strain

recrystallization does not occur, and recrystallized grain size decreases as the amount of strain increases because more sites for grain nucleation are formed. Slower heating and higher temperatures tend to create larger grains at lower strains.

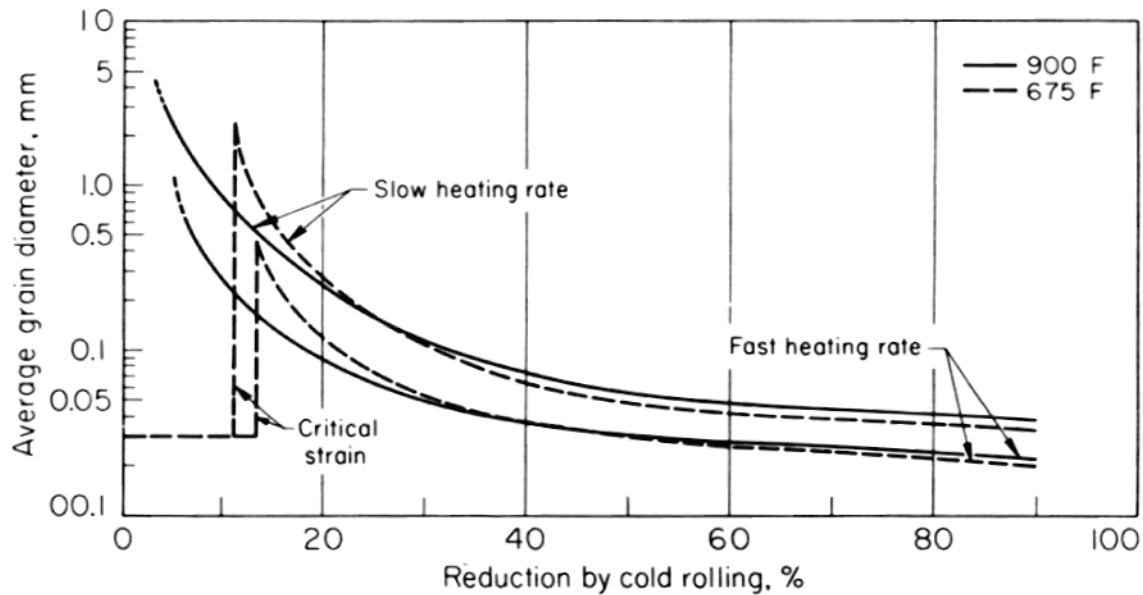


Figure 1: Effect of cold rolling strain, temperature, and heating rate on recrystallized grain size. Figure is from reference [12].

The mobility of a single-crystal grain boundary will be related to the velocity with which the specimen is inserted into the furnace. The critical range of strain found for each material for the process to work will be explained further through compositional and initial microstructure properties.

1.4 LITERATURE REVIEW

Prior to the methods developed by Fujiwara, a strain-anneal method was in use as described by Carpenter et al [12]. This method, like the method of T. Fujiwara, is a solid-state large crystal growth process and was performed on Al. In this case the Al was

99.6% pure, with Si (0.19%) and Fe (0.14%) as the major impurity elements (wt% or at% not provided). The strain-anneal method involves straining a material by a very specific amount as to reach a critical strain for recrystallization, but to limit the number of nucleation sites as much as possible. The Al specimen is then placed in a furnace which is very gradually heated from 450 °C to 550 °C at a rate of 15 to 20 °C per day, followed by a 1 hour anneal at 600 °C to increase mobility and consume any remaining grains. This allows for one to several grains to nucleate and grow to consume the specimen, but the results are not consistent.

The first incarnation of the methods developed by T. Fujiwara was reported in 1938 [1]. This experiment used two methods to produce single-crystal aluminum wire of commercial purity and 1mm in diameter. The first method used a furnace with a temperature gradient along its length. The wire was placed inside and the temperature was raised, effectively passing a temperature gradient along the specimen. The second method involved a moving furnace at a set temperature. The furnace moved along a track by a motor so that the wire specimen was entered at a speed of 10 cm/hr. The wire was unannealed or strained other than the strain produced during wire drawing, which is not specified. Single-crystals 13 cm long were reported for both iterations.

The next development reported by T. Fujiwara was in 1939, when a method for producing single crystals of any desired orientation was published [2]. The same aluminum wire and setup was used as before, with the drive motor replaced with a water-drip system to reduce vibrations. A kernel crystal was created by entering the wire into the furnace, stopping, and pulling the wire out of the furnace. A Laue image of the crystal produced was taken and used along with the orientation desired to determine an

appropriate amount of bending in the polycrystalline region ahead of the single-crystal front. The bent specimen was then reentered into the furnace and, as the kernel single crystal continued to grow along the specimen and past the bent segment, its orientation remained constant, so that the bending oriented the crystallographic growth as desired. The initial growth, bending, and continued growth steps are illustrated in Figure 2.

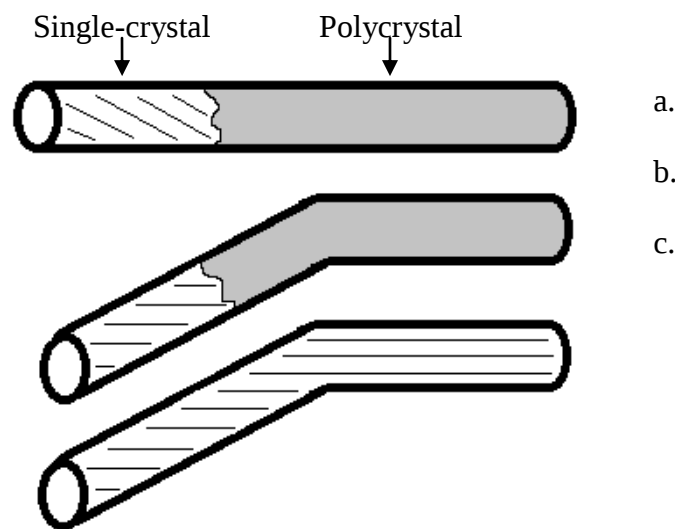


Figure 2: Example of how wire may be bent to orient a kernel crystal to grow in a desired direction, showing kernel initiation (a), bending polycrystalline region ahead of single crystal to orient crystal (b), and continued growth of crystal, which remains in its chosen orientation as it grows into the rest of the specimen (c). Lines in single-crystal region represent crystallographic planes.

The next step for Fujiwara was the development of a method to produce single-crystal aluminum plate with any desired orientation [3]. The sheet aluminum was first rolled to a thickness of 0.3 mm and cut to strips of 5mm wide and 150 mm long. Two slits were cut along the length on one end leaving three fingers of material. The specimen was then annealed at 580 C for 5 hours to remove any strain and to fully

recrystallize the material. The specimen was stretched to 2% and 2 of the three fingers were chemically removed with an acid solution at their base to create a specimen with uniform strain along its length, including a section of reduced width. The reduced width section is created to provide a location for initiation of the kernel grain and space so that the specimen can be bent and twisted as needed to orient the kernel grain. The specimen was reentered into the furnace slowly as before, to allow the initiated and oriented grain to grow and fill the length and width of the specimen.

Fujiwara further developed techniques to create single-crystal wires and plates of iron with controlled crystallographic orientations [4,5]. For these applications, the specimen was placed in a sealed tube under vacuum (0.013 Pa) to prevent oxidation of the iron at high temperatures as it was guided into the furnace.

In 1949, T.J. Tiedema [13] at the Foundation for Fundamental Research in Holland reproduced much of the work of T. Fujiwara for publication, because of a lack of access to the Japanese records at the time, and presented details not given in past publications. Tiedema used plate and wire aluminum of 99.5% purity. The drawn wire was found to have the characteristic [111] drawing texture prior to annealing in a moving furnace at a rate of 6.7 cm/min and temperature of 550 °C. The wire was then stretched to approximately 2% and its end annealed to initiate a single crystal in a furnace at a temperature of 630 °C. The wire insertion rate was 4 cm/hr. The initially produced kernel crystals typically had a [210] orientation $\pm 3^\circ$ to the wire axis. The last anneal by slow insertion into the furnace, after bending the wire appropriately, was performed at 630 °C and at a 2 cm/hr entry rate. Sheet aluminum, with dimensions 1mm thick, 2 cm wide and 30 cm long, was turned into single crystals in a similar way, with an anneal

after rolling at 550 °C and at a 9 cm/min entry rate. It was then strained to 2%, a kernel initiated at 630 °C and a 3 cm/hr entry rate, bent to orient the kernel grain, and grown through the specimen at 630 °C and 2 cm/hr. Further research by Tiedema et al [14] looked at the issue of island grains, which may remain after growth of the single crystals. These were found to have spinel-twin orientation relationships, within a few degrees of the growing single-crystal. Grains very close in orientation may become absorbed into the single-crystal by some lattice distortion, but those up to a few degrees do not have enough driving force to reorient. Because of this, it was found that the $\langle 111 \rangle$ direction is not suitable for growing in wire since the wire has a $[111]$ texture. Other included grains, which have undergone growth, unlike those just mentioned, are found to likely be grains that experienced little deformation in the initial straining and have roughly equivalent energy to the growing crystal, and thus do not have the energy drive to join the single-crystal.

In 1951, T. Mukai used the method developed by Fujiwara to create thick specimens of aluminum [15]. The material was rolled and cut to 3 mm thick, 6 mm wide, and 120 mm long. It was then annealed at 530 °C for 5hrs before stretching to 4% strain and was chemically machined to have one tong, or finger, as done previously. A salt bath was used, instead of an electric furnace as before, and the entry rate was 1mm/hr. The specimens could be withdrawn and bent as before to obtain the orientation desired.

Around the same time, T. Fujiwara et al [6] reported, in greater detail, their work from 1944 to the publication date, 1952. This included the improvements already mentioned, such as the use of a salt bath and annealing prior to straining at 550 °C. The temperature 5 mm above the molten salt was at 490 °C and the temperature of the salt

ranged from 570-600 °C. Entry rates for the different geometries varied from 8-18 mm/hr. These parameters depended on the stage of production: kernel initiation, growth through bent region, and growth along the full width specimen, with typically slower rates and higher temperatures used for the latter stages. The final stage was often completed in an electric furnace as before.

In 1952, H. Fujiwara [16] explained the process of bending to orient the seed in further detail and provided an improvement to the process to limit the amount of strain added in the bending process. This called for the twisting, x bending, and y bending of a specimen to be carried out on different sections of the finger. The maximum amounts of bending that can be obtained in each step without harming the progression of the kernel crystal was discussed. H. Fujiwara et al [17] reported, in 1955, successfully creating single crystals of desired orientation in thin foil of thickness 0.06 mm by the same method presented previously.

Williamson et al [10] provide the first analysis of the fundamentals behind the technique by T. Fujiwara. Since the growth of a single crystal involves the suppression of nucleation of competing large crystals, their analysis examines some of the factors affecting nucleation and growth that can be applied to this technique. By considering the temperature gradient along the specimen, velocity of entry into the furnace, temperature at the growth front of the single crystal, and the activation energies for grain nucleation and growth, a better understanding of the phenomenon can be found. The probability of nucleation should be small to avoid competing crystals, so the ratio of the activation energies for nucleation and growth, Q_n/Q_g , should be greater, preferably much greater, than unity. A material with a certain Q_n/Q_g value above 1 will have critical values for

temperature gradient and velocity, and a material with a Q_n/Q_g less than 1 will not ever produce continuous single crystals no matter the amount of reduction in velocity. It is also reported that the critical velocity is also affected by the initial microstructure, in that a preferred texture misoriented 30-40° from the growing crystal is preferred for faster growth rates, and small angle texture misorientations exhibit more difficulty in growing because of the slower rates required. A high angle grain boundary can be seen as having many more vacant sites for atoms to transfer to compared to a low angle boundary, making transition and growth easier. In materials without a preferred texture, each grain is approached by the single-crystal individually, although the consumption rate of each grain still depends on their individual orientations with respect to the single-crystal. Edge grains will possess more inhomogeneities than interior grains from straining, and thus are more likely to act as nucleation sites. This is also true for inclusions, alloying inhomogeneities, or other defects, which may cause stress concentrations. The initial annealing of the material is also found to be critical, since grains that have only been recovered will act as additional nucleation sites during the final annealing treatment. The authors conclude that they successfully produced single-crystals 1mm thick, 1.3 cm wide, and 60 cm long in high purity Al (99.992%), commercial purity Al (99.7%), and Al alloys with less than 2% of copper, zinc, or silver at a furnace temperature of 0.9 T_m (entry velocity not given).

In response to the work of Williamson et al [10], N. Gane [11] composed a letter to the editor reporting to have created single-crystals in several aluminum alloys. Gane used a salt bath set about 30 °C below the solidus temperature, T_s , which was covered with steel sheet just above the molten salt and used air jets to cool the portion of the

specimen just outside the salt bath to obtain a steep temperature gradient. A flash anneal was performed to create a fine grained, completely recrystallized microstructure prior to testing. Required strain was reported to not be critical and varied from 0.3-1.25%. Rates were estimated for pure Al at 1.0 cm/hr, and 0.5 cm/hr for Al alloys. Single-crystals 25 cm long were reported for Al with 5.0% Cu, 7.0% Zn, 1.3% Si, and 4.2% Ge, and single-crystals 5 cm long for 4.5% Mg. More specific information on the growth of the single-crystal alloys was not provided.

A review of solid state growth of single crystals was conducted by K.T. Aust [18] and includes a discussion of grain boundary mobility and the effects of impurities. Aust cites previous studies and draws many of the same conclusions as before, with a broader scope. The migration of grain boundaries is largely limited by the number of steps along the grain boundary, meaning that higher angle boundaries will allow for faster migration rates. This also implies that coherent twin boundaries will exhibit very low mobility, as has been observed. Impurities will also create a drag effect since the solute atmosphere must diffuse along with the boundary. The driving force for grain growth is a reduction in energy, which could result from a reduction of interfacial energy of the boundary or a variation in free energy of the crystals involved.

Chapter 2 Experimental Procedures

2.1 SETUP AND INSTRUMENTATION

The experimental setup can be seen in Figure 3 and Figure 4. Figure 4 highlights the various parts of the setup. It consists of a motor assembly, slider rails, truck, electric tube furnace, cooling plates, and insulation components.

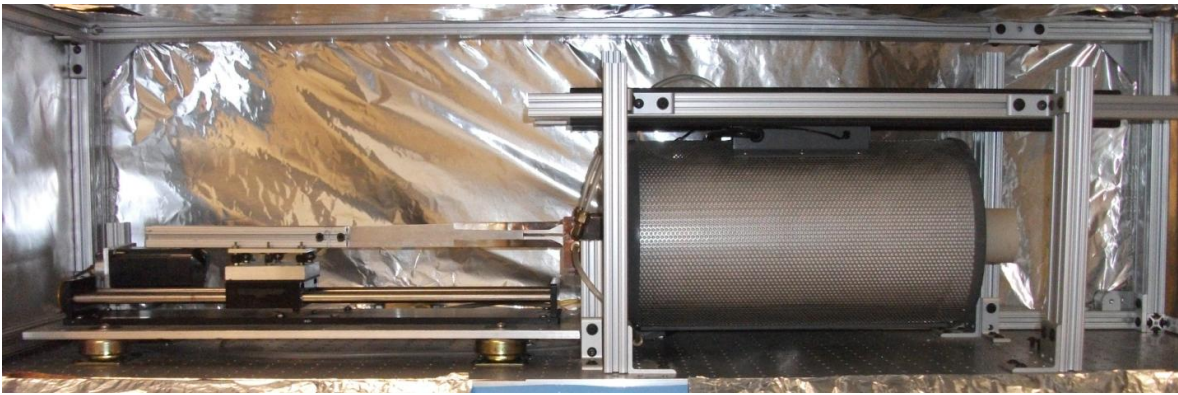


Figure 3: Image of experimental setup.

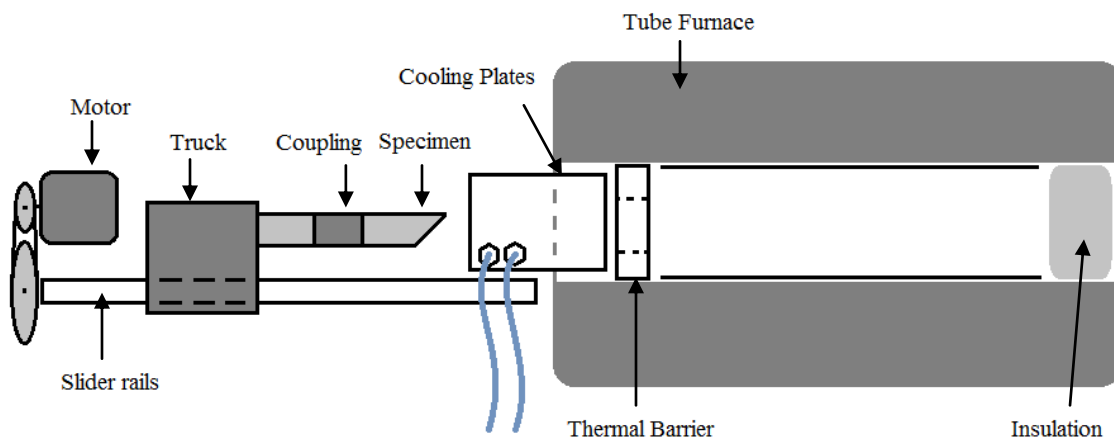


Figure 4: Schematic of testing assembly.

2.1.1 Motor/gearing/track assembly

The stepper motor used in this application is the 23MD (Sinking, .0625"/Thread, .225 °/Step) controlled by a PCL 601 – SMC60 Programmable Controller from Anaheim Automation, who also provided the slider rail assembly. The specimen is held to an arm extending from a sliding truck with a stainless steel foil sleeve coupling. The truck is positioned on smooth sliders and a screw gear provides the forward and reverse movement. The long screw gear is attached to a gear and belt system which is needed to decrease the speed at which the specimen can travel because of limitations in the minimum speed of the stepper motor's controls. The belt system also helps to reduce vibrations on the specimen from the motor since the motor and screw gear are connected through a rubber belt and not directly coupled. A larger view of this setup can be seen in Figure 5.

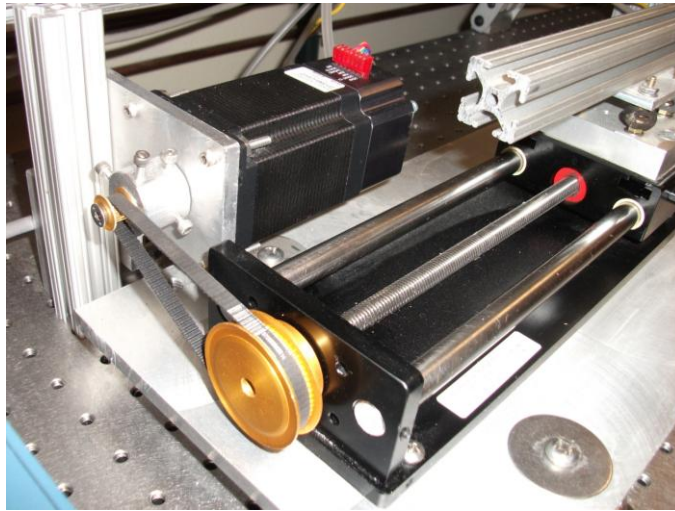


Figure 5: Image of the motor, belt system, screw gear, sliders, and truck.

2.1.2 Computer control

A computer programmed control module, as mentioned previously, governs the motion of the truck. This uses a computer program provided with the control module by the manufacturer. The motion of the motor can be controlled manually with the program, or a sequence can be programmed to run autonomously from the computer. The program features commands for speed, acceleration, distance, position, and time. Basic computer functions such as loops and Boolean conditions can be used to create the desired output. An explanation of the code used is provided in Procedures.

Control panel

The control module and its power supply are contained in the control panel. The power supply is a Dell PS-5141-1D. The control panel contains switches for toggling between various operations, and provides the connections from the computer to the motor. To change the program on the control module, or to manually specify a distance or position to move to, the power to the controller must be on and then the program can be initiated. The motor can then be connected if a manual adjustment of the truck position is desired. Any time the motor is connected and the control module is changed from 'off' to 'on', the program uploaded on the module will begin. After the program has been uploaded from the controller, edited as needed, and sent back to the controller, the program may be closed, the motor toggle selected to the 'connected' position if not already, and the power to the controller toggled 'off' to 'on' to initiate the program uploaded to the controller. The furnace and cooling system are controlled independently.

2.1.3 Cooling plates

Water-cooled copper cooling plates are oriented on both sides of the entering specimen to remove heat conducted to the specimen outside the furnace entry, as seen in Figure 6. This is done with a water chilling system that circulates the water from the copper plates to the chilling unit. The water circulating was kept at a constant set point of 7 °C for these experiments. The gap between the cooling plates is about 1 cm, which is enough to cool the air around the specimen but not obstruct the movement of the specimen or its holder. Specimen contact with the plates, or any other part of the assembly, during testing should be avoided to prevent damage to the specimen. Contact may cause local deformation and strain, thus potentially creating additional grain nucleation sites.

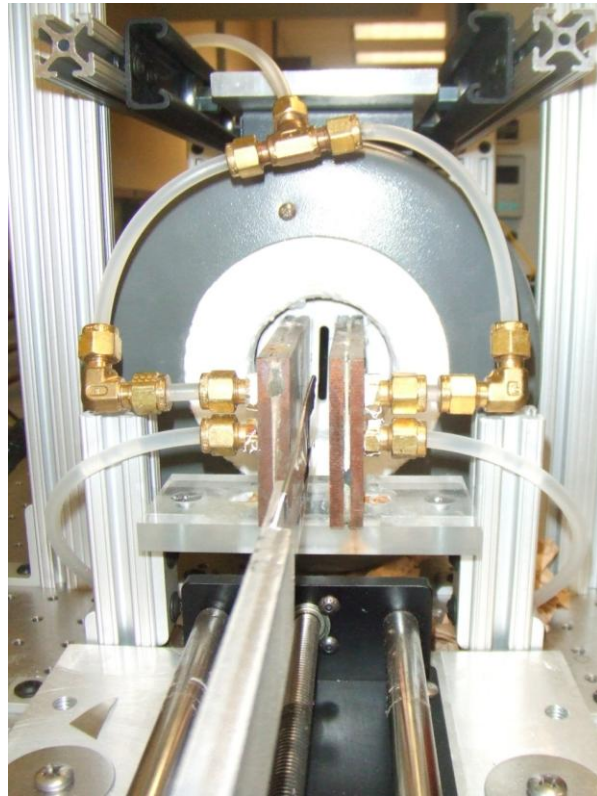


Figure 6: Image of the cooling plate setup at the furnace entry.

2.1.4 Furnace

The furnace used is an electric tube type manufactured by Thermolyne with an output of 1350 Watts. Since no changes are needed to the temperature during the test, the furnace is simply controlled by selecting a set point, reported as the test temperature. A machined ceramic barrier acts as to isolate the hot zone of the furnace from the entry region with cooling plates. Thermal insulation is also placed at the opposite end of the furnace to reduce heat escaping, helping to maintain a constant temperature in the furnace.

2.1.5 Air current suppression

An aluminum framework and shielding were placed over the entire motor track assembly and furnace to help maintain a constant temperature in the test area. Stray air currents from the room were found to affect the temperature at the entrance of the furnace, occasionally disturbing the growth of a crystal. Vents allowed for excess heat made by the furnace to escape, while still reducing the overall airflow in the test region.

2.2 TEMPERATURE PROFILES

Temperature profiles of the furnace entry were measured in two ways: one with an unshielded thermocouple to determine the temperature gradient of the air going from the cooling plate region into the furnace, and another with shielded (1.5mm diameter) thermocouples embedded in a piece of Al 1100 at different points to observe the temperatures experienced by the specimens over the same region of travel. Type K thermocouples were used for all analyses.

The shielded, embedded thermocouples were individually calibrated along with a signal amplification device that was connected to a National Instruments analog-to-digital converter to allow for automatic data acquisition by a computer. The thermocouples were placed in an ice bath of deionized water, taking care to have them individually suspended in the solution and not contacting the sides of the container. Allowing them to stabilize in room temperature created a second calibration point. A separate thermocouple reader was used to determine the temperature of the room. A third data point was taken with the thermocouples submerged in boiling deionized water.

Measurements were found to be accurate within 0.3% over the range of temperatures calibrated, accounting for the effect of barometric pressure on the day of calibration on the boiling temperature of water. A linear relationship between signal and temperature was found for each thermocouple and amplifier combination, and this was used to determine the various temperature outputs.

For both the unshielded and shielded/embedded thermocouple temperature profiles, the thermocouples were attached to the armature to which the specimen is normally attached, and the armature and slide were controlled by the stepper motor so the thermocouples would enter the furnace at a constant set speed, just as is done in a test to grow a single crystal. The output from the thermocouples was acquired by a computer using National Instruments SignalExpress software at a rate of 2 Hz, and was provided as temperature as a function of time. The temperature as a function of distance was calculated by relating the speed of travel of the thermocouples to the time given in the output.

The thermocouples embedded in test pieces of aluminum had two configurations, as shown in Figure 7. The vertical configuration was used to detect large temperature gradients in the vertical direction of the furnace. The horizontal configuration was used to examine the horizontal temperature profile along the specimen as it entered the furnace.

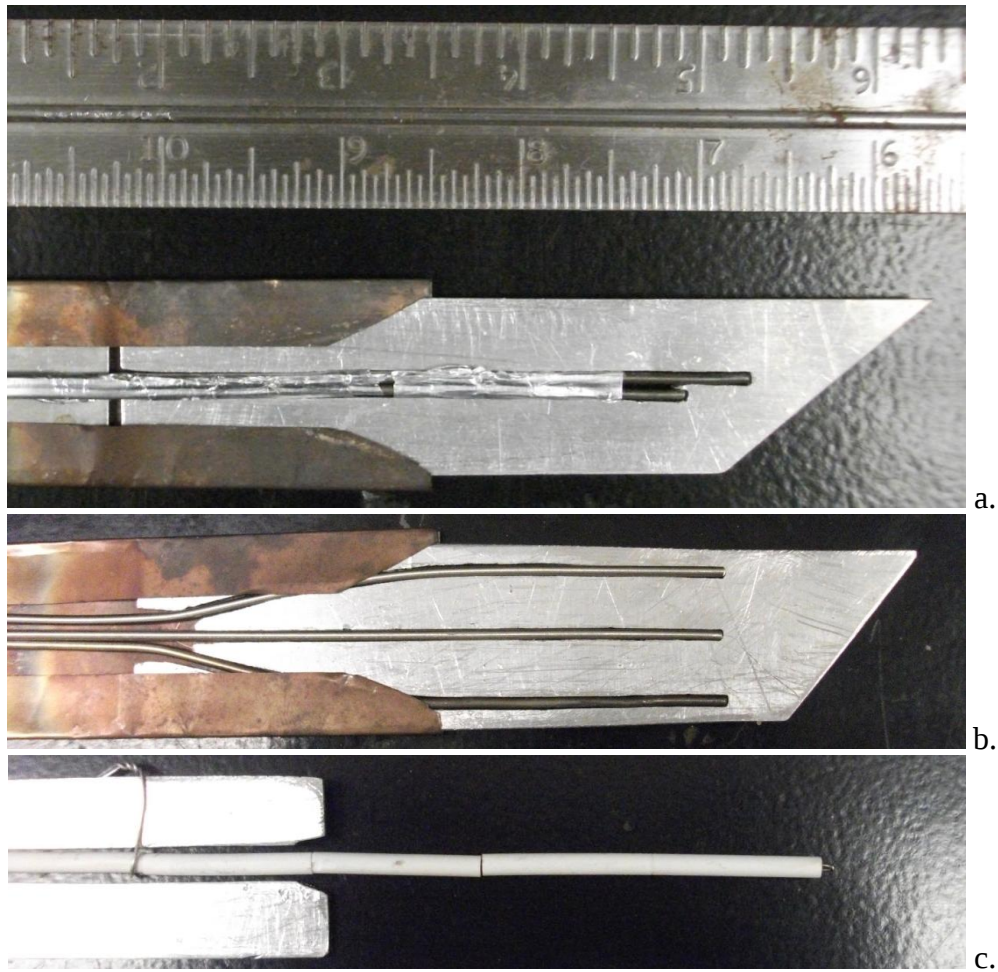


Figure 7: Images of thermocouple profile setups for (a) shielded, embedded, horizontal profile, (b) shielded, embedded, vertical profile, and (c) horizontal, unshielded thermocouple profile. Scale in inches.

The unshielded thermocouple test was performed by suspending the thermocouple from the armature, as shown in Figure 7c. This gave enough rigidity to the thermocouple to remain in position as it traveled into the furnace and minimized the amount of heat loss from the furnace by conduction through the thermocouple.

The results of the temperature profiles are shown in Figure 8 and Figure 9. A comparison shows the effect of conduction along the test piece; the temperature gradient

for the unshielded thermocouple is much steeper. Other studies typically only reported the ambient temperature profile, i.e., that of the lone, unshielded thermocouple, but this does not demonstrate the conditions that the specimen accurately sees, as is shown.

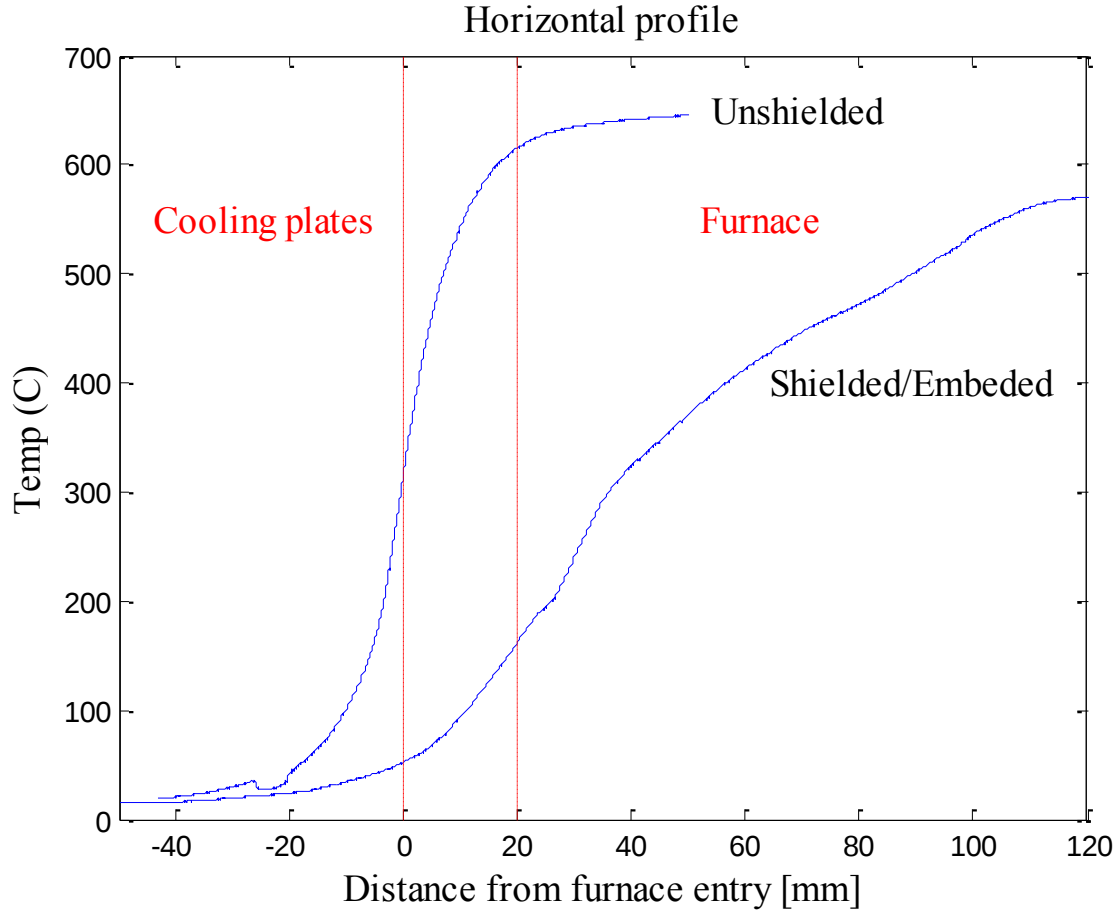


Figure 8: Plot of unshielded and shielded thermocouple temperature profiles through the furnace entry region as a function of distance. Small irregularities, such as the unshielded thermocouple's drop at -30 to -20 mm and shielded at about 25 mm, are from incidental contact with the cooling plates or ceramic thermal barrier.

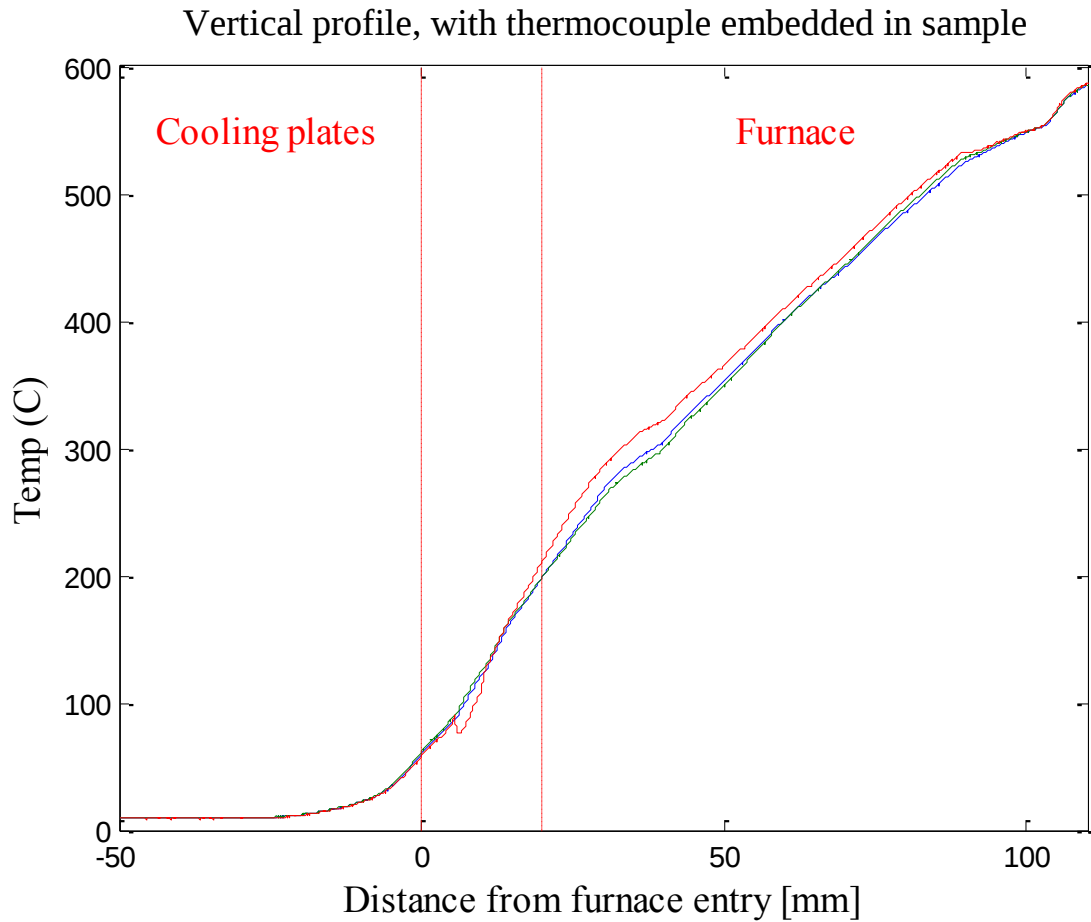


Figure 9: Temperature profile as a function of distance from the entry for shielded, embedded thermocouples showing variations in the vertical direction. The red curve on the top represents the top thermocouple as seen in Figure 7b; the middle, blue curve, represents the middle thermocouple, and the green bottom curve is the bottom thermocouple. Small irregularities in the curves are from incidental specimen or thermocouple contact with the cooling plates or ceramic thermal barrier.

In Figure 9 it can be seen that the temperature in the vertical direction typically only varies by a maximum of approximately 10 °C. Because of this, the vertical profile will be assumed constant and only the horizontal temperature profiles will be further considered.

2.3 TESTING PROCEDURES

2.3.1 Material Characterization

Three materials were studied in this investigation: 99.999% high-purity Al (Al HP), commercial-purity aluminum (AA1100) and an Al-Mg alloy containing 3 wt% Mg (Al-3Mg). The Al HP material was received from Angstrom Sciences Inc. (Duquesne, PA) as a 76.2-mm diameter, 3.2-mm thick disk. The AA1100 material, a standard commercial-grade material, was obtained as 1.2-mm thick rolled sheet. The Al-3Mg material was received from Kaiser Aluminum and Chemical Corporation's Center for Technology (Pleasanton, CA) as 4.1-mm thick sheet. Compositions of Al-3Mg and AA1100 were determined by inductively coupled plasma mass spectrometry conducted by Bodycote, formerly West Coast Analytical Service, Inc. (Santa Fe Springs, CA), except for the Mg content in the Al-3Mg material, which was provided by its manufacturer. The composition of Al HP was supplied by its manufacturer Angstrom Sciences Inc, and represents a typical analysis of this material's composition, not specific to the lot of material tested in the present study. The chemical compositions of these three materials are provided in Table 1.

Table 1: Compositions of materials in parts per million, by weight.

Material	Al	Cr	Cu	Fe	Mg	Mn	Si	Ti	Zn
Al-3Mg	bal	23.4	16.2	1230	29,900	30.1	<200	134	233
AA 1100	bal	-	1000	5100	-	55	1400	99	52
Al HP	bal	0.0435	0.48	0.19	0.17	-	1.13	0.0815	0.0235

Impurity elements, particularly Fe, can form intermetallic particles in the matrix of Al materials. These particles are harder and more brittle than the matrix and may slow

or halt the progression of a single crystal if they are large. The sizes and area fractions of intermetallic particles were measured using optical microscopy. Images were digitally acquired at magnifications of 1000x, which provided a resolution of 0.021 $\mu\text{m}/\text{pixel}$ and an image area of 82 by 66 μm , and at 500x, which provided a resolution of 0.043 $\mu\text{m}/\text{pixel}$ and an image area of 164 by 132 μm . These resolutions were sufficient to observe particles of approximately 0.1 μm in diameter and larger. Each image from the Al-3Mg and AA1100 specimens at 1000x typically contained over 300 particles, and at 500x over 1000 particles. Particle density in the Al HP material was approximately half that observed in the Al-3Mg and AA1100 materials. Average particle diameters were approximately 0.8 μm for AA1100, 0.5 μm for Al-3Mg, and 0.7 μm for Al HP. Since the size and density of particles is within an order of magnitude for the three materials, and the average particle size is small, the effect of particles on the growth of single crystals in all three materials is thought to be small.

2.3.2 Preprocessing of materials

All three materials were first processed from their as-received conditions before straining and final preparation for the Fujiwara process. Importance was placed on obtaining a fine grained, fully recrystallized microstructure of approximately the desired thickness of 1mm, and overall dimensions suitable for the size of the furnace and apparatus setup.

For Al HP, processing involved first rolling to 50% engineering strain in steps of approximately 8% strain using a Durston DRM 130 rolling mill. The Al HP material was

then recrystallized at 450°C for 30 minutes. This material was further rolled to a final thickness of approximately 1 mm using a pack rolling technique. Pack rolling was done by placing the specimen between two leaves of a 304 stainless steel sheet folded over on itself. The sides facing inwards, where the specimen was placed, had a #8 mirror finish, and the thickness of the sheet was 0.91 mm. Pack rolling provided a uniform thickness and good surface finish to the specimens. For more details on the pack rolling technique used, see Brewer et al [19]. A second annealing treatment was performed at a higher temperature of 580°C for 5 hours to fully recrystallize the material after rolling. The AA1100, because it was received as rolled sheet of approximately the desired thickness of 1 mm, was simply sheared into strips of the correct size and annealed at 580°C for 5 hours to fully recrystallize. The Al-3Mg was received as sheet of approximately 4 mm in thickness and was subsequently prepared by rolling to approximately 50% engineering strain in steps of approximately 8% reduction and then was recrystallized at 400°C for 30 minutes. This material was further rolled to a thickness of approximately 1 mm, again at approximately 8% reduction per step. Pack rolling was used for the final rolling stages. The final anneal was performed at 580°C for 5 hours.

The specimens were subjected to tensile plastic straining by either an ATS series 1600 universal testing machine or MTS test frame of similar design. Straining was performed at a rate of 0.02 in/min. The amount of strain desired varied for each material, as will be discussed in the Procedures and Results. Because of a sensitivity to the amount of strain required for Al-3Mg found after performing several tests, the Al-3Mg specimens were first machined into a “dog-bone” coupon shape before the final anneal prior to straining to obtain better control of the straining process. Specimens were machined to a

gauge length and width of 114 mm and 18 mm, respectively, and the grip region was 28 mm across. These set gauge dimensions produced a more even strain across the gauge cross section.

The initial design of the experiment called for a long finger to be created to be used for orienting the crystal as it grows, but since designating a specific orientation is not necessary for this study, instead a wedge shape was created on the end of the specimen by cutting the specimen at approximately 45°. This was to allow a grain to initiate at the tip of the wedge and grow out and across the width of the specimen. The cut was made with a Struers Minitom diamond saw at a speed of 200-300 rpm and light force using approximately 200 grams of weight. Burs from cutting were removed by lightly sanding with 600 grit silicon carbide sandpaper. Deformation created by the saw was removed by electropolishing in ASM III-7 electrolyte [20] containing 200 mL H₂O, 380 mL ethanol (95%) and 400 mL H₃PO₄ using a voltage range of 15-30 volts and a current density approximately 0.2 A/cm². This was performed gradually over the length of the specimen until the cut surface was smooth. Because of the relative ease of creating large crystals of Al 1100 and Al HP, electropolishing was only used for Al-3Mg.

2.3.3 Experimental Testing

Testing was performed by first attaching the specimen to its holder and measuring the distance required for it to enter completely into the furnace. The starting position was adjusted as necessary with the controller software to place the tip of the specimen approximately 2-4 cm from the furnace entrance. The distance to travel is converted to a

number of steps for the motor and the controller program is adjusted accordingly. The horizontal travel of the truck for each motor step equates to 9.922×10^{-4} mm when the motor is directly connected to the screw gear. The gearing installed reduces this by a 4:1 ratio, giving a step size of 2.481×10^{-4} mm. Also adjusted is the rate of entry, if desired. A sample, annotated code for the operation of a test is provided in Table 2.

Table 2: Example program commands for control of drive motor.

Line	Command	Comments
1	Position register=0	Sets current position to 0
2	Direction CW	Determines motor direction. CW=in (with gearing), CCW=out (with gearing).
3	Acceleration=5000 steps/(sec*sec)	Acceleration of the motor set
4	Base speed=5000 steps/sec	Speed of motor desired
5	Max speed=5000 steps/sec	Maximum speed of motor desired
6	Go relative 100 steps	Distance to travel in steps at set speed, direction, etc. Steps 6-9 are used to enter specimen into furnace and back out to check clearances before test is run.
7	Finish move	
8	Direction CCW	Direction changed to move specimen out.
9	Go to position 0	Command to move back to starting position.
10	Label=38	Initiation of loop
11	Wait 60000 msec	Time to wait
12	Outer loop=45 times to 38	Wait time looped 45 times=45 minute wait. Loop used because wait time limited to an input of 60000 max.
13	Direction CW	Direction changed to go towards furnace.
14	Acceleration=100 steps/(sec*sec)	Acceleration value changed.
15	Base speed=15 steps/sec	Base speed changed.
16	Max speed=15 steps/sec	Max speed changed.
17	Go relative 563200 steps	Distance specimen will enter furnace in steps.
18	Finish move	Movement stopped once distance reached.
19	Acceleration=1500 steps/(sec*sec)	Acceleration value changed.
20	Base speed=1500 steps/sec	Base speed changed.
21	Max speed=5000 steps/sec	Max speed changed.
22	Direction CCW	Direction changed to move specimen out.
23	Go to position 0	Command to move specimen back to starting position.
24	End of program	

Macrostructures were observed by etching in ASM 1M caustic etchant [21]. This consists of 100 mL distilled H₂O and 10–20 g NaOH. The etchant was first heated to 60–70 °C, and etching times were typically 90-120 seconds. Low contrast and surface oxidation for the Al-3Mg samples meant that they had to be sanded and polished prior to etching. This was done by first securing them to a metal block with *Crystalbond 555* from Ted Pella, Inc. to prevent them from bending while sanding. Sanding with silicon carbide sandpaper was done by hand using grits 320, 600, 1200, 2400, and 4000 using water as a lubricant. Grain sizes were measured using ASTM Standard E112 mean-lineal-intercept method [22].

The orientation of large grains and single crystals was determined with Laue backscatter x-ray diffraction. For this, a voltage of 35 kV, current of 20 mA, and time of 60 seconds were used to obtain the Laue patterns on an image plate. Images were taken using an image plate, scanned with a *FujiFilm BAS-1800 II* scanner operated by *Image Reader BAS-1800II V1.02* software, and processed using *OrientExpress 3.4* crystal orientation software. Orientations were then plotted together on a stereogram triangle using Matlab R2010a.

2.3.4 Test Parameters

The three materials were tested under different conditions and parameters to determine the effects of these on the growth of large crystals in the Fujiwara process. A summary of these parameters and their approximate values can be seen in

Table 3. Each material was tested to determine the critical range of strain that is required for recrystallization, and tested over a range of travel rates to determine the fastest rate that will allow grains to grow directionally along the specimen.

Table 3: Test parameter ranges.

Material	Temperature of furnace (°C)	Engineering strain (%)	Entry rate (mm/hr)
Al HP	640	2 - 4	29 - 54
Al 1100	600 - 630	2 - 7	29 - 210
Al-3Mg	550 - 590	1-10	1 - 29

Temperature ranges were selected to be close to the solidus or melting temperature of the material without going over. The temperature reported here is the set-point temperature, the maximum within the furnace, and not necessarily what the specimen experiences internally. The amount of critical strain required was determined by testing specimens covering a wide range of strains. The optimum was determined by comparing grain size to pre-strain, and the minimum was determined when a specimen exhibited only a partially recrystallized microstructure, as will be shown in Experimental Results. Entry rates were adjusted to be slower or faster until significant, or directional, growth was observed or ceased to occur.

Chapter 3 Experimental Results

3.1 INITIAL MICROSTRUCTURES

The microstructures after rolling, annealing, and straining were different for each material because the as received condition and dimensions varied. The initial microstructures of the Al HP, Al 1100 and Al-3Mg contained grain sizes of approximately 3mm, 30 μm , and 200 μm , respectively. A fine-grained initial microstructure is difficult to obtain for Al HP because of its lack of impurity elements and particulates. Particle dispersions from impurity elements are needed to pin grain boundaries, decreasing the tendency for grains to grow large under typical annealing treatments. Variations in the amount of strain applied prior to annealing may be responsible for some of the difference in grain size for Al 1100 and Al-3Mg. The effect of solute drag by Mg atoms on grain boundaries is also expected to slow grain growth in the Al-3Mg material.

3.2 EXAMPLE IMAGES OF RESULTS

Characteristic microstructural results after Fujiwara processing can be seen in Figure 11 through Figure 13. Figure 11 shows an Al-3Mg specimen that underwent significant crystal growth, producing some grains which span the width of the specimen. These grains did not continue to grow along the entire specimen, but were preempted by new crystals nucleated along the way. Specimens that exhibit directional growth are ones

that have one crystal dimension much greater than the other, or may have growth oriented relative to the temperature gradient. This implies that the linear grain growth rate may proceed at a rate equal to or greater than the entry rate. This gives information about the mobility of the grain boundary. A schematic of a specimen with directional growth and the temperature gradients inside a cylindrical furnace that may give rise to this microstructure are shown in Figure 10. Smaller directional grains, such as those in Figure 10, are the result of a faster entry rate in which grains were not provided the time to grow out across the width of the specimen before growing along its length.

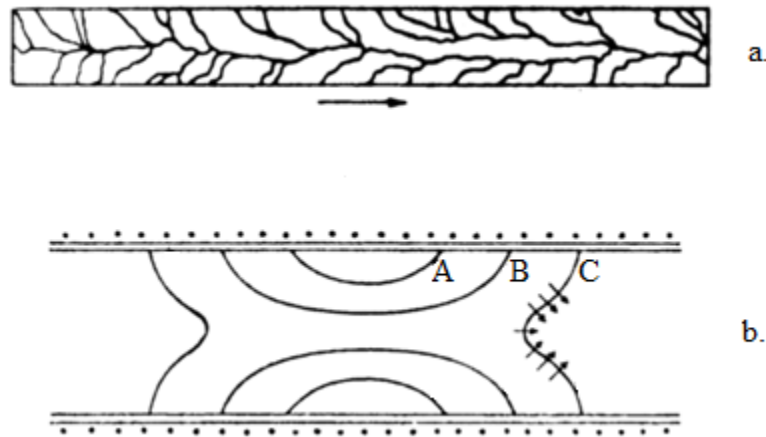


Figure 10: (a) Schematic showing grain boundaries formed in a specimen pulled into a cylindrical furnace. (b) Isotherms within a cylindrical furnace are shown, where temperatures are $A > B > C$, and arrows represent the crystal growth direction if c is greater than the temperature required for grain growth to proceed. Figure is from reference [10].

The lack of directional growth along the entire specimen's length in Figure 11 is evidenced by the small crystals near the pointed end of the specimen. Figure 12 shows an Al-3Mg specimen which grew one large grain over most of its length, with exceptions at the beginning point of the specimen and a few island grains. Directional growth is most clearly observed in Al 1100, as is shown in Figure 13. Grains nucleated at the specimen

edges and grew toward the center of the specimen and along its length for a considerable distance.

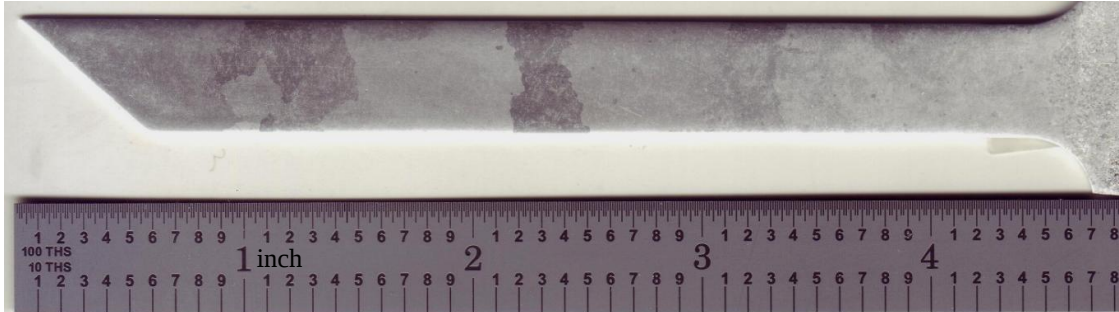


Figure 11: Al-3Mg specimen showing discontinuous crystal growth. Scale in inches.

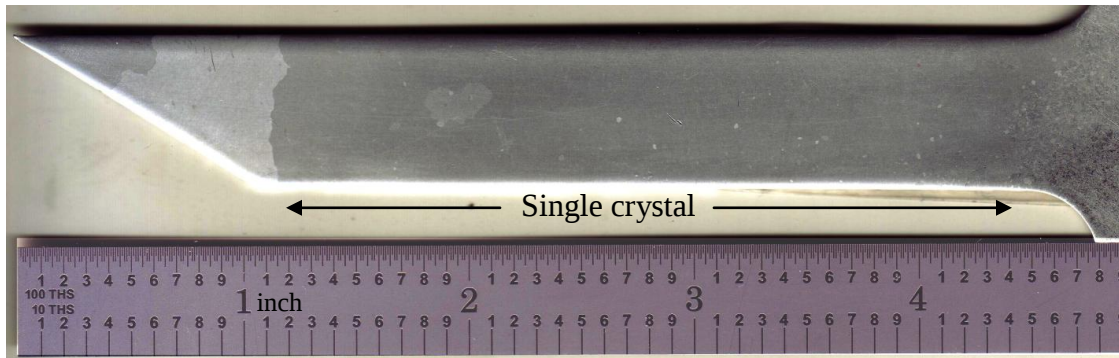


Figure 12: Al-3Mg specimen with large single crystal. Scale in inches.

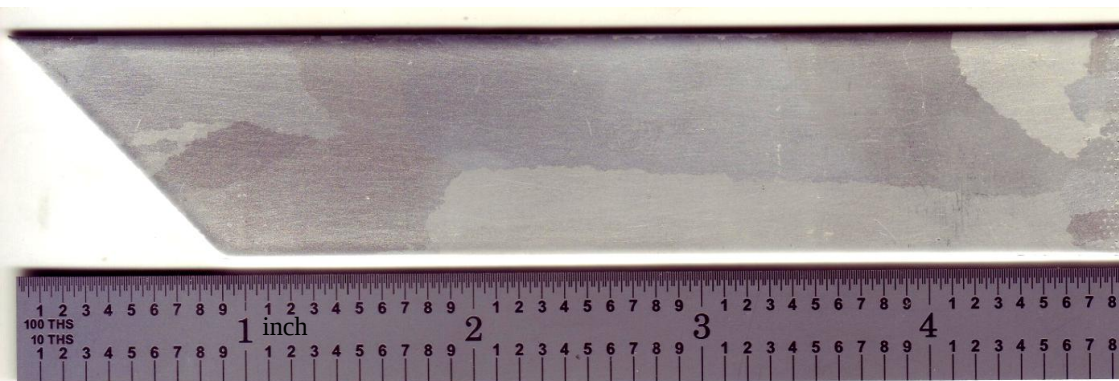


Figure 13: Al 1100 specimen with directional crystal growth. Scale in inches.

Since the largest grains typically fill the width of the specimen, strongly directional growth is more easily observed when using faster entry rates, but for Al-3Mg, any increase in entry rate resulted in discontinuous grain growth, so smaller directional grains that follow the growth patterns shown in Figure 10 are not observed.

3.3 TEST RESULTS SUMMARY

Table 4 and Table 5 show a summary for all tests and results from the three materials. The homologous temperature T_H , for each material is calculated from the test temperature divided by the melting or solidus temperature. For Al HP this is 660°C, Al 1100 approximately 660 °C, and Al-3Mg approximately 610 °C [23]. The pre-strain is the cold strain applied prior to controlled entry in to the steep temperature gradient of the furnace. Furnace entry rate is provided in mm/hr. Average grain length is measured along the long axis of the specimen, parallel to the direction of entry into the furnace. Grain width is along the long-transverse direction of the specimen.

Table 4: Test results matrix for Al HP and Al 1100.

Material	Pre-strain [%]	TH	Entry rate [mm/hr]	Specimen		Avg. grain length [mm]	Average grain length normalized by specimen's width	Single-Crystal produced [Y/N]
				length [mm]	width [mm]			
Al HP	2.1	0.91	53.6	100	26	3	0.12	N
Al HP	3.76	0.97	28.6	100	26	10	0.38	N
Al HP	2.525	0.97	28.6	100	26	12.7	0.49	N
Al HP	2.25	0.97	28.6	100	27	90	3.33	Y
Al HP	2.1	0.97	28.6	100	27	75	2.78	Y
Al HP	2.225	0.97	28.6	110	27	110	4.07	Y
Al HP	2.03	0.97	28.6	95	32	75	2.34	Y
Al 1100	5.4	0.91	53.6	100	24	0.1	0.01	N
Al 1100	4	0.95	53.6	100	24	0.1	0	N
Al 1100	5	0.95	53.6	100	24	0.1	0	N
Al 1100	6.87	0.95	53.6	100	24	8.3	0.35	N
Al 1100	3.93	0.95	53.6	120	24	60	2.5	Y
Al 1100	2.33	0.95	53.6	110	24	62	2.58	Y
Al 1100	3.4	0.95	53.6	110	24	26.7	1.11	Y
Al 1100	4.3	0.95	28.6	110	24	105	4.38	Y
Al 1100	3.15	0.95	28.6	260	24	83.3	3.47	Y
Al 1100	3.45	0.95	28.6	260	24	102.5	4.27	Y
Al 1100	4.1	0.95	28.6	260	24	100	4.17	Y
Al 1100	4.2	0.95	28.6	260	24	90	3.75	Y
Al 1100	2.9	0.95	28.6	260	24	190	7.92	Y
Al 1100	3.26	0.95	53.6	120	24	25	1.04	Y
Al 1100	3.26	0.95	107.2	120	24	12.5	0.52	N
Al 1100	3.33	0.95	214.3	120	24	0.1	0	N
Al 1100	3.33	0.95	160.7	120	24	13	0.54	N

Table 5: Test results matrix for Al-3Mg.

Material	Pre-strain [%]	TH	Entry rate [mm/hr]	Specimen		Avg. grain length [mm]	Average grain length normalized by specimen's width	Single-Crystal produced [Y/N]
				length [mm]	width [mm]			
Al-3Mg	8.8	0.9	28.6	160	21	0.4	0.02	N
Al-3Mg	9.8	0.9	28.6	160	21	0.3	0.02	N
Al-3Mg	6.1	0.95	28.6	160	23	1	0.04	N
Al-3Mg	3.4	0.95	28.6	160	23	1.4	0.06	N
Al-3Mg	3.07	0.95	28.6	50	23	1.3	0.06	N
Al-3Mg	2.54	0.95	28.6	50	23	3.8	0.16	N
Al-3Mg	2.3	0.95	28.6	50	23	8	0.35	N
Al-3Mg	1.77	0.95	28.6	50	23	6.4	0.28	N
Al-3Mg	2	0.95	28.6	100	22	5.9	0.27	N
Al-3Mg	1.48	0.95	28.6	100	24	6.4	0.26	N
Al-3Mg	1.75	0.96	28.6	100	24	8.5	0.35	N
Al-3Mg	1.75	0.96	14.3	100	24	9.5	0.4	N
Al-3Mg	1.5	0.96	14.3	110	13	10.9	0.84	N
Al-3Mg	1.91	0.96	14.3	110	13	9.5	0.73	N
Al-3Mg	1.57	0.96	14.3	110	13	6.4	0.49	N
Al-3Mg	1.4	0.96	14.3	110	13	19.1	1.47	Y
Al-3Mg	1.15	0.96	14.3	110	13	10.2	0.78	N
Al-3Mg	1.4	0.96	14.3	110	13	3.8	0.29	N
Al-3Mg	1.42	0.96	14.3	110	18	9.5	0.53	N
Al-3Mg	1.15	0.96	14.3	110	18	8.5	0.47	N
Al-3Mg	1.71	0.96	3.6	110	18	9.5	0.53	N
Al-3Mg	1.42	0.96	2.7	110	18	25.4	1.41	Y
Al-3Mg	1.7	0.97	1.8	110	18	8.5	0.47	N
Al-3Mg	1.46	0.97	1.8	110	18	12.7	0.71	N
Al-3Mg	1.44	0.97	1.8	110	18	25.4	1.41	Y
Al-3Mg	1.4	0.97	1.8	110	18	14.3	0.79	N
Al-3Mg	1.38	0.97	1.8	110	18	36	1.97	Y
Al-3Mg	1.42	0.97	1.8	110	18	20	1.11	Y
Al-3Mg	1.47	0.97	0.9	110	18	25	1.39	Y

Successful Fujiwara tests, labeled as “Single-crystal produced” in Table 4 and Table 5, were classified as such if the average grain length in the direction along the specimen normalized to the specimen width was greater than 1. Due to the size of the specimens and large grain sizes, a minimum of 3 measurements were taken along lines parallel to the length of the specimen at different points across the width. These measurements were averaged to obtain the average grain length using a mean-lineal-intercept method as mentioned previously. If the specimen only contained one or a few grains comprising its entire length, each spanning the width of the specimen, each grain’s length was measured individually and the average was taken as the average grain length. Width was used to normalize the grain size data because a large length to width ratio would suggest directional growth. If the average grain length is longer than the width of the specimen, this suggests that the grain has a preference for growing along the specimen and is not growing due to normal grain growth. This is limited by the practical dimensions of the specimen, since not all widths can be tested, but it provides a consistent guideline for labeling the experiments. Thickness was approximately constant, at about 1mm, for each material and test. Of the 52 tests performed, only 3 Al 1100 specimens that exhibited definitive directional growth did not fit the criterion. This is likely because of fast entry rates, which do not allow the grains time to grow along the specimen length. Directly comparing measurements of the longest average grains attainable for Al HP and Al 1100 may be misleading because of limitations in the specimens’ lengths. It is likely that, given all other conditions and preparations are performed correctly, both the Al HP and Al 1100 are capable of producing single-crystals of any length which the experimental apparatus can accommodate.

3.4 CRITICAL STRAIN DETERMINATION

The amount of pre-strain that is required for recrystallization is different for each material. Figure 14 shows an Al-3Mg specimen which contained a strain gradient across its width prior to recrystallization. This occurred by bending of the specimen during tensile straining. From this it can be determined that the critical strain range is within the strain range applied across the width of this specimen. At the lowest strain, at the bottom, the grains are unrecrystallized or only partially recrystallized. At the largest strain, large recrystallized grains have formed.

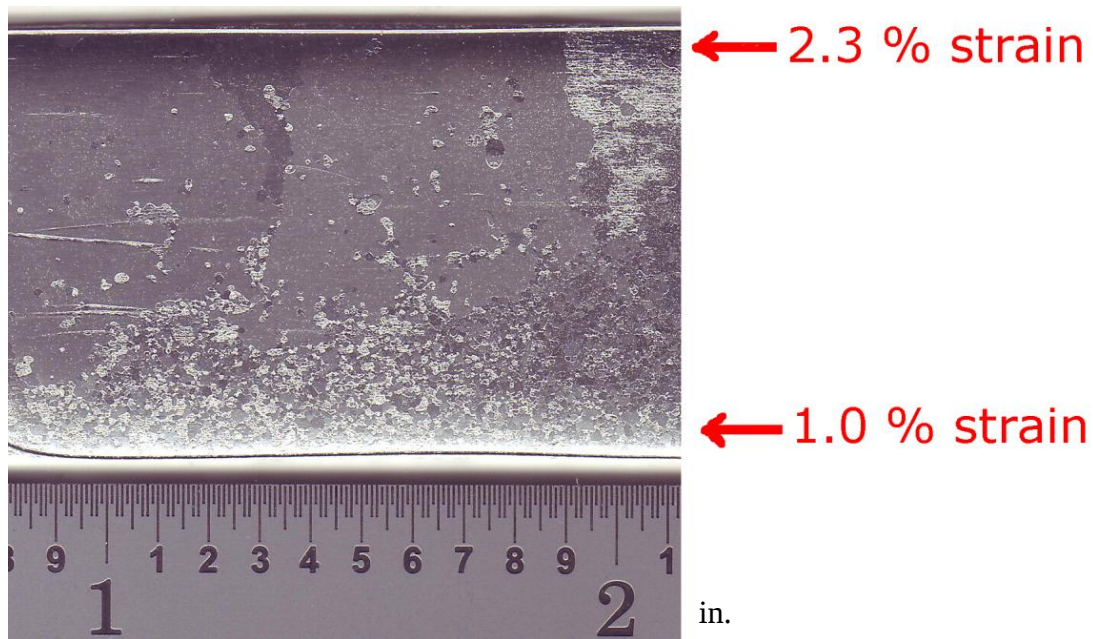
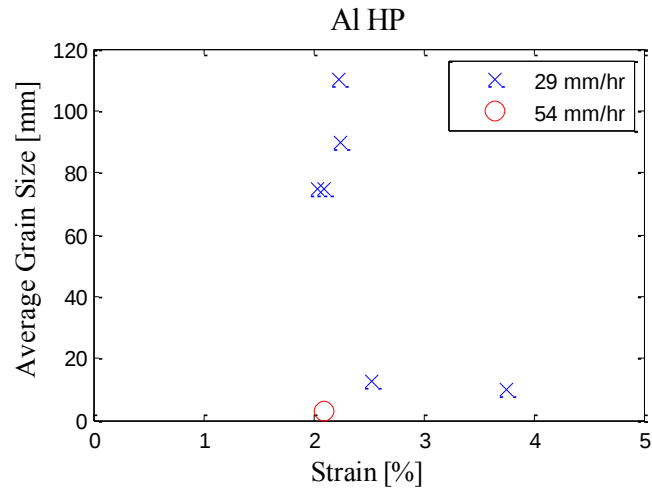
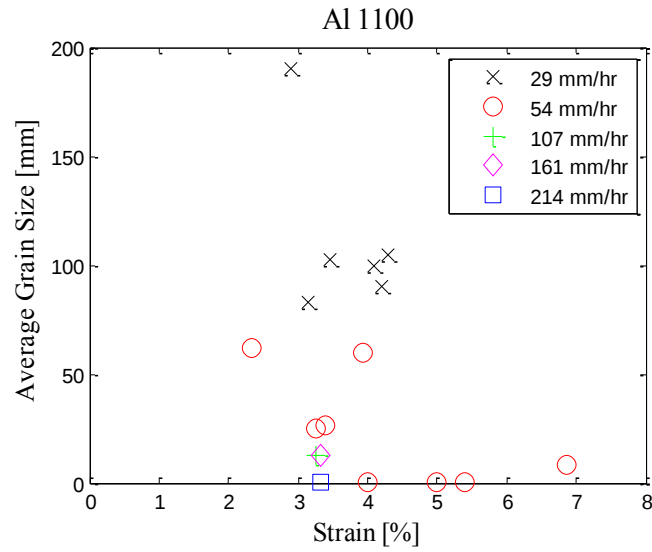


Figure 14: Al-3Mg specimen with varying strain across its width. The bottom edge exhibits a strain of approximately 1 % engineering strain while the top has a strain of 2.3%. Major scale marks are inches.

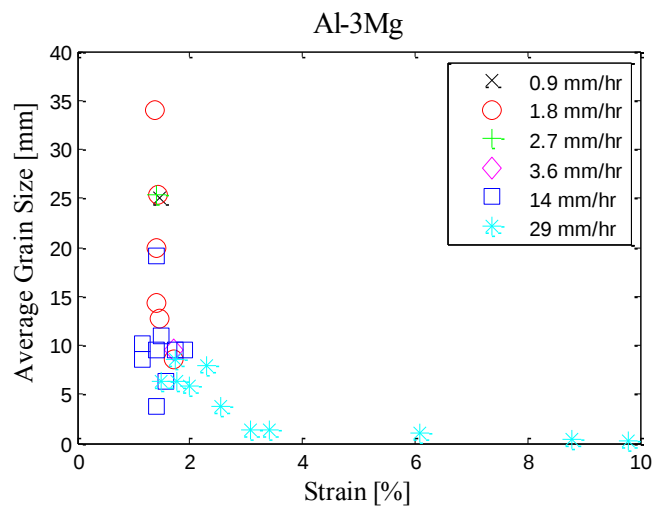
Critical strain ranges for recrystallization were determined for each material by processing through the Fujiwara method using varying amounts of pre-strain. The results from each material are provided in Figure 15.



a.



b.



c.

Figure 15: Average grain length vs. pre-strain is reported for each material and corresponding entry rate for (a) Al HP, (b) Al 1100, and (c) Al-3Mg.

These follow the trends observed in strain-annealing as introduced previously. Al HP displays a similar trend, but the range of strains for which it was tested for was smaller. The average grain length is also shown to be a function of entry rate, with slower rates generally producing larger grains, but the small sample size in these experiments does not reveal this trend for all rates studied. Also of note are the acceptable ranges of strain for each material. The critical strain for Al HP is $2.2 \pm 0.1\%$, Al 1100 $3.6 \pm 0.7\%$, and Al-3Mg $1.45 \pm 0.05\%$.

The temperature profile from a specimen with embedded thermocouples was used along with an Al 1100 specimen that was halted as it entered the furnace to determine the approximate recrystallization temperature, which was found to be $360\text{ }^{\circ}\text{C}$.

3.5 EFFECT OF ENTRY RATE

The entry rate was increased or decreased, as described previously, to determine the speed at which large crystals are able to continuously grow. Figure 16 shows how each of the three materials' grain sizes are affected by the rate of entry. Figure 16 only includes specimens with the largest average grain length for each entry rate, ie. the specimens that were strained at or near their critical strain.

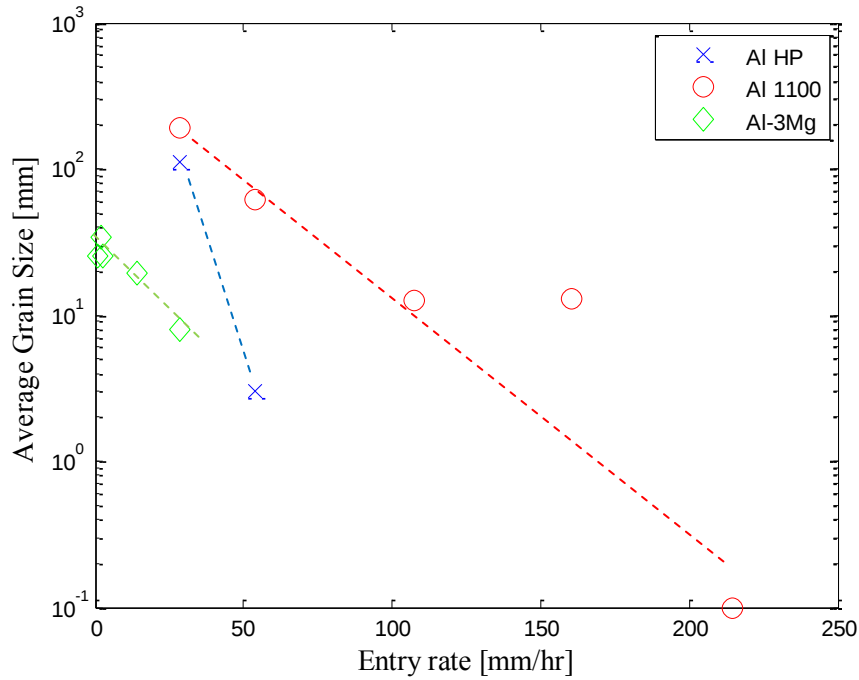


Figure 16: Average grain length as a function of entry rate for each of the three materials seen on a semi-log plot. Only the specimen with the largest average grain length for each rate is reported here.

When the logarithm of grain length is plotted as a function of entry rate, a nearly linear relationship is observed. Furthermore, the resulting slope for Al-3Mg and Al1100 are very similar. This could mean that the relationship between grain length and entry rate could be a function of initial microstructure or impurity content, since those factors were similar for Al1100 and Al-3Mg, but was not similar for Al HP. The fastest entry rates observed for repeatable single crystal production for Al HP was 29 mm/hr, Al 1100 29 mm/hr, and Al-3Mg 1.8 mm/hr. Each of these rates provided normalized average lengths of at least 2.

3.6 SINGLE-CRYSTAL ORIENTATIONS

Orientations of single crystals are shown in Figure 18 and are represented on standard triangles for cubic systems, with Figure 17 providing a schematic of the orientations referenced. The three triangles for each material represent the long, growth direction LD, which is the direction the specimens were strained, the short transverse direction ST, also seen as the thickness direction or normal to the broad side of the specimen, and long transverse LT, which is the direction along the width of the specimen. Figure 19 gives a representation of large grains of Al-3Mg that formed but did not continue growing along the length of the specimen, i.e. grains that spanned the width of the specimen but did not grow to a length longer than the value of the width of the specimen. This will be used later in the Discussion for comparison purposes.

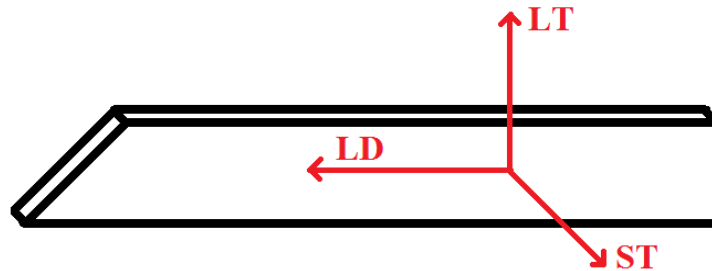


Figure 17: Schematic of orientations relative to example specimen.

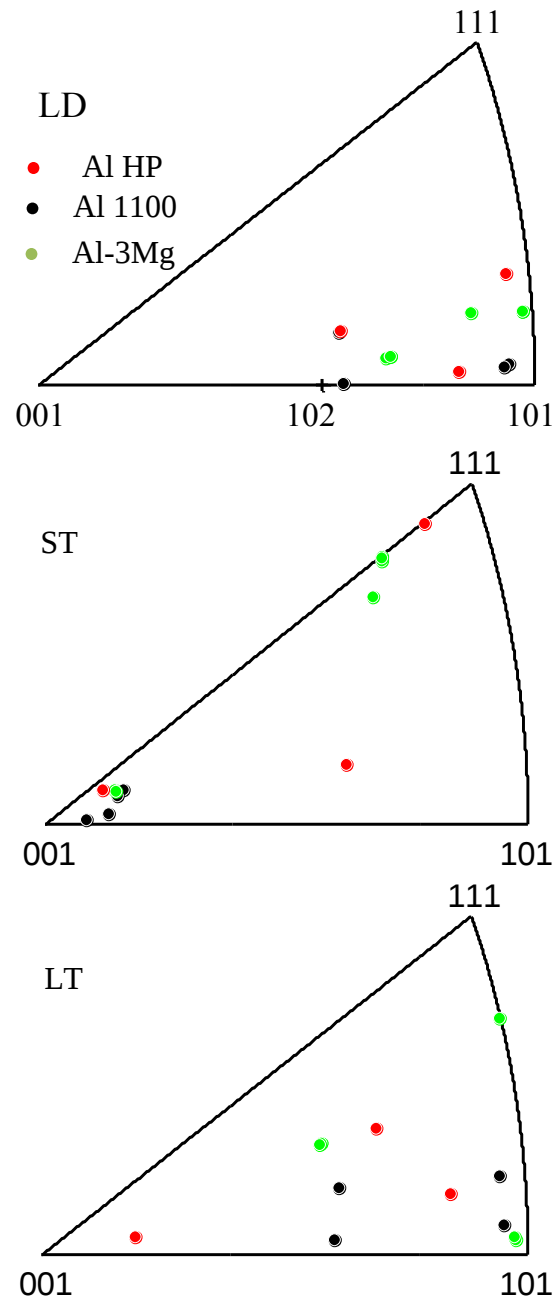


Figure 18: Crystallographic orientations of Al HP (red), Al 1100 (black), and Al-3Mg (green).

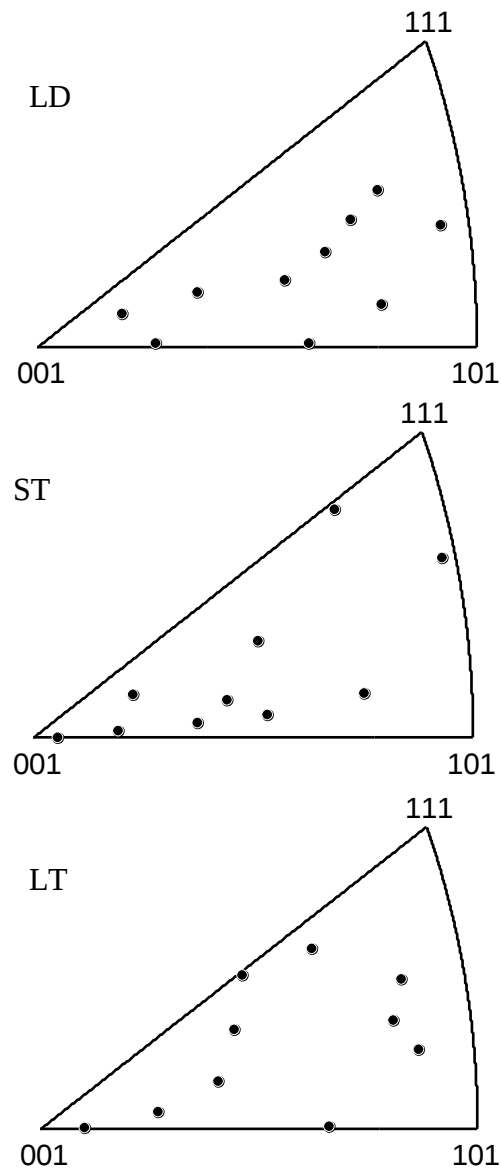


Figure 19: Orientations of a sample of 10 Al-3Mg large crystals from various specimens that did not continue growing along the specimen length. See Figure 11 for an example.

Chapter 4 Discussion

4.1 CRITICAL STRAIN COMPARISON

Figure 20 shows the grain length (along specimen length) vs. pre-strain data for all three materials to allow for an easier comparison between them.

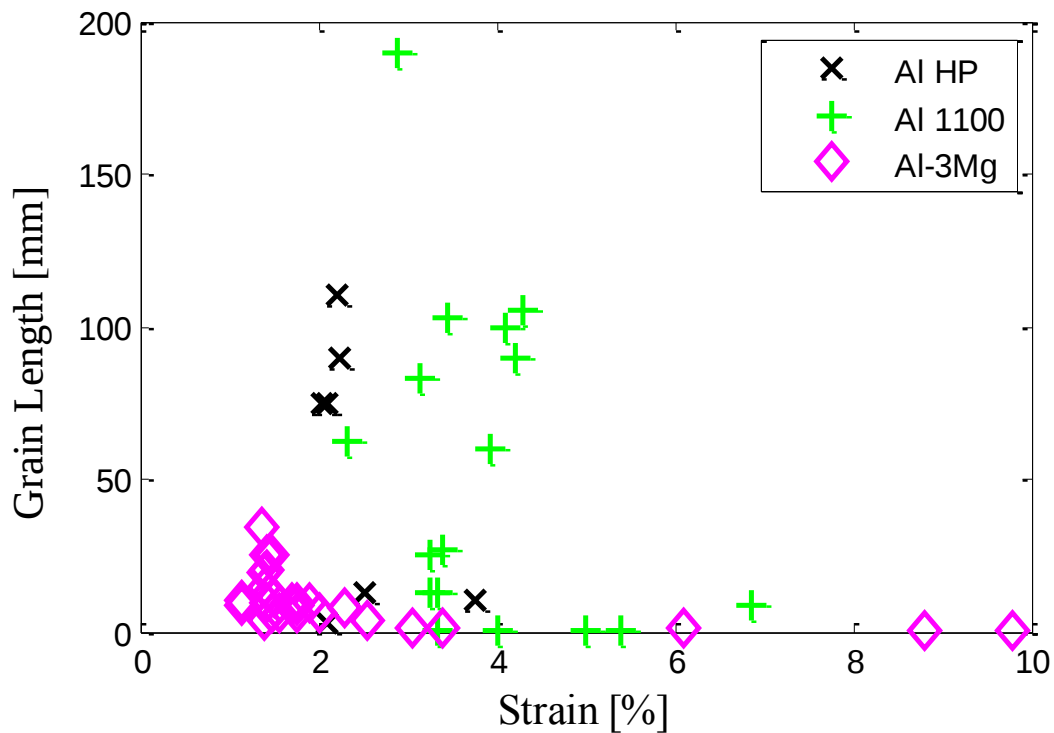


Figure 20: Grain length (along specimen length) dependence on pre-strain for all three materials and entry rates

It is clear that Al 1100 requires the most pre-strain, while Al-3Mg requires the least. The alloy content of Al-3Mg may explain why it requires the least strain. Mg is

commonly added to increase strength of Al, and Al-Mg alloys exhibit work-hardening properties. This means that for the same amount of strain, Al-3Mg will have more stored strain energy in its lattice than either of the other materials because of a higher dislocation density. This idea would suggest that Al HP should have the highest required strain, but this is not the case. One possible reason is because of initial microstructural features. Al HP has a much smaller impurity and particulate content than the other materials. Particulates will help to pin dislocation movement and further increase the strain energy stored, i.e. the dislocation density within the material. This would require a higher critical strain for Al HP, but these particles and alloying or impurity elements also serve to restrict grain growth. Since all three materials were annealed for the same amount of time at approximately the same homologous temperature, the Al HP underwent significantly more grain growth because of its low impurity content. A fine grain structure will lead to a more uniform distribution of plastic strain. Large grains, each with its own preferred slip system(s) based on the direction of applied loading, that fill an appreciable amount of the specimen gauge width, will experience different amounts of slip. This will produce a non-uniform amount of plastic strain between different grains. This could occur in the pre-straining stage of the Fujiwara process, significantly altering recrystallization behavior locally. The Fujiwara process works best on fully recrystallized, fine-grained material [10], the latter of which Al HP was not. Normal grain growth limits subsequent single crystal growth in this circumstance. A large-grained microstructure will provide less driving force for grain growth than will a smaller-grained structure, as will be discussed later.

It appears that, as the required pre-strain increases, the range of acceptable strains for large grains to grow also increases. For recrystallization to occur, a certain amount of energy must be built up within the material. The activation energy for nucleation of recrystallization should be higher than the activation energy for grain growth if grain growth is to be preferred [10]. Note that grain growth, in this case, is simply migration of the grain boundary across the pre-strained microstructure. Thus, a material that exhibits a range of critical pre-strain values for single-crystal production must have a much larger activation energy for nucleation of recrystallization than for grain growth. It is necessary for grain growth to dominate even when excess nucleation sites are available because of variations in local strains, such as between two large pre-strained grains with different orientations. Such adverse effects from large recrystallized grains in the pre-straining process is a reason that a fine-grained microstructure is preferred for use in the Fujiwara process. Al HP may not have been tested to a large enough range of strains and entry rates to make a definitive comparison for this discussion.

4.2 CRYSTALLOGRAPHIC ORIENTATIONS

The orientations of the single-crystals grown for each composition are shown previously in Figure 18. T. Fujiwara studied the preferred orientation of drawn wire [2], and observed that drawn wire would typically grow along a [210] or [110] direction, i.e., parallel to its axis, along the furnace entry direction. The drawn wire was known to have a [111] texture prior to testing [13]. When observing the single crystal specimens in the present study, which were previously rolled and annealed, there appears to be a similar

correlation. In Figure 18, the longitudinal direction (LD), shows a spread of data in a similar region. The [201] direction lies approximately halfway between [001] and [101], and the data for all three materials resides in the area between [201] and [101]. The data also extend away from this line in the [111] direction, just as observed in Fujiwara's experiments on Al wire [2]. Tiedema [13] reported the [210] direction as a strongly preferred direction for wire specimens, but several specimens clearly vary from this orientation. The Al 1100, which is the most similar to past materials tested and mentioned, does lie close to this line, with several orientations near the [101] direction and the others very near [201].

It appears that Al 1100 strongly prefers to orient the [001] direction parallel to the ST direction, while Al HP and Al-3Mg prefer to align in a range of directions from [001] to [111], excluding one possible Al HP outlier. Because the Al 1100 was rolled to the appropriate thickness before it was received and annealed, its deformation history is not known, and this preferred orientation may be a residual effect of this processing history. The Al HP and Al-3Mg, whose histories are better understood and are known to be similar, behaved similarly to each other.

A previous study by Lucke and Engler on cold rolled aluminum and aluminum alloys suggest that they will exhibit a cube texture, and that, depending on alloying and particulate content, the overall texture after annealing may largely stay in this orientation [24]. The cube texture is observed as having [100] planes parallel to the rolled surfaces, thus the [100] plane direction is in the ST direction. Al alloys that have undergone large deformations may form banded deformation structures when heavily cold rolled, causing additional variation in the recrystallized microstructure that forms. Later in this

discussion, mobility will be introduced as a function of misorientation angle. The three materials may exhibit similar textures, if present, although Al-3Mg's additional alloying content may lead to more variation in texture. Texture measurements were not made for the present investigation, but the ramifications of possible texture effects are worth consideration.

When the summary of single-crystal orientations is compared to the selection of orientations for large crystals that did not continue growing, it is clear that the orientation plays an important role in determining the growth of a single-crystal. Grains that did not continue growing do not show the orientation preferences that the largest single crystals do. Although some grains do fall in the same orientation regions as the single crystals, this only implies that crystallographic orientation is the best indication of which grains will grow largest, but orientation alone does not guarantee success.

4.3 GRAIN BOUNDARY MOBILITY

The driving mechanism for the motion of grain boundaries is a reduction in energy. This occurs through a series of atomic jumps in both directions across the boundary, with a net movement in one direction. The mobility is a measure of the grain boundary's ability to move in a material under an applied "pressure". It can be expressed in relating to a driving" pressure" and the velocity of the grain boundary, as given in equation 1, where v is the boundary velocity, m is mobility, and P is driving pressure, which is defined in units of pressure.

$$v \equiv m * P \quad (1)$$

Mobility may further be defined as a function of temperature with equation 2, which relates it to a mobility constant m_0 , gas constant R , absolute temperature T , and activation energy for grain boundary migration Q_m .

$$m = m_0 * \exp\left[\frac{-Q_m}{RT}\right] \quad (2)$$

Mobility will thus increase with temperature. Activation energy can be obtained by measuring observed mobility as a function of temperature, which was not done for the present study.

Huang et al [25] suggested Equation 3, to explain how the mobility constant in aluminum is a function of misorientation angle, θ , across the moving boundary.

$$m_0 = \alpha \theta^\beta \quad (3)$$

In equation 3, α and β are constants. The fastest growth rates were observed for misorientations of 30-40°. The materials in Huang's publication, preprepared single-crystals were upset to different amounts of strain to create the variations in misorientation angles. In the present study, the three materials were cold rolled, and were done so in a similar manner to each other. Any texture that may have formed is likely to be similar for the three materials, so this should not be a large factor in the observed results when comparing between the three materials.

Many factors affect the driving force for grain boundary migration, such as surface energy, elastic energy, and magnetic fields. The forces expected to be of importance in the present tests include the stored deformation energy, grain boundary energy, and chemical driving force. Many of these factors represent competing mechanisms. The equations for driving force from stored energy deformation, grain boundary energy, and chemical driving force are shown in equations 4, 5, and 6, respectively [26].

$$\text{STORED ENERGY:} \quad P = \frac{1}{2} \rho \mu b^2 \quad (4)$$

$$\text{BOUNDARY ENERGY:} \quad P = \frac{2\sigma_b}{r} \quad (5)$$

$$\text{CHEMICAL ENERGY:} \quad P = r (T_1 - T_0) c_0 \ln c_0 \quad (6)$$

The dislocation density is ρ , μ is the shear modulus, b is Burgers vector magnitude, dislocation energy is $\frac{1}{2} \mu b^2$, grain boundary energy is σ_b , radius of curvature of the grain boundary is r , alloy concentration is c_0 , annealing temperature is T_1 , and the temperature at c_0 's maximum solubility is T_0 .

Measurements were not made for dislocation density. Because only a small deformation was applied to each material for recrystallization, the deformation energy driving force is assumed to be small and approximately equal among the materials. For

this reason, the driving force from dislocation energy will not be considered as a factor when estimating mobility.

From experimentation, the approximate local radius of curvature for the moving boundary is known, and can be calculated by simply assuming the radius is half the diameter of the grain size of the materials after processing and prior to Fujiwara testing. The grain boundary energy can be estimated by the Read-Shockley equation [27],

$$\sigma_b = \phi(A - B \ln \phi) \quad (7)$$

with ϕ being the misorientation angle, $A = E_c/b$ where E_c is the energy of the dislocation core, and $B = \mu b/4\pi(1-\nu)$ where ν is the Poisson ratio. Because several of the quantities in Equation 7, particularly misorientation angle, are not known for each material, σ_b will be left as a variable in the subsequent analysis.

Impurities may drag the migrating grain boundary, but calculating the magnitude of this effect requires knowledge of impurity concentration in the boundary and activation energies for an atomic jump. The diffusion coefficients for a selection of the impurity and alloy elements found in the materials is presented in

Table 6. These data are from a range of temperatures and measurement techniques, and may vary from the true values in the present study because of differences in testing conditions. However, these data provide a reasonable guideline for the different effects of impurity elements.

Table 6: Diffusivity coefficients and activation energies for diffusion in Al of various elements.

Diffuser	D_0 (m ² /s)	Q (kJ/mol)	Reference
Si	1.38×10^{-5}	117.6	[28]
Mg	1.49×10^{-5}	120.5	[28]
Al	$1.9 \pm 0.6 \times 10^{-5}$	123.5	[29]
Cu	4.44×10^{-5}	133.9	[28]
Fe	3.62×10^{-1}	214.0	[28]
Ti	1.12×10^{-1}	260.0	[28]
Cr	6.75×10^{-1}	261.9	[28]
V	1.60×10^0	302.5	[28]

Many of the activation energies, Q, and diffusivity coefficients, D_0 , are similar to that for Al-Al, especially Mg and Si. This is not the case for Fe, Ti, Cr, and V (which is not included in the compositional analysis of the materials studied here), which are very different from Al-Al. Because boundary migration is related to diffusion, and activation energy for grain boundary migration is often between that of grain boundary diffusion and lattice diffusion [26], the Mg additions may not play a critical role in grain boundary mobility activation energy. Because Q is a critical value for determining mobility, and small additions of some elements, particularly Fe, Ti, and Cr, may drastically change this value, simply assuming an activation energy for boundary migration approximately equal to that of Al-Al or Mg-Al diffusion is not appropriate. A material reported in the literature, most similar to that of Al 1100, with 0.05 wt% Si and 0.001 wt% Fe, was found to have a grain boundary mobility activation energy of 147 kJ/mol [25]. All other impurities were listed as under 0.001 wt%. While it is unlikely for Si to increase Q, Fe diffusion in the Al might cause this effect [30]. Because the concentrations of Fe in Al 1100 and Al-3Mg are higher than for the Al-0.05wt%Si reported in the literature, the activation energy is expected to be equal to, or greater than, that provided for the material

in literature. The concentrations of Cr and Ti in Al 1100 and Al-3Mg are much lower than Fe for each of the materials, so their effect is assumed small in comparison to that of Fe.

Using equations 1,2, and 5, the mobility constant can be solved for as a function of known parameters, such as entry velocity, grain size, temperature, and the variable grain boundary energy, assuming that activation energy for migration is approximately constant for the three materials. The final equation is then

$$m_0 * \sigma_b = \frac{V * r}{2 \exp\left(\frac{-Q_m}{RT}\right)} \quad (8)$$

where V is entry rate. Entry rates used for analysis were those that produced the largest average normalized grain lengths for each material. The activation energy assumed for this calculation is 147 kJ/mol.

When this mobility coefficient is plotted against impurity or alloy concentration, keeping boundary surface energy as a variable, a clear relationship is revealed, as shown in Figure 21. The alloy or impurity concentrations were estimated based on the chemical composition data, as follows: 0.001% for Al HP, 0.8% for Al 1100, and 3.0% for Al-3Mg. This provides only an estimation of the impurity contents, because some of the impurities are in precipitate form and are not in the matrix and the effect of these cannot be easily calculated. Considering mobility of grain boundaries in the presence of particles is beyond the scope of this study.

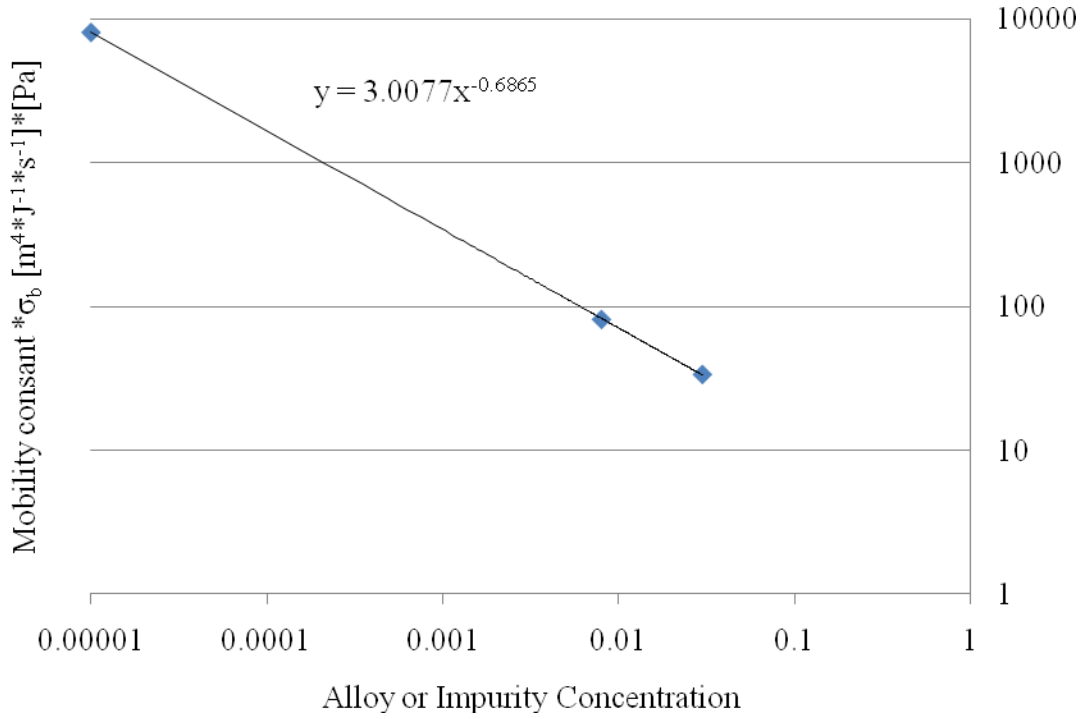


Figure 21: Mobility constant times grain boundary pressure as a function of impurity concentration.

This relationship follows that observed for mobility constant as a function of misorientation angle, which is left as a variable in the σ_b term. Thus, misorientation is not specified and is, therefore, not the cause of the trend observed. The trend follows the equation

$$m_0 = C * c_0^D \quad (9)$$

where in this case $C = 3.0077$ and $D = -0.6865$. This analysis helps explain why Al HP did not achieve entry rates faster than Al 1100, as might be expected. The Al HP's large-grained initial microstructure likely caused strain inhomogenities in the pre-straining step of the Fujiwara process, which caused localized changes to the activation energies for nucleation and growth. The large-grained microstructure also reduces driving pressure

for grain boundary mobility. This confirms the earlier hypothesis that the initial large grain structure hinders single crystal growth. This model assumes that the growth limiting factor is the same for all three materials, since Q was assumed constant.

Mobility constants times grain boundary tensions are shown in Table 7 for several materials described in the literature and the materials in this study. Misorientation angle range is provided, if known.

Table 7: Mobility constants from literature and present study.

Material	Misorientation angle	$\ln(M_0^* \sigma_b)$
High Purity Al [31]	30-40°	12.1 - 20.2*
Al-0.05wt%Si [32]	40°	12.2 – 14.5
Al-0.05wt%Si [32]	2.6-5.6	3.7 – 8.1
Al HP	Unknown	9.0
Al 1100	Unknown	4.4
Al-3Mg	Unknown	3.5

*brief drop to value of 7.5 due to coincident site lattice at 32.2° ($\Sigma=13$) not included.

The data from the literature correspond very well to the present data. From these estimations, it appears that the Al 1100 and Al-3Mg, which are expected to behave most similarly to Al-0.05wt%Si due to compositional information given, fall in the range of values for the latter material with small misorientation angles. The Al HP corresponds most similarly to the High Purity Al material. These values suggest that Al HP also has an average misorientation below the high angle range given for the High Purity Al material.

Chapter 5 Conclusions

Three materials were used to grow single-crystal specimens in the solid-state following the method of T. Fujiwara: high purity aluminum Al HP, commercially pure aluminum Al 1100, and an aluminum-magnesium alloy with 3 wt% magnesium Al-3Mg. The three materials were first processed into sheet material and fully recrystallized. A pre-strain was applied, and the specimens were slowly entered into a furnace with a steep temperature gradient. The materials were tested using a range of pre-strains and entry rates to determine the critical pre-strain for recrystallization and maximum entry rate for single crystal growth. Specimens were ground, polished, and etched to reveal their macrostructure. Laue back-diffraction patterns were obtained for select crystals to determine crystallographic orientation.

The dependence of crystal growth on pre-strain follows the same pattern typical of strain-annealing methods used for growing large grains. A critical strain is needed prior to annealing, and any increase in strain above this critical value decreases the resulting recrystallized grain size. Furnace entry rate affects the size of grains grown. Slower entry rates almost always produce larger grains, and this relationship was observed for entry rate and resulting grain size for the Al 1100 and Al-3Mg materials.

The single crystals produced preferred crystallographic orientations with [210] and [110] directions parallel to the growth direction, as observed for Fujiwara's wire specimens, known to exhibit a cube texture. Al 1100 preferred to align its short transverse direction parallel to a [100] direction, and Al HP and Al-3Mg varied in their

short transverse orientation preference from [100] to [111] directions. Rolled aluminum and low alloyed aluminum, which form a cube texture, show a preference for the [100] direction in the short transverse orientation, thus Al 1100 demonstrates a better correlation between the material texture behaviors in the literature.

The grain boundary mobility constant for each material was calculated from known experimental and material parameters, and compared to published data for similar materials. The main driving force was assumed to be grain boundary energy. This analysis produced good agreement between current and published data. A correlation was made between the mobility constants obtained and the variation in grain boundary tension with the impurity content of the materials tested. This revealed a decrease in mobility constant (times grain boundary tension) with increasing impurity content following an empirical power-law equation, but assumed a similar activation energy for grain boundary migration among all three materials.

The method of Fujiwara provided a useful way to create single-crystals of aluminum, and avoided the solidification issues involved in melt-processing single-crystal growth. This method may even be expanded from the application used here to specify the orientation of the single-crystal. Data on the mobility of grain boundaries in these materials was obtained, although further investigation using larger temperature ranges could provide the data needed to calculate activation energy for boundary migration in each material, which would allow more accurate measurement of boundary mobility values.

This study is the first to report on the effect of impurities and alloying elements on the growth of single crystals using the method of Fujiwara. Few details were available

in the literature for the process' applicability to alloys, and no analysis was provided to try to explain the differences in the results for materials with different compositions. Previous mobility studies have not used a moving temperature gradient across a deformed microstructure to obtain information about the material. This study showed that the Fujiwara process is an alternative approach to testing for grain boundary mobility information, and helped determine important factors in the growth of single crystals through this method.

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