I, Madhura A Joshi, hereby submit this original work as part of the requirements for the degree of Master of Science in Materials Science.

It is entitled:
Growth and Characterization of Magnesium Single Crystal for Biodegradable Implant Material Application

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Growth and Characterization of Magnesium Single Crystal for Biodegradable Implant Material Application

A thesis submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of Master of Science in the program of Material Science and Engineering in the Department of Mechanical and Materials Engineering of the College of Engineering and Applied Science by

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Abstract

Magnesium (Mg) is one of the most promising biodegradable materials for implants owing to its mechanical properties. But because of its highly corrosive nature, its corrosion behavior is difficult to control or predict. This document explores a new approach by using single crystal magnesium for the implant application. Directional solidification technique using vertical modified Bridgman-Stockbarger method has been used to grow the high purity Mg single crystals. They have been characterized to test their single crystallinity and high purity using metallography, X-ray diffraction, pole figure, inductively coupled plasma mass spectroscopy (ICPMS) and microCT techniques. Attempts to improve the corrosion behavior of the substrate has been made via utilizing various surface treatments such as DC anodization, micro arc oxidation (MAO) and chemical etching. In vitro and in vivo corrosion testing has been done to evaluate the corrosion performance using potentiodynamic polarization testing as well as weight loss testing. Film characteristics were studied using the various surface analysis techniques such as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Various medical devices were made for the animal model studies by the NSF Engineering Research Center for Revolutionizing Metallic Biomaterials (ERC-RMB) participant collaborators and tested for their biological behavior and compatibility.
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I would be forever in debt of all the imaginative and genius minds that helped discover, invent and innovate in order to make this world a better place.

I dedicate this thesis to my grandmother - Jayashree Aaji, who shaped my life and was the kindest person I ever knew.
Table of Contents

1 Introduction.......................................................................................................................... 1
1.1 Magnesium as a biodegradable metal .............................................................................. 1
1.2 Advantage of Mg over other biodegradable materials.................................................. 3
1.3 Single crystal growth process ....................................................................................... 4
  1.3.1 Nucleation .................................................................................................................. 4
  1.3.2 Growth mechanisms .................................................................................................. 8
1.4 Single Crystal Growth ..................................................................................................... 9
  1.4.1 Liquid- Solid Conservative processes ....................................................................... 10
1.5 Magnesium crystal structure ......................................................................................... 12
1.6 Principles of electrolytic corrosion ............................................................................... 13
  1.6.1 Corrosion of Magnesium ........................................................................................ 15
1.7 Orientation dependent corrosion of magnesium .......................................................... 16
1.8 High ductility exhibiting Mg single crystal ................................................................. 22
1.9 Surface treatments used for corrosion resistance improvement .................................. 23
  1.9.1 Anodization .............................................................................................................. 24
  1.9.2 Micro arc oxidation .................................................................................................. 24
  1.9.3 Chemical Etching ...................................................................................................... 25
2 Experimental Details - Materials, Methodology and Characterization for Pure Mg single crystal growth ........................................................................................................... 27
  2.1 Raw Material ............................................................................................................... 27
  2.2 Crucible choices ........................................................................................................... 28
  2.3 Growth system ............................................................................................................. 29
  2.4 Process details ............................................................................................................. 30
  2.5 Electro Discharge Machining (EDM) wire cut method for slicing the crystals .......... 31
  2.6 Validation methods to test for single crystallinity and purity ...................................... 31
     2.6.1 X-ray Diffraction methods ...................................................................................... 31
     2.6.2 Pole Figure analysis .............................................................................................. 37
     2.6.3 Metallography ....................................................................................................... 38
     2.6.4 Micro CT ................................................................................................................ 40
     2.6.5 Inductively Coupled Plasma Mass Spectroscopy (ICPMS) .................................... 40
2 Surface treatments ............................................................................................................. 43
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>DC Anodization</td>
<td>43</td>
</tr>
<tr>
<td>3.2</td>
<td>Micro-arc oxidation</td>
<td>44</td>
</tr>
<tr>
<td>3.3</td>
<td>Chemical etching</td>
<td>45</td>
</tr>
<tr>
<td>3.4</td>
<td>Corrosion Behavior Analysis</td>
<td>46</td>
</tr>
<tr>
<td>3.4.1</td>
<td>In Vitro Testing</td>
<td>46</td>
</tr>
<tr>
<td>3.4.2</td>
<td>In vivo testing</td>
<td>47</td>
</tr>
<tr>
<td>3.5</td>
<td>Film Characteristics and Surface Analysis</td>
<td>49</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Optical Microscopy, Scanning electron microscopy (SEM) and Energy dispersive spectrometry (EDS)</td>
<td>49</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Atomic Force Microscopy (AFM)</td>
<td>50</td>
</tr>
<tr>
<td>3.5.3</td>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Results and Discussion</td>
<td>51</td>
</tr>
<tr>
<td>4.1</td>
<td>Crystal growth and characterization</td>
<td>51</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Solidified Crystal from the melt</td>
<td>51</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Characterization of the crystallinity</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>Corrosion behavior of surface treated and un-treated surfaces</td>
<td>58</td>
</tr>
<tr>
<td>4.2.1</td>
<td>DC Anodized surface</td>
<td>58</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Micro-arc oxidized surface</td>
<td>61</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Chemically etched surface</td>
<td>62</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Weight loss measurements by immersion testing</td>
<td>63</td>
</tr>
<tr>
<td>4.2.5</td>
<td>In vivo testing</td>
<td>65</td>
</tr>
<tr>
<td>4.3</td>
<td>Characterization of the treated surfaces</td>
<td>66</td>
</tr>
<tr>
<td>4.3.1</td>
<td>DC anodized coating morphology</td>
<td>67</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Micro-arc oxidized surface morphology and coating thickness</td>
<td>68</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Chemically etched surface – Morphology and composition</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>Single Crystal used in animal studies</td>
<td>80</td>
</tr>
<tr>
<td>5.1</td>
<td>For reconstruction of the Anterior Cruciate Ligament (ACL) joint</td>
<td>80</td>
</tr>
<tr>
<td>5.2</td>
<td>Micro CT results</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>Conclusion</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>Future Work</td>
<td>85</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>Appendix</td>
<td>92</td>
</tr>
</tbody>
</table>
List of Figures

Fig. 1. Interface when the solid is formed within a liquid. ................................. 5

Fig.2. The change in the total free energy of the solid-liquid system as a function of the radius of the solid particle. ................................................................. 6

Fig. 3. Solid formation on an impurity i.e. heterogeneous nucleation. ........................ 7

Fig. 4. Rate of nucleation as a function of the liquid temperature. .......................... 8

Fig. 5. Classification of the monocomponent crystal growth process. ......................... 10

Fig. 6. (a) HCP unit cell (b) Indices of planes and directions (c) The stacking arrangement of spheres (d) ABABA stacking. ................................................................. 12

Fig. 7. Single crystal surfaces with different rotation angles. ..................................... 16

Fig. 8. (a) Potentiodynamic polarization curves of the Mg single crystals as a function of rotation angle (b) Effect of rotation angle on the pitting potential of Mg single crystals in 3.5 wt.% NaCl solution at 20 degree C. (c) Change in current as a function of time with applied potential of -1.57 V vs SCE. ................................................................. 17

Fig. 9. (a), (b) Differences in the depth caused by different grain corrosion rates, (c) Map of the orientation dependence with the corrosion resistance. .................. 18

Fig. 10. (a), (b) Regions of the polycrystalline coupon chosen for the study, (c) Specially designed electrode for testing. ................................................................. 19

Fig. 11. EBSD map of the studied area putting orientational information to the grains. .... 20
Fig. 12. Polarization curves measured from areas D and E ($\varphi$ and $\phi$) as representatives of the dark and bright regions of the surface of the Mg coupon immersed in (a) Mg(OH)$_2$ saturated solution and (b) 0.01 M NaCl solution, respectively. 24 .......................................................... 20

Fig. 13. Cyclic polarization curves for surfaces analyzed for corrosion behavior. 25 .................. 21

Fig. 14. Sample of Mg single crystal after and before deformation at 573 K to $\epsilon = 1.8$. 27 ...................... 23

Fig. 15. Layers observed in the MAO coating .......................................................... 25

Fig. 16. Different sizes of the raw material (pure Mg) used for crystal growth ..................... 27

Fig. 17. Different crucibles and the stainless steel crucible holder used for Mg crystal growth. 28

Fig. 18. Single crystal grower J5409. .................................................................................. 29

Fig. 19. The user interface on the crystal grower. .......................................................... 29

Fig. 20. EDM wire cut machine and cutting chamber. .......................................................... 31

Fig. 21. X-ray emission process. 16 .......................................................... 32

Fig. 22. Diffracting x-ray beam after falling on the set of planes. 16 ......................... 34

Fig. 23. Custom made stage for accommodating longer single crystals ...................... 35

Fig. 24. (a) Transmission Laue method, (b) Back-reflection Laue method. 16 ...................... 36

Fig. 25. Laue spots (a) Ellipses in transmission method (b) Hyperbolas in Back-reflection method (C-Crystal, Z.A. – Zone Axis, F-Camera Film, $\phi$-Angle of inclination of the zone axis with the beam). 16 .............. 36

Fig. 26. (a) Polishing set up for pole figure sample preparation, (b) Bruker AXS D8 Discover XRD machine. .............................................................................................................. 37
Fig. 27. (a) Bruker axs D8 discover chamber used for pole figure analysis (b) Crystal plane with respect to the sample plane. ................................................................. 38

Fig. 28. Sample polishing stages representative images................................................................. 39

Fig. 29. Agilent ICP-MS instrument ............................................................................................... 41

Fig. 30. Different locations of the crystal being analyzed to find elemental distribution .......... 42

Fig. 31. DC anodization set-up ........................................................................................................ 44

Fig. 32. MAO coated surface (a) Representative optical image at 30X, (b) The sparking observed during the process .................................................................................................................. 45

Fig. 33. Optical and X-ray images of the mice having implanted samples of (a) Polycrystalline Mg Unetched and Etched (b) Pure Mg Single Crystal Unetched and Etched ..................................... 48

Fig. 34. Evolution of single crystal growth...................................................................................... 51

Fig. 35. XRD diffractogram obtained from the single crystal Mg .................................................. 52

Fig. 36. XRD diffractogram obtained from the polycrystalline Mg .............................................. 52

Fig. 37. Pole figures obtained for the polished discs of 14 hour soaked Mg single crystal .......... 53

Fig. 38. Laue XRD patterns for 14 hour soaked Mg crystal obtained at (a) Top, (b) Center and (c) Bottom of the rod. The spots are identical for the scans obtained for the top, bottom and center regions. (Courtesy: Dr. Stephan Rosenkranz, Argonne National Laboratory) .......................................................... 54

Fig. 39. (a) Laue XRD pattern for polycrystalline Mg rod shown in (b). The patterns is diffused and in clear contrast with those obtained for the single crystal rods. (Courtesy: Dr. Stephan Rosenkranz, Argonne National Laboratory) ........................................................................................................ 55

Fig. 40. Polished and etched crystals for metallography.............................................................. 55
Fig. 41. Micro CT images of (a) The 2" long single crystal (b) The circular cross section. ... 56

Fig. 42. ICP-MS elemental distribution obtained across the length of the single crystal. ... 57

Fig. 43. Polarization curves of Anodized (S2-upper brown curve) and non-anodized (S1-lower blue curve) Mg single crystals in Hank’s solution. ... 59

Fig. 44. Polarization curves of Polycrystalline Mg, Polished single crystalline (S1 and 2S1) and Anodized single crystalline (2S2) Mg in 0.15M NaCl solution. ... 60

Fig. 45. Polarization curves obtained from the MAO coated samples. ... 61

Fig. 46. Potentiodynamic DC polarization curves obtained for Polished and polished + etched single crystal. ... 62

Fig. 47. Optical images of immersion test samples (a) Single crystal polished till 1200 grit, (b) Etched single crystals for 10 seconds, (c) Polycrystalline Mg, (d) MAO coated single crystal before immersion, namely before immersion, after removal from the solution. ... 63

Fig. 48. Weight loss vs. Time graph obtained from immersion test in DMEM + HEPES. ... 64

Fig. 49. Weight loss vs Implantation Time for in vivo study in the mice model. ... 65

Fig. 50. Bubble volume vs. Time data for in vivo study in the mice model. ... 66

Fig. 51. Optical images of non-anodized (S1) and anodized (S2) samples after polarization test (Mag.30X). ... 67

Fig. 52. SEM images of anodized (S2) samples (a) before and (b) after polarization test (Mag 500X). ... 67

Fig. 53. Optical microscope images of the samples after the polarization tests in 0.15 M NaCl. 68
Fig. 54. Surface and cross section SEM images of the samples MAO coated for (a)&(d) - 5 min, (b)&(e) - 7 min, (c) & (f) - 10 min. ................................................................. 69

Fig. 55. AFM scans of Mg crystal surfaces (a) 1200 Grit polished (b) Polished and 10 seconds etched (c) Polished and 30 seconds etched. ................................................................. 70

Fig. 56. XPS depth profile of pure MgSC with different surface conditions (a)1200 grit polished, (b)1200 grit polished & 10 seconds etched using NME etchant and (c) 1200 grit polished & 30 seconds etched with NME etchant. ................................................................. 71

Fig. 57. Survey Spectra for 1200 grit polished Mg single crystal (a) Before sputtering (b) After sputtering. ................................................................. 73

Fig. 58. De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished Mg single crystal. ................................................................. 74

Fig. 59. Survey Spectra for 1200 grit polished + 10 seconds etched Mg single crystal (a) Before sputtering (b) After sputtering. ................................................................. 75

Fig. 60. De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished + 10 seconds etched Mg single crystal. ................................................................. 76

Fig. 61. Survey Spectra for 1200 grit polished + 30 seconds etched Mg single crystal (a) Before sputtering (b) After sputtering. ................................................................. 77

Fig. 62. De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished + 30 seconds etched Mg single crystal. ................................................................. 78

Fig. 63. (A) Specially designed ACL ring (B) Placement of the ring at the ACL joint. 48 ........ 81
Fig. 64. (a) Time zero image of the ACL joint after the implantation of the single crystal ACL device with suture technique in cadaveric joint (b) 6 Weeks of healing of the ACL joint after the implantation of the single crystal ACL device with suture technique (c) Control : normal healthy ACL joint. ................................................................. 81

Fig. 65. Micro CT image of the leftover ring after 6 weeks (a) greyscale imaging for remaining volume calculations, (b) Corroded part of the ring can be seen in white (c) The corrosion product accumulated after pitting corrosion can be seen in a darker grey due to the density differences .82

Fig. 66. Nitrogen, Argon gas flow controller, Water flow controller, Light wand representing various process stages. ........................................................................................................ 92

Fig. 67. Controls for loading, unloading, emergency stop and alarm lights on the crystal grower 93

Fig. 68. Single crystal growth process flow chart......................................................................... 94
List of Tables

Table 1 Comparison of the bone properties with other metallic materials. \textsuperscript{11,12} ...................................... 3

Table 2 Average Pitting and repassivation potentials for Mg single crystal orientations in 0.01 M NaCl and 0.0001 M of sodium dichromate. \textsuperscript{25} ........................................................................................................ 22

Table 3 Elemental distribution calculated using ICPMS ........................................................................................................... 57

Table 4 Corrosion potential, corrosion current and approx. corrosion rate data obtained for anodized samples from the DC polarization experiments .................................................................................. 60

Table 5 Corrosion potential, corrosion current and approx. corrosion rate data obtained for MAO coated samples from the DC polarization experiments .................................................................................. 61

Table 6 Weight loss measurements from the immersion test in DMEM + HEPES .................. 64

Table 7 Variation of surface elemental concentration of samples with different MAO treatment time ........................................................................................................................................ 69

Table 8 Surface roughness parameters of the Magnesium samples obtained using AFM .......... 71

Table 9 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished sample ........................................................................................................................................ 73

Table 10 High resolution peak data for 1200 grit polished Mg single crystal before and after Argon sputtering ........................................................................................................................................ 74

Table 11 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished + 10 seconds etched sample ........................................................................................................ 75

Table 12 High resolution peak data for 1200 grit polished + 10 seconds etched Mg single crystal before and after Argon sputtering ........................................................................................................................................ 76
Table 13 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished + 30 seconds etched sample ................................................................. 77

Table 14 High resolution peak data for 1200 grit polished + 30 seconds etched Mg single crystal before and after Argon sputtering. ........................................................................................................ 78

Table 15 Volume analysis after the ring degradation .......................................................................................................................... 82
1 Introduction

This section discusses the background and rationale behind using Magnesium (Mg) single crystal as a potential biodegradable implant material. It also discusses the single crystal growth aspects and the Mg crystal structure. It delves into discussing the principles of electrolytic corrosion along with providing evidences found in the literature about the orientation dependent corrosion of Mg single crystal and gives some background about the surface treatments explored in this thesis in order to improve the corrosion behavior of Mg single crystal substrate.

1.1 Magnesium as a biodegradable metal

Biodegradable metals (BM) are defined as “Metals expected to corrode gradually in vivo, with an appropriate host response elicited by released corrosion products, then dissolve completely upon fulfilling the mission to assist with tissue healing with no implant residues. Therefore, the major component of BM should be essential metallic elements that can be metabolized by the human body, and demonstrate appropriate degradation rates and modes in the human body” by Zheng et. al. ¹.

Elemental magnesium was discovered by Sir Humphrey Davy, a British chemist, in 1808. The German scientist, Robert Bunsen started the production of Mg metal by electrolysis of fused anhydrous MgCl₂ in 1833. Physician Edward Huse made use of Mg wires as ligatures to stop the bleeding in the vessels in 1878. Slower in vivo corrosion and complete degradation of Mg was observed by him which was reliant on the size of the wire used. The Austrian physician Erwin Payr started Mg resorption experiments in 1892 and by 1900 he suggested that the oxygen and water present in the tissue, CO₂, the dissolved salts in the blood and chemical processes in the cells were having the combined effect on the corrosion of Mg in the body. Magnesium has seen a greater
interest as a biomedical implant material in recent years due to several advantages over conventionally used metallic implant materials such as stainless steel (SS) and titanium. Its most amazing property is its ability to be completely absorbed into the human body over time \(^\text{2,3}\). It is a part of several biochemical functions as it activates about 300 enzymes. After potassium, magnesium is the most abundant intracellular element \(^\text{4}\). Significant Mg content has been observed in plasma, serum, erythrocytes, brain, stomach, intestine, lung, kidney, heart, muscle, spleen and liver; and ranges from 0.87 mmol/l in plasma to 8.82 mmol/kg in the heart \(^\text{5}\).

This makes it suitable for osteosynthesis \(^\text{6}\) and to be used in degradable orthopedic or craniofacial implants. Once the bone tissue has healed, the implant is gradually absorbed into the human body. This eliminates the need for additional surgeries for implant removal and reduces the trauma and economic costs for the patient \(^\text{7}\).

Mg is also an essential element needed for the normal functioning of the human body and is required as a part of a balanced diet. For an average healthy person, daily intake of Mg varies from 310 mg/day for women to 400 mg/day for men. Thus if Mg is used as an implant material, it will eventually get dissolved in human body. The dissolution of Mg in the human body is relatively harmless \(^\text{7}\) and can in fact help meet the daily nutrient requirement.

Mg has lower Modulus (40-45 GPa) than Ti and SS and has a better modulus match with the bone. Both steel (200 GPa) and Ti (116 Gpa) have higher moduli compared to the bone \(^\text{3,8}\). Magnesium because of its lower modulus will reduce the stress shielding effect and enhance strong bone growth and healing \(^\text{2,3,6,9}\). Mg based implants are therefore better than SS or Ti in terms of facilitating stronger bone growth.
1.2 **Advantage of Mg over other biodegradable materials**

- Mg with the density of 1.738 g/cc is the lightest of all the structural metals and this value is very close to that of the cortical bone (1.75 – 2.1 g/cc).

- Mg has the highest damping capacity owing to its capacity to absorb energy. This property can be very useful for the implants involved with heavy load bearing applications which require high shock and vibration absorbing capacities.

- It is very easy to machine to achieve final stable dimensions. Medical applications require intricate shapes to be made that have to be tailored to each patient.

- Stress shielding is a big problem when an implant with the incompatible stiffness value compared to that of bone is attached to it causing the decrease in bone mass and density. The implant then transfers the load away from bone causing problems and possibly implant failure if it continues. It is a known problem with the current orthopedic implants made of stainless steel or titanium that have their density, elastic modulus and yield strength much higher than that of the bone. Pure Mg has the elastic modulus of around 45 GPa which is closer to that of the cortical bone having the modulus of around 20 GPa. On the other hand, Ti alloys have the elastic modulus of the order of 110-120 GPa.

<table>
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<tr>
<th>Properties</th>
<th>Natural Bone</th>
<th>Mg</th>
<th>Titanium based</th>
<th>Stainless Steel based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>1.8-2.1</td>
<td>1.74</td>
<td>4.5</td>
<td>8</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>3-20</td>
<td>41-45</td>
<td>110-117</td>
<td>189-205</td>
</tr>
</tbody>
</table>

*Table 1 Comparison of the bone properties with other metallic materials.*  
\[10,11\]
Biomaterials like Ti are inert in the body with little host response, good or bad. But Mg is biocompatible and non-toxic and favors bone formation. Mg is a vital ion for forming the biological apatites making up a bulk of bone mineral which is a key part to the bone formation.  

1.3 Single crystal growth process

Solidification is one of the most important techniques used to manufacture materials like metals, ceramics, inorganic glasses, thermoplastics etc. While solidifying atomic arrangement in the materials changes from short range order to long range order. Solidification of crystalline materials has two steps namely nucleation and growth. Ultrafine solid crystallites form from the liquid and they begin to grow as atoms as the liquid starts attaching to the nuclei till no liquid remains. Solidification is a vital process to study as it affects the final properties of the material.

The discovery of fire and the knowledge of its usage to melt and cast the metals is an important landmark in the history of mankind. Today, after thousands of years of discovery of fire, the solidification still remains an important process. It is a first or a second processing step while making several materials from metals and alloys like ingots, sheets, wires, rods, plates etc. This section will discuss the nucleation and growth aspects.

1.3.1 Nucleation

With respect to the solidification, nucleation refers to forming of the first nano crystallites from the melt. For example when the water begins to solidify, nano nuclei of ice crystals start forming. Nucleation is the initial stage of forming one phase from another phase.

A material solidifies when the liquid cools to just below the freezing (or melting) temperature. It is favored as the energy of the crystalline structure is less than that of the liquid for the material. This difference in the energy, which is the driving force for solidification is the free
energy per unit volume ($\Delta G_v$). While forming a solid, a solid-liquid interface is created as shown in the Fig. 1. If the surface free energy of $\sigma_{sl}$ is associated with it, then larger solid involves greater increase in the surface energy. Total change in the free energy can be given as the following equation (1) –

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \sigma_{sl} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots **
the solid re-melts instead of growing further, the free energy will again decrease as it possible as well as the embryos are thermodynamically unstable. Formation of an embryo having radius more than the critical radius is matter of chance or probability. Further growth of that embryo causes the total free energy to decrease leading to the formation of new stable solid and further growth of the nucleus. At the melting point, the chances of such stable nucleus formation are small and hence further cooling of the melt is required for the solid nucleus formation. The undercooling of $\Delta T$ is basically the equilibrium freezing temperature minus the actual liquid temperature. There are two different possibilities when it comes to nucleation – Homogeneous nucleation and heterogeneous nucleation.

1.3.1.1 Homogeneous Nucleation

As the melt cools below the equilibrium freezing temperature, two factors play a role in causing the nucleation. Atoms start losing their thermal energy increasing the possibility of cluster

![Fig.2. The change in the total free energy of the solid-liquid system as a function of the radius of the solid particle.]

As the melt cools below the equilibrium freezing temperature, two factors play a role in causing the nucleation. Atoms start losing their thermal energy increasing the possibility of cluster
formation to form large embryos. Larger difference in the volume free energy between the melt and the solid reduces the critical radius. When the undercooling becomes large enough to cause the formation of a stable nucleus, homogeneous nucleation takes place and the critical radius can be given as follows by the equation (2) where $\Delta H_f$ is the latent heat of fusion, $T_m$ is the equilibrium solidification temperature in K and $\Delta T$ is $(T_m - T)$ which is undercooling at the melt temperature of $T$. According to this equation, increasing undercooling decreases the size of the critical radius for nucleation.

$$r^* = \frac{2\sigma_s T_m}{\Delta H_f \Delta T}$$

(2)

### 1.3.1.2 Heterogeneous Nucleation

Nucleation on a surface is known as a heterogeneous nucleation. For example, it is known that water does not solidify into ice on its own until – 40 degree C temp is reached which is undercooling of 40 degree C. But in the presence of an impurity suspended or on the walls of the container holding it, solid gets a surface to form on as shown in the Fig. 3. Required critical radius is met much quicker by the radius of curvature by only a small number of atoms assembling together than required for homogeneous nucleation. It depends on the contact angle between the nucleating phase and the surface on which nucleation happens.

![Fig. 3. Solid formation on an impurity i.e. heterogeneous nucleation.](image)

13
1.3.1.3 Rate of nucleation

![Graph showing rate of nucleation as a function of liquid temperature]

**Fig. 4. Rate of nucleation as a function of the liquid temperature.**

The rate of nucleation being a function of the temperature is zero above the freezing point of the solid and as the temperature drops below the freezing point, the rate of nucleation increases up to a certain point as shown in the Fig. 4. But lowering the temperature also cause the atomic diffusion to become slower, causing the nucleation process to slow down. In case of heterogeneous nucleation, concentration of the nucleating agents also plays a role.

1.3.2 Growth mechanisms

After the formation of solid nuclei of a phase, more atoms begin to attach on the surface causing it to grow. Two types of heat have to be removed during the solidification process namely specific heat of the melt and the latent heat of fusion. Specific heat is the heat needed to change the temperature of the unit weight of the material by one degree. It should be removed first by radiation into the environment or by conduction in the crucible till the melt cools down to the freezing temperature. The manner in which the latent heat of fusion is removed from the melt decides the growth mechanism (planar or dendritic growth) and in turn the final structure of the solid.
1.4 Single Crystal Growth

Single crystal growth is in development over the years to satisfy the requirements of the various research and development areas. Original methods have been modified and refined for the purpose of customization and final application. It depends highly on the trial and error and design of the experiment. Crystal growth is an art. Amazing advances in the field of electronics have been using single crystal semiconductors along with the areas where magnetic and optical materials are heavily used. The current situation in the crystal growth area suggests that there is a gap between theoretical predictions and experimental executions of those suggestions because of the complexity of the processes and various interdependent parameters involved.

Crystal growth is a heterogeneous chemical reaction of the following types – a) solid to crystal, b) liquid to crystal c) gas to crystal. It could take place in the system except having traces of impurities the only component existing is the material being crystallized which is called monocomponent growth. It could also take place in the system where the impurities present or added dopants are at a high concentration along with the material being crystallized which is called polycomponent growth. There is no specific boundary between these two types of growth processes when it comes to the concentration of the second component, but practically speaking one could say that the concentration of the impurities should be low enough that any diffusion processes would not hinder the growth process. The differentiation is of the importance when it comes to proposing the theory and technique established for the growth.14,15

This particular thesis deals with the monocomponent growth using pure magnesium. The processes used for this type of growth can be classified as shown in the Fig. 5.
1.4.1 **Liquid-Solid Conservative processes**

Liquid-solid equilibrium is the favored method to grow single crystals because it happens by controlled freezing and related to other processes it is much easier to control. It is the most practiced to produce single crystals. But to some monocomponent materials this method cannot be utilized to begin with because the material may decompose before melting or it sublimes or its vapor pressure is too high at the melting point or the melting point might be too high for it to be considered as practical from economical point of view.

The process would be conservative if there is no material being added or removed from either the solid or liquid phase except by crystallization.

For normal freezing, whole volume of the material is liquid at the start of the process and the solid is formed from the liquid phase as the solid-liquid interface traverses through the melt. Growth takes place in a perfect case at a single site in the molten part causing it to become cooler.
than other sections. Nucleation at the site provides a crystal base on which all the later growth is deposited. Usual procedure would involve a crucible with a conical bottom to hold the molten material and moving it over a temperature gradient so that the material at the tip undergoes freezing first. Consequent movement of the solid-liquid interface takes place. Ideally the single crystal would start nucleating at the tip and if more than one crystal gets nucleated the one that grows the fastest governs the interface. Seed can also be kept at the tip before the growth begins and care should be taken that the seed should not melt before the beginning of the growth. This may be termed as Bridgman-Stockbarger method. An alternate of this technique a temperature gradient is imposed upon the crucible with the tip at the coolest temperature and the remaining part at the melting temperature. Entire crucible temperature is then designed to go down, with an intention of the growth starting at the tip again.

Czochralski or crystal-pulling method is where the material to be crystallized is liquified in the beginning in the crucible. It is isothermally heated and then there is a negative temperature gradient above the melt. A seed is introduced in the melt and made to touch the melt such that it is melted and then slowly withdrawn. Bearing in mind that temperature gradient and rate of withdrawal is planned well for the material, an interface of solid-liquid forms at the level above the molten bulk and the interfacial tension supports the liquid column created above the melt. The seed is pulled with a translational as well as rotational motion.

In the Kyropoulos method, a seed is submerged in the crucible and temperature gradient is retained in a manner that growth takes place only at the interface of the seed and the melt. The seed has to be cooled for this to occur and entire melt is cooled. It uses Czochralski method design but not the same concept as the rotating seed is not pulled and instead temperature of the entire melt is lowered. ¹⁵
1.5 Magnesium crystal structure

When solidified, metals usually tend to crystallize in three crystal structures namely body-centered cubic (BCC), face-centered cubic (FCC) or hexagonal closed packed (HCP). Mg has a hexagonal unit cell and having lattice parameters as; \( a=b=0.32 \) nm; \( c=0.52 \) nm and angles \( \alpha = \beta = 90 \) degrees and \( \gamma = 120 \) degrees. (0001) plane has the maximum atomic density of \( (1.13 \times 10^{19} \text{ atoms/m}^2) \). (11\( \bar{2} \)0) has \( (6.94 \times 10^{18} \text{ atoms/m}^2) \) and (01\( \bar{1} \)0) has \( (5.99 \times 10^{18} \text{ atoms/m}^2) \). The close packed plane has the greater binding energy due to higher atomic co-ordination and lower surface energy. Thus activation energy essential for dissolution of that plane increases increasing the corrosion resistance. \(^{17}\)

X-ray diffraction can be used to find the interatomic distances. If we assume atoms as hard spheres, the atomic packing factor (APF) of the HCP structure is 0.74 and the co-ordination number is 12 which means each atom is surrounded by 12 atoms. The APF can be calculated using the following equation (3).

\[
\text{APF} = \frac{\text{Volume of atoms in a unit cell}}{\text{Volume of the unit cell}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3)
\]

Four indices (Miller-Bravais indices) are used with the letters \( h, k, i, l \) for HCP structure. They are based on the co-ordinate system of 4 axes like in the Fig. 6 (a) namely \( a_1, a_2, a_3 \) making an angle of 120 degrees with each other and a \( c \) axis at 90 degrees to them. The unit cell is made
of the equal and co-planar vectors $a_1$ and $a_2$ making an angle of 120 degrees and $c$ being the third axis at 90 degrees to both of them as shown with the dark lines in Fig. 6 (a). To show the hexagonal symmetry usually the hexagonal form is shown including the third axis, $a_3$ is shown in the basal plane. Index “i” is related to $h$ and $k$ as $h+k = -i$. The reciprocals of the intercept of the crystal plane on $a_1$, $a_2$, $a_3$ and $c$ give the $h$, $k$, $i$, $l$ of that plane. The HCP structure gets its name as it is one of the 2 combinations possible for the spheres to be packed in space with maximum possible density and have a periodicity as shown in Fig. 6 (c). In HCP the second layer of atoms is stacked on the voids of the first layer and the third layer of atoms is stacked above the atoms in first layer (ABABABAB...) as shown in Fig. 6 (d).

1.6 Principles of electrolytic corrosion

Corrosion takes place as due an electrochemical reaction between the metal and its surroundings. Almost all corrosion types involve exchange of electronic charge in an electrolyte involving an anodic and a cathodic reaction. The anodic reaction remains of the form of the following eq. (4)

\[ M \rightarrow M^{n+} + n\varepsilon \] .................................................. \( 4 \).................................................. \( 4 \)

There are different types of corrosion some of which are described briefly in the following section. Uniform corrosion requires the metal to be metallurgically and compositionally unchanging and the electrolyte to be reachable to all its surface so that the removal of the metal becomes uniform all across the surface. Galvanic corrosion takes place when two metallurgically different metallic parts are coupled together with an electrolyte and one of them corrodes more than the other one. Crevice corrosion takes place due to the presence of an isolated area of metal created by a shielded volume acting as an anode and the rest of the metal acting as a cathode.
Pitting corrosion takes place due to confined attack on the passive film creating a self-service crevice. Environmentally induced cracking involves three subtypes namely stress corrosion cracking (SCC), corrosion fatigue cracking (CFC) and hydrogen induced cracking (HIC). SCC takes place with a static tensile stress mode with particular environmental situation like passive film under oxidizing condition. CFC takes place with cyclic stresses in corrosive environment while HIC, hydrogen diffuses through the lattice by the reaction (5) while producing hydrogen atoms during cathodic reactions.

\[ 2H^+ + 2e^- \rightarrow H_2 \] \hspace{2cm} (5)

Intergranular corrosion (IGC) involves preferential corrosion at the grain boundaries due to selective segregation or depletion of impurities.\(^{19}\)

Thermodynamics (\(E_{\text{corr}}\) or Corrosion potential) can predict the energy changes governing the spontaneity of an electrochemical reaction and if the corrosion is possible. But the rate at which the reaction will proceed can only be determined by the kinetics (\(I_{\text{corr}}\) or corrosion current). The free energy change of \(\Delta G\) can be associated with an equilibrium electrochemical potential \(E\) by the relationship given in the equation (6)

\[ \Delta G = -nFE \] \hspace{2cm} (6)

Where, \(n\) = number of electrons being exchanged, \(F\) = Faraday’s constant that is 96500 Coulombs per equivalent. The sum of the half-cell potentials namely \(e_a\) being anodic oxidation potential and \(e_c\) being cathodic reduction potential, \(E\) can be the given as \(e_a + e_c\). The case where reactants and products are in their standard state meaning their activity is unity, like in case of dilute of highly dissociated solutes, or in solid state, the half-cell potentials have the value of \(e^0_a\) and \(e^0_c\).
In the absence of unit activity, half-cell potentials can be calculated from Nernst equation by considering a following equation as general equation for half-cell reaction (7).

\[ aA + mH^+ + ne^- = bB + dH_2O \]  

The Nernst equation can be written as follows (8) \(^{19}\).

\[ e = e^0 + \frac{2.3RT}{nF} \log \left( \frac{A^a (H^{+m})}{B^b (H_2O)^d} \right) \]  

1.6.1 Corrosion of Magnesium

Mg is an attractive metal. It has low density, high strength to weight ratio but Mg alloys have poor corrosion resistance. Metals give away electrons while reacting with body fluids forming positive ions. Standard electrode potential provides a comparison of the relative ease with which this electron loss occurs from metals; more negative value corresponding to higher tendency to form metal ions than that of hydrogen which further corresponds to quicker degradation in aqueous solution. Mg has a standard potential of -2.37 V which makes it a really active metal. The corrosion is also pH dependent. Magnesium ion is stable in the solution till the pH value of 11 is reached after which Magnesium Hydroxide becomes stable causing passivation. Our human body has the pH of 7.4. It causes Mg to corrode in the body. Its reaction with the aqueous environment in our body causes it to oxidize and produce magnesium hydroxide with a release of hydrogen gas. The corrosion process is independent of the oxygen concentration. The overall reaction can be seen below –

\[ Mg + 2H_2O = Mg(OH)_2 + H_2 \] \[ \Delta G^* = -359 \text{ kJ/mol} \]  

The partial reactions may be seen below -

\[ Mg(s) = Mg^{2+} (aq) + 2e^- \text{ (Anodic)} \]  

15
2 H₂O\(_{(aq)}\) + 2e\(^-\) = H₂\(_{\text{g}}\) + 2OH\(^-\) (Cathodic) ................................................................. (11)

Mg\(^{2+}\)\(_{(aq)}\) + 2OH\(^-\) = Mg(OH)\(_{2}\) (Product formation) ................................................................. (12)

But when the chloride concentration in the surrounding environment goes beyond 30 mmol/l, Mg(OH)\(_{2}\) converts to magnesium chloride which is very soluble \(^{20,21}\). The in vivo chloride concentration is 150 mmol/l \(^{22}\).

1.7 Orientation dependent corrosion of magnesium

Very few papers have been published on corrosion behavior as a function of orientation of single crystal. They can be summarized as follows.

![Fig.7. Single crystal surfaces with different rotation angles. \(^{23}\)](image)

Shin et al have tried identifying the how the surface orientation affects the corrosion performance of magnesium single crystal by having single crystal surfaces with ten different rotation angles of the plane normal from [0001] direction to [10\(\bar{1}\)0] with the intervals of 10 degrees as seen in the

Fig.7. The specimens used were cut from the single crystal of pure magnesium grown using modified vertical Bridgman method. Graphite crucible was used and the furnace was lowered at
the speed of 5mm/h under inert environment. Laue back-reflection method was used to orient the crystals in the desired way and then they wire cut. They were polished using SC papers and annealed in an evacuated Pyrex tube to eliminate defects introduced while polishing. Then they were etched using methanol and nitric acid in the 2:1 ratio.

The potentiodynamic testing was performed on the cold mounted samples polished with 1000 SC papers. The tests were performed at 20 degree C in 3.5 wt% NaCl with distilled water. SCE and graphite were utilized as reference and counter electrodes. The samples were immersed for 1 hour for achieving steady open circuit potential. The scan rate was 0.166 mV/s. All planes displayed pitting & the pitting potential changed for every orientation. It first reduced from -1.57 V to -1.64 V from 0 degree to 40 degree rotation angle. After that it went up to -1.60 V when the rotation angle was increased to 90 degrees as seen in the Fig. 8 (b). The current density was also recorded as a function of time at the constant voltage of -1.57 V vs. SCE.

Fig. 8. (a) DC polarization curves of the Mg single crystals for every angle of rotation (b) Effect of rotation angle on the pitting potential of Mg single crystals in 3.5 wt% NaCl solution at 20 degree C. (c) Change in current as a function of time with applied potential of -1.57 V vs SCE.  

The change in the current density values indicate the onset and propagation of pits. When the film formed effectively inhibited the corrosion causing Cl⁻ ions in the solution, the current density did not increase as much and then plateaued when the film managed to control and reduce
the Cl− penetration as seen in Fig. 8 (c). Rotation angle of 0 degrees corresponding to (0001) plane had the highest pitting corrosion resistance 23.

Liu, Qiu et al studied the pure Mg specimens of size 12 mm X 16mm X 2 mm samples to observe the influence of orientation on the corrosion in 0.1 N HCl. The sample was submerged in the solution for 15 hr after initial polishing with 1200 grit SC paper, 6 and 0.5 micron diamond paste, rinsing with distilled water and light etching using a 3% Nital solution. Active corrosion took place with vigorous hydrogen evolution for the whole time. The neighboring grains had corroded dissimilarly to dissimilar depths. The grains were too large for the AFM working range, hence an innovative method was used to estimate the corrosion behavior through corrosion depth.

![Image](image_url)

**Fig.9. (a), (b) Differences in the depth caused by different grain corrosion rates, (c) Map of the orientation dependence with the corrosion resistance.** 17

The EBSD technique was used by the authors to get the orientation of each grain. The neighboring grains got corroded dissimilarly due to having dissimilar orientations and an arrow was marked for each neighboring pair from the grain which was corroded deeper to the shallower grain. Shallower depths meant it had a better corrosion resistant relatively. Such pairs were taken from different samples and same trend was observed in relative corrosion behavior. This qualitative sampling of many grains formed a map of the orientation dependence with the corrosion resistance as seen in the Fig.9. Area near the (0001) pole had the most arrowheads pointed towards
it indicating highest corrosion resistance as per the method developed to analyze. It was followed by (1120) orientation and then (0110) orientation.  

Fig. 10. (a), (b) Regions of the polycrystalline coupon chosen for the study, (c) Specially designed electrode for testing.  

Song and Xu studied a polycrystalline Mg sample. The coupon was cold mounted and mechanically polished using SC papers then oil based diamond suspensions having 9, 3 and 1 µm particle size. It was followed by the liquid polishing made of extremely fine colloidal silica.  

The metallographic photo of the Mg specimen Fig. 10 (a) shows the dark and bright regions of different textures and accordingly they were divided into B, C, D, E and G. Spots D and E (ϕ and φ) were selected for the electrochemical testing representing dark and bright regions. A special electrochemical cell was created using a 1 mm diameter plastic syringe in order to be able to measure activities of each grain as shown in Fig.10(c). Pt wire was the ref electrode with only the tip exposed and Pt mesh was the counter electrode. Mg coupon was submerged in 0.01 M NaCl and Mg(OH)₂ liquids. The sample was immersed for 5 minutes to stabilize OCP. Scan rate was 0.1 mv/s from -0.1 V to +0.1 V w.r.t OCP.
The polarization curve in Fig. 11 noticeably suggest that area D represented by $\phi$ is anodically more stable and more corrosion resistant as it’s OCP is about 60 mv higher in both cases. Fluctuation around the corrosion potential in case of NaCl solution suggests that severe corrosion may occur around this area as NaCl is more corrosive due to chloride ions. The EBSD analysis displays the dissimilar texture of the sample on the stereographic triangle corresponding to the different crystal axes of the grains was observed as shown in the Fig. 12. Grain D colored between red and purple is very close to (0001) and green colored grain E is nearly (1120) oriented.

![Polarization curves](image1)

Fig. 11. Polarization curves measured from areas D and E ($\phi$ and $\varphi$) as representatives of the dark and bright regions of the surface of the Mg coupon immersed in (a) Mg(OH)2 saturated solution and (b) 0.01 M NaCl solution, respectively.  

![EBSD map](image2)

Fig. 12. EBSD map of the studied area putting orientational information to the grains.
meaning close to a prismatic plane. This clearly shows that basal plane is much more corrosion resistant than prismatic or other planes in the solutions used.  

![Cyclic polarization curves for surfaces analyzed for corrosion behavior.](image)

McCall et al have tried studying the crystallographic pitting in Mg single crystal for the aqueous solution of 0.01 M NaCl and $10^{-4}$ M dichromate. (0001), (10̅10), (1120) surfaces were studied under open circuit and anodic polarization. Magnesium single crystal was acquired from Alfa Aesar and Laue back reflection method was used to determine surface orientation and a exchangeable arrangement was used to move it to EDM wire cut set up. With the help of a goniometer by rotating the crystal, patterns were obtained and indexed using a standard Greninger chart and stereographic projections were plotted for each pattern with the Wulff net. Stereographs and standard projections comparison for each surface were within the accuracy of 1 to 2°. They were then prepared for electrochemical testing. Surface preparation consisted stepwise polishing and final polishing with colloidal silica oxide. The residue was eliminated by sonicating in acetone for 2 min and rinsing with Millipore water and drying with compressed air. Platinum mesh was used as the counter electrode, SCE as the reference and the OCP was measured for changing times 30 min to 3 hours. The scan rate was 0.1 mV/s and the beginning of steady pitting was observed
with the severe increase in current and current hysteresis upon direction reversal in the cathodic way. The pitting and repassivation potentials were recorded for all three surfaces as seen in Table 2. For (10\(\bar{1}\)0) and (11\(\bar{2}\)0) surfaces the pitting was commenced only marginally more electropositive than their OCP’s but for the (0001) surface it was similar to its OCP which was more electronegative related to those for the prismatic surfaces pitting potentials. The polarization curves can be seen in the Fig. 13. The effect of Cl\(^-\) concentration was also observed by varying it between 0.01 to 0.1 M and it did not affect the \(E_{\text{pit}}\) or \(E_{\text{repassivation}}\) values. Effect of solution pH was also observed in absence of sodium dichromate, Mg exhibited extended passive region and no pitting was observed for concentration of chloride ion as high as 0.6 M \(^{25}\).

Table 2 Average Pitting and repassivation potentials for Mg single crystal orientations in 0.01 M NaCl and 0.0001 M of sodium dichromate \(^{25}\)

<table>
<thead>
<tr>
<th>Mg (hkil)</th>
<th>Pitting Potential vs SCE</th>
<th>Repassivation Potential vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>-1.45 ± 0.062</td>
<td>-1.551 ± 0.019</td>
</tr>
<tr>
<td>(10(\bar{1})0)</td>
<td>-1.424 ± 0.008</td>
<td>-1.53 ± 0.011</td>
</tr>
<tr>
<td>(11(\bar{2})0)</td>
<td>-1.4 ± 0.022</td>
<td>-1.53 ± 0.014</td>
</tr>
</tbody>
</table>

1.8 High ductility exhibiting Mg single crystal

Mechanical properties in terms of ductility shown by Mg single crystal are significantly different than those shown by polycrystalline Mg. At elevated temperatures, Mg single crystals have shown very large elongations (over 300%) in nominal strain. The ductility is strongly dependent on crystal orientation. \(^{26}\) A single crystal sample that was tensile tested at 573 K showed extremely high ductility where activation of single slip was observed where the activated slip plane was found to be prismatic. Uniform elongation in the gage was observed without necking as seen in Fig.14. \(^{27}\) Polycrystalline Mg on the other hand shows low ductility of around 5-20% at room
temperature. At room temperature, deformation takes place by slip on the basal plane in direction \( <11\overline{2}0> \). Such high ductility at particular orientations increases formability as well as impact resistance of the material improving the implant response to shock loading situations.

![Sample of Mg single crystal after and before deformation at 573 K to \( \epsilon = 1.8 \).](image)

**Fig. 14. Sample of Mg single crystal after and before deformation at 573 K to \( \epsilon = 1.8 \).**

The focus of this thesis remains on the effect of single crystallinity on corrosion behavior of Mg.

1.9 **Surface treatments used for corrosion resistance improvement**

In spite of its numerous advantages there are some remaining difficulties in controlling the rate of dissolution of Mg in human body to match this daily value, over extended periods of several weeks or months. Mg is a highly active metal and corrodes quite fast, in fact it has been traditionally used as a sacrificial anode for this reason. Hence, controlling corrosion rate of Mg is challenging. Several Mg alloying have been developed in this direction, that have better corrosion behavior, but addition of other alloying elements often raises concerns regarding their biocompatibility and toxicity in the body. Hence, it is always preferable if pure Mg can be used while achieving good corrosion control. Corrosion of polycrystalline materials tends to be higher
at grain boundaries and surfaces as they represent high energy regions. Hence, elimination of grain boundaries should reduce the corrosion potential of even unalloyed Mg. Accordingly, high purity (99.9%) Mg single crystals were grown in our lab- Nanoworld at UC using modified Bridgman-Stockbarger technique in an inert Ar atmosphere. To further modify the corrosion behavior and delay the dissolution of Mg, 3 different surface treatments were done on the discs namely DC anodization, micro-arc oxidation(MAO) and chemical etching. Coatings that offer some corrosion resistance can delay the initiation of the biodegradation process which is very important when it comes to a biodegradable implant. Ideally the film forms should also offer good wear resistance as it shouldn’t be damaged easily while the implantation occurs.

1.9.1 Anodization

Anodization involves an electrolytic oxidation process where the metal surface becomes an anode and reacts with the electrolyte forming a thick oxide. The anodization improves the corrosion properties of the substrate, increases the oxide thickness, and improves adhesion properties to the paint. The anodization of Mg can be done by passing either direct current (DC) or an alternating current (AC) through the electrolyte of choice. Hydrogen is released at the cathode and Mg being the anode gets oxidized. Some of the influencing factors can be the electrolyte composition, voltage/ current density being applied, substrate composition. The electric field acts as a driving force for transporting the cations and anions in the electrolyte.

1.9.2 Micro arc oxidation

Micro arc oxidation (MAO) is also known as plasma electrolytic oxidation (PEO). It passivates the substrate by increasing the thickness of the oxide layer on its surface. It is an anodization method that takes place at the voltages more than the dielectric breakdown voltage of
the oxide layer already present on the metal substrate as after reaching a certain thickness, the barrier film acts as a resistor to the current as shown in Fig.15. Owing to the porous nature of the film, parts offering less resistance causes sparks discharge. The local temperatures are reached up to 20000 K and sparking is observed causing partial melting of the surface forming a ceramic oxide coating eventually. MAO coatings have several superior properties like high hardness, good wear resistance, moderate corrosion resistance, better thermal stability and dielectric properties. It increases the adhesion of organic or polymeric top-coats.\textsuperscript{31,34,35} The formation of MAO coatings involve several electro-chemical, plasma chemical and thermal chemical reactions. They are usually prepared with constant current density and measurements of cell voltage vs. time gives the presence of different stages of the process. The prime stages of MAO coatings can be stated as a) formation of anodic barrier layer, b) dielectric breakdown of barrier layer, c) localized increase in film thickness at sparking locations, d) pore formation in the oxide, e) sustained growth of the oxide film, f) formation of larger sparks.\textsuperscript{35}

![Fig.15. Layers observed in the MAO coating.](image)

### 1.9.3 Chemical Etching

Etching reveals structural details by attacking the metal surface preferentially. Sample surface has to be prepared initially to be flat and free of scratches. Mostly used etching technique is solution etching and that can be classified as follows-
1.9.3.1 Acid and Basic Reagents – Immersion, Swabbing

Sample is held in the etching solution with a gentle agitation to avoid air bubbles sticking on the surface and for continuous supply of the reagent. For swabbing, surface is gently swabbed with the soft cotton dipped in etchant.

1.9.3.2 Electrolytic – Direct Current, Alternating Current.

The specimen is anode, electrolyte is the etchant and cathode is a material that does not interfere by not dissolving in the etchant. 36
2 Experimental Details - Materials, Methodology and Characterization for Pure Mg single crystal growth

For the magnesium single crystal growth, modified vertical Bridgman-Stockbarger method was used. In the year 1931, P.W. Bridgman was issued a patent titled “Crystals and their manufacture”\textsuperscript{37}. In 1939, D. C. Stockbarger was issued a patent titled “Method for the manufacture of crystalline bodies”\textsuperscript{38}. The furnace used was designed by First Nano – CVD equipment corp. by modifying the processes described by the late Dr. Bridgman and Dr. Stockbarger\textsuperscript{39}.

2.1 Raw Material

The raw material was purchased from Alfa Aesar. Magnesium slugs of 1”, 2” length of 99.95% purity were used as shown in Fig.16. They were used for growing pure Mg single crystals of varying lengths. Different crucible designs were used for different dimension.

Fig.16. Different sizes of the raw material (pure Mg) used for crystal growth.
2.2 Crucible choices

Graphite was used as the crucible material as it does not react with Magnesium at elevated temperatures and it is easy to process and form a smooth surfaced cylindrical hole with a tip ideal for single crystal growth. The different crucible designs used can be seen as follows in the Fig.17. The graphite crucible sat inside the stainless steel crucible holder which had a hollow shape machined inside it so that the graphite crucible could fit exactly inside it. Crucible holder was designed with a lid on top with a small hole so that evaporation of Magnesium would be minimized.

Fig.17. Different crucibles and the stainless steel crucible holder used for Mg crystal growth.
2.3 Growth system

A specially designed single crystal grower J5409 (Fig. 18) was used that worked on the directional solidification principle was used to grow the crystals. It was made by First Nano CVD Equipment Corporation. It consists of 2 zones having precise temperature controls. The furnace also provides linear motion as well as rotational motion.

Fig. 18. Single crystal grower J5409.

Fig.19. The user interface on the crystal grower.
2.4 Process details

Temperature - The growth process was decided to be carried out at 760 degree C after several trials of the furnace runs. The melting point of Mg is 650 degree C. The high temperature ensured complete melting of the Mg slugs being used.

Soaking time – This was an important parameter. Different soaking times were tried during the process development ranging from 2 hours to 14 hours (2, 4, 6, 8, 14 hrs). 2 and 4 hours soaking times were not favorable hence more time was spent running experiments with the soaking times of 6, 8 and 14 hours. After several runs, 14 hours soaking time was found to be the most favorable and yielded maximum success.

Crucible movement – Extremely slow movement rates are usually recommended to ensure highest quality of the crystal. In order to strike a balance between quality and practicality. 30 mm/ hour movement rate was used. Due to this movement, the crucible undergoes a temperature gradient allowing directional solidification.

Pressure – Tube pressure was maintained at 720 Torr in inert Argon atmosphere as explained in section 2.4.

More details on the growth process are provided step by step in the Appendix section.
2.5 Electro Discharge Machining (EDM) wire cut method for slicing the crystals

The EDM wire cut machine and the cutting chamber can be seen in the Fig. 20. It was used in order to cause minimum damage to the crystals caused due to external forces.

Fig. 20. EDM wire cut machine and cutting chamber.

2.6 Validation methods to test for single crystallinity and purity

For validating single crystallinity of a grown crystal, conventionally Laue diffraction technique is used. But due to unavailability of the Laue diffractometer, we had to use other complimentary methods to prove the single crystallinity of the sample.

2.6.1 X-ray Diffraction methods

X-ray diffraction plays an important role in characterizing the single crystal.

2.6.1.1 X-ray Generation

X-rays are electromagnetic radiation having wavelength much shorter than the visible light, occupying the region between ultraviolet rays and gamma rays on the complete spectrum. The ones used for diffraction have wavelengths between 0.5 Å to 2.5 Å. X-ray production takes place when an electrically charged particle having enough kinetic energy, slows down speedily. These charged particles, which are electrons, in this case come from the x-ray tube having and electron
source and two metal electrodes with a very high voltage retained between them. It pulls the electrons to the anode which is a target causing them to strike it. X-rays get generated at the point of impact but most of the kinetic energy gets converted into heat and only less than 1% gets converted to the X-rays. The rays emitted from the target have a combination of different wavelengths of different intensity which depends on the tube voltage and the target being used. The radiation consisting of multiple wavelengths is called polychromatic, continuous, white or Bremsstrahlung radiation. When the voltage of the tube is raised beyond a certain critical value, which is dependent upon the target metal, a sharp maxima appears at certain wavelengths, on the intensity vs wavelength curve, forming a characteristic spectrum of the target metal. It’s origin lies in the target material. If the impacting electron on the metal has enough energy, it knocks out an electron from the K shell to bring the atom into an excited state creating a vacancy, which gets filled by one of the outer shell electrons falling into it and emitting energy in the process. This energy has a definite wavelength and called characteristic K radiation. Depending on what shell electron fills the radiation it can be called Kα or Kβ, if it is being filled by the L or M shell electrons as seen in the Fig.21.

![Fig.21. X-ray emission process.](image-url)
2.6.1.2  Bragg’s Law

Diffraction occurs due to the phase relations between two or more waves. Two important points worth mentioning are: the difference in the path length of the waves leads to the phase difference and change in phase causes change in amplitude. Two rays remain in phase if the path difference is zero or when it differs by the whole number multiple of wavelength. Path length difference occurs when a crystal diffracts X-rays. Fig. 22 shows how atoms in a crystal are arranged in a set of planes, parallel to each other and normal to the plane of paper with a certain distance apart from each other say “d”. If it is assumed that a monochromatic X-ray beam falls on the crystal at an angle Θ (Bragg Angle) which is an angle between the incident beam and the crystal plane. Diffracted beam will consist of many number of scattered rays, reinforcing each other, without interacting with the atom. If we look at rays 1 and 2, they are scattered by the atoms K and L. Only the diffracted beam amongst all the scattered beams is shown in the Fig. 22. KM is perpendicular to 2L and KN to L2’. For the rays 1K1’ and 2L2’, the path difference can be given as follows (12)

\[ ML + LN = d \sin \Theta + d \sin \Theta = 2d \sin \Theta \] ............................ (12)

If this path difference is in the whole multiples (n) of the incident wavelength (λ) then the scattered rays 1’ and 2’ will be completely in phase which is what the Bragg’s law states as shown in the eq (13). It was formulated by W.L. Bragg and it is a must condition for the diffraction to happen.

\[ n\lambda = 2d \sin \Theta \] ............................ (13)
As the Bragg’s law puts very strict rules on \( \lambda \) and \( \Theta \) for any crystal, with monochromatic beam of X-rays, a random placement of single crystal will not produce diffracting conditions for the beam. One can either vary wavelength (\( \lambda \)) or Bragg angle (\( \Theta \)).

### 2.6.1.3 Powder diffraction

The crystal is reduced to a fine powder or already in the form of microscopic grains and a beam consisting of a fixed wavelength is used where each particle is a small crystal or assembly of small crystals, which are oriented randomly w.r.t. the beam. The powder is basically a single crystal, rotated about all possible axes such that every set of lattice planes will be in a diffracting condition. Here \( \lambda \) is fixed and \( \Theta \) is varied. X-ray scans were carried out at different locations along the as grown crystals without changing the orientation using a Panalytical Xpert XRD system at 45KV, 40mA using a Cu K\( \alpha \) radiation with 1° source slit to characterize crystal quality and confirm single crystallinity.
- Custom stage machining

In order to accommodate bigger samples on the machine a new stage had to be fabricated from aluminum on site. The original stage that came with the machine was too small for the samples. The final product can be seen as follows in Fig.23. Under Doug Hurd’s expertise this stage was manufactured at the University of Cincinnati machine shop.

![Custom made stage](image)

**Fig.23. Custom made stage for accommodating longer single crystals.**

2.6.1.4 Laue Diffraction

Here the Θ is fixed and the λ varies. It was first used by Von Laue. White radiation involving the continuous spectrum falls on the crystal making the Θ fixed for all set of planes, which then selectively diffracts those λ’s satisfying the Bragg’s law. Based upon the source, crystal and film (now camera) position, transmission Laue and back-reflection Laue are the two variants of the Laue method (Fig.24). Diffracted beams form a pattern or arrangement of spots which lie on definite curves (ellipses or hyperbolas). All the spots lying on the same curve are from the planes from one zone as all those reflections lie on the surface of an imaginary cone having it’s axis as
the zone axis, with one side of the cone being tangent to the transmitted beam (Fig. 25). When $\phi$ becomes more than $45^\circ$, back-reflection pattern is used.

![Diagram of Laue spots](image)

**Fig. 24.** (a) Transmission Laue method, (b) Back-reflection Laue method. 

14 hour soaked single crystal Mg rod and a polycrystalline Mg rod was (raw material control) were studied using the back reflection Laue method using the Multiwire Laue XRD system at Argonne National Laboratory. The scans were made at the top, middle and bottom of the single crystal along the length at 20 kV voltage and 15 mA current.
2.6.2 Pole Figure analysis

Fig. 26. (a) Polishing set up for pole figure sample preparation, (b) Bruker AXS D8 Discover XRD machine.

Inclination of the normal to a particular plane in a crystal with respect to a respective plane can represent orientation of a plane in the crystal Fig.27 (b). If a crystal is at the center of an imaginary sphere then the points at which the plane normals intersect that sphere would be called poles. A pole figure basically is a stereographic projection having an orientation with reference to the crystal showing varying pole density along with the pole orientation for the planes of interest in the crystal 16.

Pole figure analysis of the single crystals discs were done at Dr. Sergey’s lab at NCAT with the help of Dr. Sergey and Dr. Svitlana. It was done to get more information about the orientation of the sample. The sample preparation involved extensive steps as shown in the Fig.26 (a). The samples were cut using the EDM wire cut machine into the disc shapes and polished using the diamond papers with isopropanol with 9 micron, 6 micron, 1 micron and 0.3 micron grit sizes. After polishing, they were mounted on the stage in Bruker AXS Discover D8 XRD system as shown in Fig.27 (a). The stage could rotate in chi and phi angles in order to scan the whole sample.
and probe the planes. The Mg lattice parameters and planes of interest were specified as input. The XRD pole figures of the 14 hour soaked Mg crystal discs were obtained.

![Bruker axs D8 discover chamber used for pole figure analysis](image)

**Fig. 27.** (a) Bruker axs D8 discover chamber used for pole figure analysis (b) Crystal plane with respect to the sample plane.

### 2.6.3 Metallography

Metallography is a great way to control the quality of the product through studying the microstructure. Proper surface preparation of the specimen is needed for correct interpretation. It should be flat, scratch-free. The stages of preparation include the following steps some of which are shown in the Fig. 28 -

- **Sectioning** – Removing the sample of interest from the main piece. In this case, depending on the end goal such as observing the grain boundaries present across the length or corrosion testing, the samples of the crystal were either directly used or sectioned using EDM wire cut machining.
- Mounting – Embedding the samples in the polymeric medium in order to be able to handle it easily, to prevent it from breaking and preserve the edges. Select samples were embedded in epoxy resin (Buehler Inc.) and cured at room temperature.

- Fine Grinding – Removing the deformed surface caused by sectioning and the polymer material on the surface.

- Rough Polishing – Limiting the deformation done by fine grinding step. 600 grit SC carbide paper was used for this step.

- Final Polishing – Removing the deformation produced by rough polishing. The deformation produced by this stage is minimal and removable by etching. 1200 grit SC paper was used for this step. This was followed by final polishing for 15-30 minutes on a lapping cloth under oil to get a mirror finish using 6, 1 and 0.25 micron diamond paste. Samples were then etched with nitric acid based etchant to reveal if any grain boundaries were present.

- Ultrasonic cleaning – It is an effective way to reduce the embedded SC particles and the dirt during polishing. Disc samples were kept in the acoustically transparent glass beaker in the sonicator and the cleaning solution used was ethanol after each step.

![Sample polishing stages representative images.](image)

**Fig. 28. Sample polishing stages representative images.**
2.6.4 Micro CT

Micro CT scans were done at Dr. Collins lab in NCAT on single as well as polycrystal Magnesium. The machine used was the phoenix nanotom® m nanoCT® system by GE. A general plan consisting of an X-ray source, a specimen of interest, X-ray to electronic signal conversion and a rotating device or a rotating scanner is used. It is useful as it images a 3D specimen nondestructively\textsuperscript{40}.

2.6.5 Inductively Coupled Plasma Mass Spectroscopy (ICPMS)

The yearly business for ICP-MS is less than 7\% of the overall atomic spectroscopy market even though ICP-MS offers much more than other techniques. Price and the requirement of a highly skilled individual to operate it could be the reasons. Dr. Pablo Campo-Moreno helped us carry out the testing and analysis.

2.6.5.1 Background

The way it works is liquid samples are introduced using a spray chamber and a nebulizer which turn the samples into an aerosol. A high temperature plasma discharge is used and the atomized sample gets injected to the base of the plasma through the sample injector. Plasma is produced by passing a strong magnetic field through the copper coil on a tangential gas flow through the concentric quartz tubes. The sample loses liquid as it goes through the various heat zones of the plasma torch. The sample turns from the liquid aerosol into the gas and when it reaches the analytical zone of the plasma, it is in the form of excited atoms and ions comprising of the total elemental composition of the original injected sample. The temperature at that zone is 6000 to 7000 K. The energy of plasma removes the electron from the outermost orbital of an atom to generate an ion. The transportation and detection of these ions make the ultra-trace detection of
elements possible. Every element has its isotopes meaning they have same atomic number but not the same atomic masses and they generate ions with differing masses which show up at different places on the spectral scan. The analyzer allows analyte ions of a specific mass to charge (m/z) ratio through towards the detector and filters out unwanted non-analyte, interfering and matrix components. 41

2.6.5.2 Experimental details

Agilent 7700 SERIES instrument was used for measurements shown in Fig.29. Wire cut EDM technique was used to get the sections from three different locations Top, middle and bottom as shown in the Fig.30. Those were dissolved separately in 25 ml volume ultra-pure trace metal grade nitric acid. The weights were precisely measured using a highly sensitive weighing balance. Acid digestion bombs were used to contain the mixture which were made of teflon. After all 3 magnesium pieces were completely digested, 3 dilutions of varying concentrations were prepared for every mixture namely 10%, 1%, 0.1%.
Fig. 30. Different locations of the crystal being analyzed to find elemental distribution.
3 Surface treatments

Magnesium has acquired more interest of the researchers recently due to the several advantages it has to offer over the conventionally used metallic and polymeric implant materials. The advantages such as more compatible mechanical properties with that of the bone, its non-toxic nature, ability of the body to excrete it harmlessly as well as its bone regeneration capacity are some of them which have been already discussed before. In spite of having all these advantages, the high dissolution rate of Mg still remains one of the big issues faced. By using its single crystalline form we hope to better the corrosion resistance of the material. But to provide additional protection, different surface treatments were tried and tested. They include DC anodization, micro arc oxidation (MAO) and chemical etching. Preliminary corrosion behavior comparison was done with the help of in vitro and in vivo tests. For all the surface treatments, identical circular discs with flat plane orientation close to [0001] were cut using wire electro-discharge machine (EDM) from the as-grown single crystal ingots.

3.1 DC Anodization

The pure polycrystalline Mg from Alfa Aeser (6.35 mm dia. rod), and single crystal Mg (6.5 mm dia. rod) were cut in the form of discs of 2 mm thickness using wire EDM. They were then connected to the copper wires using a conductive silver epoxy. Electrical continuity was tested. Then the samples were embedded in epoxy resin (Buehler Inc.). The samples were polished after the curing of epoxy with progressively finer SiC paper (Buehler Inc.) up to 1200 grit size. The anodizing experiments were done in a 200 mL solution having 1 M NaOH and 0.1 M Na₂SiO₃ with the remaining distilled water. The power supply was purchased from Circuit Specialist Inc. Anodizing was carried out at 80 V on pure Mg single and poly crystals for 2 hours and 6 hours. To maintain the uniform temperature and distribution of chemicals the bath was slowly stirred.
with a magnetic stirrer. The anodized samples were then left out for air drying. Test setup is shown in Fig. 31.

![Test setup](image)

**Fig. 31. DC anodization set-up.**

### 3.2 Micro-arc oxidation

For this surface treatment the pure Mg single crystals grown in our lab were used as the substrate. Samples of the same were cut using EDM wire cut machine into discs of 6.5mm diameter X 2 mm thickness. These experiments were done at Dr. Yun’s lab at NCA&T with the help of Dr. Leon. They were then connected with a copper wire and conducting silver paste in one side and then mounted in epoxy. It was then polished by silicon carbide paper successively up to 1200 grit and then subjected to MAO. These samples were used for polarization and cross section studies. An aqueous solution of 10 g/L Na₂SiO₃, 2g/L NaOH, 6g/L KF, 5g/L Na₂HPO₄ was used as an electrolyte. A steel rod was used as a cathode. A constant current of 100 mA was provided by EAC-S 1-phase AC power source (ET System® Electronic system GmbH). The frequency was
250 Hz with avg. voltage of 86 V and RMS voltage 146 V. The MAO was done for different times namely 5, 7 and 10 minutes at room temperature. Sparks were observed on the surface as seen in the Fig. 32 (b) indicative of the dielectric breakdown Coatings done for all 3 different times had the same greyish surface appearance through the microscope as seen in Fig. 32 (a).

3.3 Chemical etching

Samples from the polycrystalline Mg and from the grown pure Mg single crystal were cut using EDM wire cut machine into discs of 6.5 mm diameter X 2 mm thickness. The discs were successively hand polished using the 600 grit and 1200 grit SC paper in IPA. After every pass, the individual discs were sonicated in ethanol for 2 minutes and then air dried. After that they were chemical etched for 10 seconds. The chemical etchant used was made of Nitric acid, Methanol and Ethanol (NME) in the ratio 1:2:1. After etching the samples were immediately rinsed using ethanol and air dried. The samples were etched mounted or unmounted depending on the experiment that they were followed by.
3.4  Corrosion Behavior Analysis

*In vitro* as well as *in vivo* analysis was done on the samples with and without surface treatments.

3.4.1  *In Vitro Testing*

Weight loss measurements along with potentiodynamic DC polarization measurements were made.

3.4.1.1  Immersion testing in DMEM + HEPES

Polycrystalline Mg crystals (approx. 6.35 mm dia X 1.8 thick), polished and chemically etched single crystal (avg 6.5 mm dia X 1.8 thick) and MAO coated single crystal (approx. 6.5 mm dia X 1.8 thick) samples in the form of discs were tested in buffered solution of Dulbecco's modified eagle's medium (DMEM) from Life Technologies (Item: 12430047) for their weight loss over 72 hours. pH was monitored every few hours. The experiment was conducted at room temperature. The samples were cleaned using chromate solution after removal. Optical images of the samples before immersion, after removal and after cleaning to remove the corrosion product were taken.

3.4.1.2  Potentiodynamic polarization tests

DC polarization studies were conducted using a Gamry computer controlled corrosion test system to study the corrosion behavior of the samples using a flat cell.

For DC anodized samples, to simulate corrosion in body fluids, 0.15 M NaCl aqueous solution and Hank’s solution were used as corrosive environments at room temperature for the tests. Hank’s solution was purchased from Thermo Scientific - Hyclone laboratories. An Ag/AgCl
electrode was used as the reference electrode and a platinum mesh was used as the counter electrode. A potential window of Eocp ± 0.25 V was applied where Eocp is the open circuit potential. The scan rate was kept at 1 mV/s. The samples were immersed in the solution for the duration of 5 minutes before testing.

For MAO coated samples, the solution used was Hank’s solution purchased from the same source, at room temperature. Saturated Calomel electrode was used as reference electrode and platinum mesh was used as a counter electrode. Before starting the test the open circuit potential was monitored for 1200 seconds. The scan rate was kept at 1 mV/s.

DMEM+HEPES solution at room temperature was used to study the corrosion behavior of the etched crystals. The samples used were connected with a copper wire and conducting silver paste in one side and then mounted in epoxy (EpoKwick® Epoxy System Buehler Inc.). Mounted samples were divided into two groups namely polished till 1200 grit by SC papers and polished till 1200 grit by SC papers + chemically etched for 10 seconds by the NME etchant. The samples were immersed in the DMEM+HEPES for 20 minutes. The open circuit potential (E_{ocp}) data was recorded with time. Saturated calomel electrode (SCE) was used as the reference electrode and platinum mesh was used as a counter electrode. The scan rate of 1 mV/s.

3.4.2 *In vivo testing*

For biomedical applications of biodegradable materials, one of the most important questions to be addressed is the corrosion behavior of the materials *in vivo* and the possible toxicity of the materials to the host. Hence, a subcutaneous mice implant model was used for this study. Mg pellets were implanted in subcutis that could be easily accessed, monitored and measured. Gas bubble generated in the subcutis will form a bulge under the skin, and can be easily observed and
measured with calipers. This experiment was performed at Dr. Dong’s lab with the help of his research group at the Vontz Center for Molecular Studies, University of Cincinnati.

**Implantation:** The Mg pellets having around 6.5 mm diameter x 2 mm thickness, were weighed, rinsed with PBS and sterilized under UV radiation. Mice were anesthetized, surgically prepped, given pre-emptive analgesic prior to the implantation. An incision of 5 mm was created on right side of the back and the pellet was inserted subcutaneously. The skin wound was closed in one layer with wound clips. 2 sets of samples were implanted containing following samples (Fig. 33)

*Set 1*(Polished till 1200 grit by SiC papers) Polycrystalline Mg and single crystal 14 hour soaked

*Set 2*(Polished till 1200 grit by SiC papers and then Etched with nitric acid + ethanol + methanol mixture for 10 seconds) Polycrystalline Mg, and single crystal 14 hour soaked.

![Fig. 33. Optical and X-ray images of the mice having implanted samples of (a) Polycrystalline Mg Unetched and Etched (b) Pure Mg Single Crystal Unetched and Etched.](image-url)
3.5 Film Characteristics and Surface Analysis

DC Anodization, MAO and Chemical etching formed films on the Mg single crystal surface exhibiting different properties. In order to evaluate them in a better manner the following testing was done.

3.5.1 Optical Microscopy, Scanning electron microscopy (SEM) and Energy dispersive spectrometry (EDS)

Optical microscopy is an important exploratory techniques that is easy to use. Because of the low cost of the instrument compared to the other microscopes such as SEM, it is a technique of choice where higher magnifications are not actually required to get the necessary surface information.

SEM provides information about topographical features, morphology, compositional difference, crystal orientation with secondary and backscattered electrons making it a necessary technique to analyze material properties.

For DC anodization, SEM and optical microscope imaging of pre- and post-tested samples by DC Polarization was conducted using a Hitachi TM3000 SEM operating at 15 KV and a Keyence VHX-5000 digital microscope.

After MAO coating of the samples SEM images of all sample surfaces and cross sections were obtained using Philips FEI XL30 ESEM with EDS. A 3 point EDS elemental analysis was performed and Mg, Si, O, P, K, F, Na were recorded.

After chemical etching the single crystal discs for 10 seconds using the nitric acid based etchant, the samples were imaged under the backscatter mode.
3.5.2 Atomic Force Microscopy (AFM)

For the AFM measurements, Veeco Dimension 3100 atomic force microscope was used. The surface roughness parameters were calculated using the Nanoscope Analysis software. According to the AFM measurements, 1200 grit polished sample shows the highest average roughness followed by 10 seconds etched and 30 seconds etched samples. The area scanned was 105 micron X 105 micron. The tip used was Ultrasharp silicon cantilever NSC 16/50. The measurements were done under the tapping mode.

3.5.3 X-ray Photoelectron Spectroscopy (XPS)

In order to understand the compositional characteristics of the protective film formed after etching of pure Mg single crystals, XPS depth profile analysis was carried out. Survey spectra before and after depth profiling were recorded along with the high resolution peak studies on the same position. Sputtered crater dimensions created for depth profiling were 2mm X 4mm. The pure Mg single crystal samples with different surface conditions were examined in K-Alpha™+ XPS System by Thermo Scientific brand of Thermo Fisher Scientific. The XPS experimentation was done by RJ LEE group. The approximate sputtering rates were determined by using the trial sample for each surface condition. Argon ion sputter rates were calibrated using 1000A SiO₂ standard on a silicon substrate. The disc shaped samples made using EDM wire cut machine had the diameter of 6.5 mm and the thickness of 1.8 mm each. Three different surface conditions for the discs were subjected to XPS studies namely: surface polished till 1200 grit SC paper, surface polished till 1200 grit and etched using NME etchant for 10 seconds, surface polished till 1200 grit and etched using NME etchant for 30 seconds.
4 Results and Discussion

The results of the research that was described in the previous sections have been described in this section.

4.1 Crystal growth and characterization

The following section talks about the progress in Mg crystal grown using modified vertical Bridgman-Stockbarger Technique at Nanoworld Labs. Results obtained from the steps taken for the crystal characterization have also been discussed\textsuperscript{42}.

4.1.1 Solidified Crystal from the melt

The evolution in the size of the solid grown can be seen below Fig. 34 using pure Mg raw material in different sizes. Different raw materials gave different crystals. The 1” and 2” slugs resulted in the best quality crystals. After solidification, the crystals were tested using different validation methods as discussed in the section 2.

Fig. 34. Evolution of single crystal growth.\textsuperscript{42}
4.1.2 Characterization of the crystallinity

Different complimentary techniques such as X-ray powder diffraction, pole figure analysis, Laue diffraction and Metallography were used to verify the single crystallinity of the solidified crystals.

4.1.2.1 X-ray Diffraction (XRD)

![XRD diffractogram obtained from the single crystal Mg.](image1)

**Fig. 35.** XRD diffractogram obtained from the single crystal Mg.

![XRD diffractogram obtained from the polycrystalline Mg.](image2)

**Fig. 36.** XRD diffractogram obtained from the polycrystalline Mg.

XRD scans done on the entire surface of the cylindrical crystal using the method described in the section 2.6.1 gave result as shown in Fig.35. The peaks were persistent at the same 2θ across the sample lengthwise, which definitely is an indication of the same orientation, existing throughout the sample. Fig.35 is just a representative diffractogram amongst the many that were
recorded for different crystals. XRD scan carried out on the polycrystalline polished Mg sample from 15 to 120 degrees of 2Θ showed the allowed reflections expected from HCP lattice as shown in Fig. 36.

4.1.2.2 Pole Figure Analysis

The XRD pole figures obtained for the polished disc using the procedure described in the section 2.6.2 can be seen in the Fig.37. The number of spots for each set of planes depends on the

Fig.37. Pole figures obtained for the polished discs of 14 hour soaked Mg single crystal.
plane multiplicity and the spots obtained are in accordance with the multiplicities expected for the planes shown in the figure which again is a clear indication of the fact that the sample tested was a single crystal.

4.1.2.3 Laue Diffraction

As discussed in 2.6.1.4 Laue back-reflection method was used to scan the single and polycrystalline Mg samples. The 14 hour soaked single crystal resulted in distinct spots which remained consistent along the length of the crystal indicating the presence of single crystallinity as seen in Fig. 38. Polycrystalline sample resulted in a diffused pattern due to the presence of several randomly oriented grains as seen in Fig. 39.

![Laue XRD patterns](image)

**Fig. 38.** Laue XRD patterns for 14 hour soaked Mg crystal obtained at (a) Top, (b) Center and (c) Bottom of the rod. The spots are identical for the scans obtained for the top, bottom and center regions. (Courtesy: Dr. Stephan Rosenkranz, Argonne National Laboratory)
Fig. 39. (a) Laue XRD pattern for polycrystalline Mg rod shown in (b). The patterns is diffused and in clear contrast with those obtained for the single crystal rods. (Courtesy: Dr. Stephan Rosenkranz, Argonne National Laboratory)

4.1.2.4 Metallography

Most single crystals do not show grain boundaries. Some crystal grown for lower soak durations did show small grains around the rod periphery and were not used for this study. Following are some of the initial crystals that were produced using magnesium slugs of 1” length as shown in Fig. 40.

Fig. 40. Polished and etched crystals for metallography.
4.1.2.5 MicroCT

As there is hardly any difference between the density of polycrystalline and single crystal Mg, micro CT would not give any grain boundary information. But as it can differentiate between the voids, cracks, different phases, it still indicates according to the images obtained for the 14 hour soaked 2” long crystal (Fig. 41) that there was an ideal melting of the slug to form the single crystal without any shrinkage cavities. The visual anomaly is due to the handling of the sample as it is on the external surface.

Fig.41. Micro CT images of (a) The 2” long single crystal (b) The circular cross section.
The raw material which was used for the growth of the single crystal is 99.95% pure. The certificate of analysis provided by Alfa Aesar contains the following information about the impurities – Aluminum 2 ppm, Manganese 11 ppm, Nickel 3 ppm, Copper 1 ppm, Iron 10 ppm, Silicon 17 ppm. The following Fig. 42 contains the trend lines for Al, Mn, Ni and Cu with the data points shown in Table 3. As there were some problems with the Si and Fe standards being used for the experiment for calibration, the correct data was not obtained for Si and Fe. 1 % and 0.1% dilutions did not show all the trace elements present due to low concentration. Only 10% dilution could give interpretable values hence only that graph has been plotted.

**Table 3 Elemental distribution calculated using ICPMS**

<table>
<thead>
<tr>
<th>Position</th>
<th>Weights in mg</th>
<th>% Al</th>
<th>% Mn</th>
<th>% Ni</th>
<th>% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>118.672</td>
<td>0.00204</td>
<td>0.003726</td>
<td>0.000658</td>
<td>0.006229</td>
</tr>
<tr>
<td>Middle</td>
<td>232.964</td>
<td>0.001415</td>
<td>0.003871</td>
<td>0.000378</td>
<td>0.002637</td>
</tr>
<tr>
<td>Bottom</td>
<td>182.132</td>
<td>0.00226</td>
<td>0.004631</td>
<td>0.000388</td>
<td>0.00135</td>
</tr>
</tbody>
</table>

**Fig. 42. ICP-MS elemental distribution obtained across the length of the single crystal.**
4.2 Corrosion behavior of surface treated and un-treated surfaces

This section talks about the results obtained from the potentiodynamic DC polarization tests done on the Mg substrate with different surface treatments.\textsuperscript{42}

4.2.1 DC Anodized surface

The DC anodized samples were tested in Hank’s solution and in 0.15 M NaCl.

4.2.1.1 In Hank’s solution

Fig. 43 shows the DC polarization results for a single crystal sample (S1) and Sample (S2): single crystal disc Anodized cut from the same crystal as S1. Anodizing conditions were 80V DC for 2 hours in 200 ml of (75 ml of 0.1 N sodium silicate and 125 ml of 1 M sodium hydroxide). Both samples were subjected to polarization in Hank’s solution at room temperature. The anodized sample showed more noble corrosion potential compared to the non-anodized and the corrosion currents in both the samples were comparable.

Tafel analysis was carried out on the polarization data corrosion rate was determined. Table 4 summarizes these results. 2 hour anodized sample S2 shows slightly reduced corrosion tendency compared to non-anodized sample S1.
4.2.1.2 In 0.15 M NaCl solution

Fig. 44 shows the polarization curves obtained from polycrystalline Mg, single crystalline Mg and anodized single crystalline Mg. Tafel analysis was carried out on the polarization data and $I_{\text{corr}}$ and corrosion rates were determined. Table 4 summarizes these results. Non-anodized single crystal samples S1 and 2S1 show slightly lower corrosion rates (51 and 46 mpy respectively) compared to the polycrystalline material (60 mpy) that can be attribute to absence of grain boundaries. Anodized sample 2S2 shows lowest corrosion current and corrosion rate (29 mpy) compared all the samples. The above results suggests that the resistive layer formed on the Mg surface by anodizing treatment after 6 hours was slightly beneficial towards reducing corrosion in 0.15M NaCl solution.
Table 4 Corrosion potential, corrosion current and approx. corrosion rate data obtained for anodized samples from the DC polarization experiments.\textsuperscript{42}

<table>
<thead>
<tr>
<th>Sample</th>
<th>In Hank’s Solution</th>
<th>In 0.15 M NaCl solution</th>
<th>2S2 – Anodized single crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1</td>
<td>S2</td>
<td>Polycrystal Mg</td>
</tr>
<tr>
<td>Ec\textsubscript{corr} \textup{ (V vs Ref)}</td>
<td>-1.51</td>
<td>-1.45</td>
<td>-1.56</td>
</tr>
<tr>
<td>I\textsubscript{corr} \textup{ (\mu A/cm\textsuperscript{2})}</td>
<td>60</td>
<td>55</td>
<td>31.9</td>
</tr>
<tr>
<td>Approx. Corrosion rate \textup{ (mpy)}</td>
<td>108</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>
4.2.2 Micro-arc oxidized surface

Potentiodynamic DC polarization curves of the samples with and without the coating are shown in the Fig. 45. Corresponding corrosion results are summarized in Table 5. All coated samples show slightly lesser corrosion current than the uncoated sample. On the anodic branch of the curve obtained from single crystal polished in water, it can be seen that the film is constantly being formed and broken on the surface as we see the current density varies back and forth.

![Polarization curves obtained from the MAO coated samples.](image)

**Table 5** Corrosion potential, corrosion current and approx. corrosion rate data obtained for MAO coated samples from the DC polarization experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Single Crystal Polished</th>
<th>5 mins MAO treatment time</th>
<th>7 mins MAO treatment time</th>
<th>10 mins MAO treatment time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr (V vs. SCE)</td>
<td>-1.49</td>
<td>-1.73</td>
<td>-1.6</td>
<td>-1.57</td>
</tr>
<tr>
<td>Icorr (µA/cm²)</td>
<td>24.8</td>
<td>11</td>
<td>16.6</td>
<td>9.77</td>
</tr>
<tr>
<td>Approx. Corrosion Rate (mpy)</td>
<td>49</td>
<td>20</td>
<td>30</td>
<td>17</td>
</tr>
</tbody>
</table>
4.2.3 Chemically etched surface

Potentiodynamic DC polarization curves of the polished and polished + etched samples are shown in the Fig. 46. The corrosion potential was increased towards noble direction from -1.84 V vs SCE for the polished crystal to -1.78 V vs SCE for the etched crystal. The corrosion rate found of the etched crystal was 1197 mpy which was almost 12.5 times lower than that of the polished crystal being 15000 mpy.

![Potentiodynamic DC polarization curves obtained for Polished and polished + etched single crystal.](image)

As corrosion measured using D C polarization is a surface phenomenon with accelerated corrosion, these results would not be completely correlated with the predicted corrosion behavior of the single crystal implants in the body. The bulk corrosion of Mg single crystal would give very different results than surface corrosion as in the bulk along the thickness more than one plane gets exposed to the corrosive media.
### 4.2.4 Weight loss measurements by immersion testing

The immersion test results show that in DMEM+HEPES solution at room temperature, single crystalline sample polished till 1200 grit corroded the most followed by etched single crystal, MAO coated single crystal and polycrystalline Mg. The optical images of the samples obtained before immersion, after removal from the solution at 15, 30, 72 hrs time intervals and after cleaning those with chromate solution can be seen in Fig.47. 

**Fig. 47.** Optical images of immersion test samples (a) Single crystal polished till 1200 grit, (b) Etched single crystals for 10 seconds, (c) Polycrystalline Mg, (d) MAO coated single crystal before immersion, namely before immersion, after removal from the solution.\(^{42}\)

The optical images of the samples obtained before immersion, after removal from the solution at 15, 30, 72 hrs time intervals and after cleaning those with chromate solution can be seen in Fig.47. **Fig. 48** shows the weight loss graph obtained using the data listed in Table 6.
Fig. 48. Weight loss vs. Time graph obtained from immersion test in DMEM + HEPES.\textsuperscript{42}

Table 6 Weight loss measurements from the immersion test in DMEM + HEPES\textsuperscript{42}

<table>
<thead>
<tr>
<th>Weight Loss (mg)</th>
<th>Mg Single Crystal Polished</th>
<th>Single Crystal Etched (10 seconds treatment time)</th>
<th>Polycrystalline Mg Polished</th>
<th>MAO coated Single Crystal (10 mins treatment time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 15 hrs</td>
<td>5.925</td>
<td>8.511</td>
<td>4.568</td>
<td>7.336</td>
</tr>
<tr>
<td>After 30 hrs</td>
<td>13.672</td>
<td>12.929</td>
<td>5.192</td>
<td>7.33</td>
</tr>
<tr>
<td>After 72 hrs</td>
<td>19.113</td>
<td>14.794</td>
<td>6.129</td>
<td>10.222</td>
</tr>
<tr>
<td>Approximate Corrosion rate after 72 hrs (mpy)</td>
<td>500</td>
<td>405</td>
<td>162</td>
<td>275</td>
</tr>
</tbody>
</table>
4.2.5 *In vivo* testing

Polycrystalline Magnesium pellets were implanted as control samples. It seems that with and without chemically etching process, the polycrystalline Mg pellets got corroded by exhibiting the weight lost by 5% and 9% respectively, in 56 days. Although the mice bearing Mg polycrystalline pellets without the etching treatment were constantly forming small gas bubbles. On the other hand, 14 hour soaked Mg single crystal pellets without the chemically etching treatment, corroded much faster and their weight reduced by 52% in 56 days, as seen in Fig.49. Mice bearing these pellets also formed large volumes of gas under skin. The chemical etching treatment significantly slowed down the corrosion showing weight reduced by 7% in 56 days. The weight loss measurement was not possible in between as the mice need to be sacrificed in order to harvest the implanted pellets. The weight loss behavior observed would not be linear between 0 days to 56 days. As we have data only at 2 time points, the connecting geometry turns out to be a line. Mice bearing the polished and etched Mg single crystal pellet formed much small gas bubbles under

Fig.49. Weight loss vs Implantation Time for *in vivo* study in the mice model.12
skin in the first 14 days and did not form noticeable gas bubbles after that (Fig.50). Hence, the chemical etching treatment significantly improved quality of the Mg single crystal samples. Even though the weight loss was measured after 56 days of implantation time, the bubble volume was monitored throughout the experiment. Corrosion rate can also be correlated to the volume of the hydrogen bubble generated as seen in Fig.50.

![Bubble Volume vs Time](image)

**Fig.50. Bubble volume vs. Time data for in vivo study in the mice model**

4.3 Characterization of the treated surfaces

The treated surfaces were characterized using techniques such as optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).
4.3.1 DC anodized coating morphology

Fig. 51 shows optical images of film surface after DC polarization tests. The samples show a difference in appearance with greater corrosion induced surface damage appearing in uncoated samples. To further investigate the nature of microscopic damage, SEM imaging was carried out on anodized disc (S2) before and after DC polarization (Fig. 52). Anodizing in this particular case seems to restrict the corrosion to localized form compared to general corrosion for non-anodized samples. This indicates that the film is not completely uniform and protective, though it does help in reducing the corrosion rates.

![Fig. 51. Optical images of non-anodized (S1) and anodized (S2) samples after polarization test (Mag 30X).](image)

![Fig. 52. SEM images of anodized (S2) samples (a) before and (b) after polarization test (Mag 500X).](image)
Fig. 53 shows the optical images of the samples after the polarization tests in the 0.15 M NaCl solution. Polycrystalline sample shows a lot of pits on the surface compared to other samples. Anodized sample shows uniformly distributed small pits. Single crystal has lesser number of pits compared to the anodized samples.

**Fig. 53. Optical microscope images of the samples after the polarization tests in 0.15 M NaCl**
(A) Polycrystalline Mg (B) Anodized Mg for 6 hours (2S2) (C) Single crystal Mg (2S1) (D) Single crystal Mg (S1) (Magnification 30 X).

### 4.3.2 Micro-arc oxidized surface morphology and coating thickness

Fig. 54 shows the surface and cross-section morphologies of the coatings for 3 different times namely 5, 7 and 10 minutes. Pore size seems to be smaller for 5 min and 7 min treatment time and increase for 10 min treatment time Fig. 54 – a, b, c.

The coating thickness increases from the minimum of 1.8 microns for 5 min time to 4.7 microns for 10 min time. For the 10 min time the film seems to be a bit discontinuous in the cross-section image. It could be due to the pore going through and through the coating. In the EDS analysis (Table 7), elements Mg, Si, O, P, K, F, Na were seen as expected owing to their presence in the electrolyte used. The Mg content seems to be the lowest for 5 min treatment time (33.91 at. %) then increasing for 7 min treatment time (45.19 at.%) and decreasing a little for 10 min treatment time (41.51 at%). Though further analysis is required, it is perhaps indicative that the coating formed for 7 min and 10 min had more deep through and through pores exposing the Mg.
single crystal surface below which is being detected in the EDS. Opposite trend is observed for oxygen content supporting the above description.

![Fig. 54. Surface and cross section SEM images of the samples MAO coated for (a)&(d) - 5 min, (b)&(e)- 7 min, (c) & (f) – 10 min.](image)

**Table 7 Variation of surface elemental concentration of samples with different MAO treatment time**

<table>
<thead>
<tr>
<th>Avg Atom%</th>
<th>5 mins</th>
<th>7 mins</th>
<th>10 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>42.77</td>
<td>38.06</td>
<td>40.65</td>
</tr>
<tr>
<td>F</td>
<td>2.13</td>
<td>2.73</td>
<td>3.19</td>
</tr>
<tr>
<td>Na</td>
<td>2.11</td>
<td>1.47</td>
<td>1.56</td>
</tr>
<tr>
<td>Mg</td>
<td>33.91</td>
<td>45.19</td>
<td>41.51</td>
</tr>
<tr>
<td>Si</td>
<td>12.31</td>
<td>8.46</td>
<td>8.90</td>
</tr>
<tr>
<td>P</td>
<td>6.54</td>
<td>3.98</td>
<td>3.95</td>
</tr>
<tr>
<td>K</td>
<td>0.21</td>
<td>0.32</td>
<td>0.24</td>
</tr>
</tbody>
</table>
4.3.3 Chemically etched surface – Morphology and composition

Magnesium single crystal surface was etched using the NME etchant. As-polished Mg single crystal till 1200 grit, polished and etched single crystal for namely 10 seconds and 30 seconds were used for the morphology and composition analysis.

4.3.3.1 Surface roughness measurements by AFM

The surface roughness parameters were calculated using the Nanoscope Analysis software. According to the AFM measurements, 1200 grit polished sample shows the highest average roughness followed by 10 seconds etched and 30 seconds etched samples as seen in Table 8. Average maximum peak heights and average maximum peak depths follow the same trend in AFM results. It indicates that the etchant affects the surface roughness of the crystal making it smoother as the etching time increases in this case. The AFM scans can be seen in Fig.55.

Fig.55 AFM scans of Mg crystal surfaces (a) 1200 Grit polished (b) Polished and 10 seconds etched (c) Polished and 30 seconds etched.
Table 8 Surface roughness parameters of the Magnesium samples obtained using AFM

<table>
<thead>
<tr>
<th></th>
<th>1200 grit</th>
<th>10 sec etch</th>
<th>30 sec etch</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS Surface roughness $R_q$</td>
<td>106</td>
<td>51</td>
<td>36</td>
</tr>
<tr>
<td>Average Surface roughness $R_a$</td>
<td>78</td>
<td>67</td>
<td>48</td>
</tr>
<tr>
<td>Average Max Height $R_{pm}$</td>
<td>83</td>
<td>73</td>
<td>53</td>
</tr>
<tr>
<td>Average Max Depth $R_{vm}$</td>
<td>-111</td>
<td>-56</td>
<td>-33</td>
</tr>
</tbody>
</table>

4.3.3.2 Surface film composition by X-ray Photoelectron Spectroscopy (XPS)

As the film formed by etching were too thin to be analyzed using EDS to get a better idea about the film thickness and composition, a more surface sensitive technique of XPS was used.

Fig. 56. XPS depth profile of pure MgSC with different surface conditions (a) 1200 grit polished, (b) 1200 grit polished & 10 seconds etched using NME etchant and (c) 1200 grit polished & 30 seconds etched with...
4.3.3.2.1 Depth profiles

Composition as well as approximate thickness of the film can be calculated using the XPS technique. The depth profiling on the samples helped get an idea about the film thickness. The XPS depth profiles for the samples tested namely surface polished till 1200 grit SC paper, surface polished till 1200 grit and etched using NME etchant for 10 seconds, surface polished till 1200 grit and etched using NME etchant for 30 seconds can be seen below in Fig. 56.

The depth profiling shows the presence of C, O, Mg on the substrate. The point at which the two component profiles cross is where there is no longer a continuous layer of either component and that could be assumed to be the boundary between the two components. The XPS depth profiling of these 3 samples revealed the presence of a film mainly made of Mg and O of nanometer thickness on the etched samples – 15 nm for the 10 seconds etched sample and 70 nm for the 30 seconds etched sample. The crossover between the profile of Mg and O is around 2 nm which shows a very thin oxide film for the 1200 grit polished sample. The samples were being milled at the angle of 45 degrees, thus some regions are being shadowed showing the gradual change in the slope after the initial sharp change for all three profiles. High resolution XPS scans reveal the etching film was mainly made of MgO and Mg(OH)₂ as explained in the next section. The carbon present in all three cases was found to be adventitious.
4.3.3.2.2 Survey Spectra and High Resolution Spectra

- For 1200 grit polished Mg single crystal

Fig. 57. Survey Spectra for 1200 grit polished Mg single crystal (a) Before sputtering (b) After sputtering.

The survey spectra of 1200 grit polished sample prior to argon sputtering reveals that Mg, O and C are the elements present on the sample surface. After argon sputtering to the depth of 188 nm, the survey spectra obtained shows that majorly Mg is present along with the small percentage of O. The B.E. peak at 285.1 eV of elemental C disappears after etching in the survey spectra indicating that carbon on the surface is adventitious. In order to know the bonding of the elements present in and across the depth of the sample of our interest, high resolution Mg1s, O1s and C1s core level XPS peaks were analyzed along with the depth profile analysis.

Table 9 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished sample

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg1s</td>
<td>1303.89</td>
<td>14.62</td>
<td>Mg1s</td>
<td>1303.88</td>
<td>81.25</td>
</tr>
<tr>
<td>O1s</td>
<td>531.89</td>
<td>47.61</td>
<td>O1s</td>
<td>532.08</td>
<td>15.91</td>
</tr>
<tr>
<td>C1s</td>
<td>285.1</td>
<td>37.37</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The high resolution de-convoluted peaks for Mg1s, O1s and C1s before and after argon sputtering for 1200 grit polished sample can be seen in Fig. 58.

After comparing the peak binding energy values with the ones from the NIST database we can say following things about this sample. The Mg1S peak for the sample surface at 1302.61 indicates the presence of Mg(OH)$_2$ and 1303.38 indicates the obvious presence of elemental Mg. After etching, the presence of elemental Mg increases to 77 atomic%.

![De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished Mg single crystal.](image)

**Table 10 High resolution peak data for 1200 grit polished Mg single crystal before and after Argon sputtering**

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Possible Species</th>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Possible Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s Scan A</td>
<td>529.18</td>
<td>12.92</td>
<td>Mg(OH)$_2$</td>
<td>O1s Scan A</td>
<td>531.12</td>
<td>3.49</td>
<td>MgO</td>
</tr>
<tr>
<td>O1s Scan B</td>
<td>531.61</td>
<td>34.53</td>
<td>MgO</td>
<td>O1s Scan B</td>
<td>534.66</td>
<td>1.93</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Mg1s Scan A</td>
<td>1303.38</td>
<td>33.41</td>
<td>Mg</td>
<td>Mg1s Scan A</td>
<td>1303.36</td>
<td>77.37</td>
<td>Mg</td>
</tr>
<tr>
<td>Mg1s Scan B</td>
<td>1302.61</td>
<td>10.19</td>
<td>Mg(OH)$_2$</td>
<td>Mg1s Scan B</td>
<td>1304.34</td>
<td>13.82</td>
<td>MgO</td>
</tr>
<tr>
<td>C1s aromatic</td>
<td>290.01</td>
<td>3.92</td>
<td>Aromatic</td>
<td>C1s Scan A</td>
<td>282.98</td>
<td>1.9</td>
<td>Si-C</td>
</tr>
<tr>
<td>C1s C-C</td>
<td>284.61</td>
<td>5.02</td>
<td>C-C</td>
<td>C1s Scan B</td>
<td>290.36</td>
<td>1.4</td>
<td>MgO/CO$_2$</td>
</tr>
</tbody>
</table>
- For 1200 grit polished + 10 seconds etched Mg single crystal

The survey spectra in Fig. 59. Survey Spectra for 1200 grit polished + 10 seconds etched Mg single crystal (a) Before sputtering (b) After sputtering. for 1200 grit polished + 10 seconds etched sample shows the presence of Mg, O and C elements on the surface. After etching away the depth of 559 nm only pure Mg is found to be present in the survey spectra. It indicates the elemental C is being adsorbed from the environment due to the presence of carbon dioxide. The B.E. peak of core level C(1S) of elemental C at 285.08 eV confirms this. The high resolution de-convoluted peaks for Mg (1s), O(1s) and C(1s) before and after argon etching can be seen in Fig. 60.

![Survey Spectra](image)

Fig. 59. Survey Spectra for 1200 grit polished + 10 seconds etched Mg single crystal (a) Before sputtering (b) After sputtering.

Table 11 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished + 10 seconds etched sample

<table>
<thead>
<tr>
<th></th>
<th>Before sputtering</th>
<th>Atomic %</th>
<th>After sputtering</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Peak BE</td>
<td></td>
<td>Name</td>
<td>Peak BE</td>
</tr>
<tr>
<td>Mg1s</td>
<td>1303.9</td>
<td>18.89</td>
<td>Mg1s</td>
<td>1303.38</td>
</tr>
<tr>
<td>O1s</td>
<td>531.92</td>
<td>51.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1s</td>
<td>285.08</td>
<td>28.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 12 High resolution peak data for 1200 grit polished + 10 seconds etched Mg single crystal before and after Argon sputtering

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Possible Species</th>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Possible Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s Scan A</td>
<td>531.54</td>
<td>42.1</td>
<td>MgO</td>
<td>O1s Scan A</td>
<td>531.16</td>
<td>2.4</td>
<td>MgO</td>
</tr>
<tr>
<td>O1s Scan B</td>
<td>530.88</td>
<td>12.61</td>
<td>Mg(OH)$_2$</td>
<td>Mg1s Scan A</td>
<td>1303.33</td>
<td>78.59</td>
<td>Mg</td>
</tr>
<tr>
<td>Mg1s Scan A</td>
<td>1303.76</td>
<td>19.51</td>
<td>MgO</td>
<td>Mg1s Scan B</td>
<td>1304.65</td>
<td>14.96</td>
<td>MgO</td>
</tr>
<tr>
<td>Mg1s Scan B</td>
<td>1303.06</td>
<td>2.22</td>
<td>Mg</td>
<td>C1s Scan A</td>
<td>282.84</td>
<td>2.2</td>
<td>Si-C</td>
</tr>
<tr>
<td>C1s Scan A</td>
<td>284.71</td>
<td>18.31</td>
<td>C-C</td>
<td>C1s Scan B</td>
<td>290.56</td>
<td>1.85</td>
<td>MgO/CO$_2$</td>
</tr>
<tr>
<td>C1s Scan B</td>
<td>289.56</td>
<td>5.25</td>
<td>MgO/CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 60. De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished + 10 seconds etched Mg single crystal.
- For 1200 grit polished + 30 seconds etched Mg single crystal

The survey spectra for 1200 grit polished + 30 seconds etched sample shows the presence of Mg, O and C elements on the surface as seen in Fig. 61. After etching away the depth of 559 nm only pure Mg is found to be present in the survey spectra. The high resolution de-convoluted peaks for Mg 1s, O1s and C1s before and after argon etching can be seen in Fig. 62.

![Survey Spectra for 1200 grit polished + 30 seconds etched Mg single crystal](image)

**Fig. 61. Survey Spectra for 1200 grit polished + 30 seconds etched Mg single crystal (a) Before sputtering (b) After sputtering.**

Table 13 Atomic % of elements on the surface revealed after the survey scans for 1200 grit polished + 30 seconds etched sample

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
<th>Name</th>
<th>Peak BE</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg1s</td>
<td>1303.28</td>
<td>16.8</td>
<td>Mg1s</td>
<td>1303.33</td>
<td>100</td>
</tr>
<tr>
<td>O1s</td>
<td>531.34</td>
<td>51.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1s</td>
<td>284.95</td>
<td>31.47</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 62. De-convoluted XPS peaks before and after argon sputtering for 1200 grit polished + 30 seconds etched Mg single crystal.

Table 14 High resolution peak data for 1200 grit polished + 30 seconds etched Mg single crystal before and after Argon sputtering.

<table>
<thead>
<tr>
<th></th>
<th>Before sputtering</th>
<th></th>
<th></th>
<th></th>
<th>After sputtering</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Peak BE</td>
<td>Atomic %</td>
<td>Possible Species</td>
<td>Name</td>
<td>Peak BE</td>
<td>Atomic %</td>
</tr>
<tr>
<td></td>
<td>C1s Scan A</td>
<td>284.44</td>
<td>13.57</td>
<td>C</td>
<td>C1s Scan A</td>
<td>294.15</td>
<td>1.01</td>
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<tr>
<td></td>
<td>C1s Scan B</td>
<td>285.04</td>
<td>9.81</td>
<td>C-C</td>
<td>C1s Scan B</td>
<td>290.41</td>
<td>2.97</td>
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<tr>
<td></td>
<td>C1s Scan C</td>
<td>289.11</td>
<td>2.91</td>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O1s Scan A</td>
<td>531.09</td>
<td>43.92</td>
<td>MgO</td>
<td>O1s Scan A</td>
<td>530.98</td>
<td>3.06</td>
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<td></td>
<td>O1s Scan B</td>
<td>532.34</td>
<td>10.31</td>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg1s Scan A</td>
<td>1303.43</td>
<td>14.82</td>
<td>Mg</td>
<td>Mg1s Scan A</td>
<td>1303.16</td>
<td>59.88</td>
</tr>
<tr>
<td></td>
<td>Mg1s Scan B</td>
<td>1302.79</td>
<td>4.65</td>
<td>Mg(OH)₂</td>
<td>Mg1s Scan B</td>
<td>1303.47</td>
<td>33.08</td>
</tr>
</tbody>
</table>
The binding energy values were obtained from the NIST database.

**O1s**
MgO : 529.6 – 532.1 eV
531.2 eV $^{43}$
Mg (OH)$_2$ : 530.9 eV $^{44}$

**Mg1s**
Mg : 1303-1303.5 eV
1303.4 eV $^{45}$
Mg(OH)$_2$ : 1302.7 eV $^{44}$
MgO : 1303.9 eV $^{46}$

**C1s**
C – 284.1 – 285.1 eV
284.6 eV $^{47}$

**SiC**
281.3-283.8 eV
282.9 eV $^{48}$

**MgO/CO$_2$** : 290.3 eV $^{49}$

The film formed due to etching was mainly made magnesium oxide and magnesium hydroxide according to XPS results.
5 Single Crystal used in animal studies

For the particular experiment we collaborated with the Dr. Savio Woo’s group involving his students Dr. Kathryn Farraro, Kwang Kim, Jonquil Flowers. The experiments were carried out in the Musculoskeletal Research Center, Department of Bioengineering, Swanson School of Engineering, University of Pittsburgh.

5.1 For reconstruction of the Anterior Cruciate Ligament (ACL) joint

A specially designed ring was used by Dr. Woo’s group to bridge the gap between two torn ends of the ACL to function as the internal support as shown in the Fig. 63. The ring should ideally degrade as the ACL heals and starts bearing more load. It is supposed to be used along with cells or bioscaffolds releasing the biological agents from time to time to facilitate healing. Single crystal Mg (99.95% pure - 8 mm diameter and 2 inch length) was used as the starting material to fabricate the ring made in the nanoworld lab. The drawing and the picture of the device and how it can be used to repair the ACL can be seen in the Fig. 6350. The ring design was designed for the goat ACL depending on the anatomical dimensions of the mid-substance of the ACL. Surgical implantation technique involved suture technique developed in Dr. Woo’s lab.
The Mg single crystal ring was observed 6 weeks after implantation by sacrificing the animal (Fig. 64). Micro-CT analysis was carried out. The Fig. 64 (a) shows the time zero image of the ACL implanted in cadaveric goat stifle joint. The Fig. 64 (b) shows the ACL joint after 6 weeks of implantation and the Fig. 64 (c) shows how a normal healthy ACL joint looks like in a goat as a control. The visual observation of the image after 6 weeks of the implantation shows the remnants of the ring in the greyish black color. The ring doesn’t seem to be structurally intact.

Fig. 64. (a) Time zero image of the ACL joint after the implantation of the single crystal ACL device with suture technique in cadaveric joint (b) 6 Weeks of healing of the ACL joint after the implantation of the single crystal ACL device with suture technique (c) Control: normal healthy ACL joint.
5.2 Micro CT results

These studies were done at the Musculoskeletal Research Center (MSRC) in the Department of Bioengineering at the University of Pittsburgh. Femur ACL Tibia complex (FATC) was embedded in the MMA polymer and subjected to micro CT imaging with voxel size of 10 microns. Analysis and imaging was done by Dr. Kathryn Farraro from University of Pittsburgh. After volume analysis following results were obtained as shown in Table 15. The images in Fig. 65 were used for the volume analysis.

<table>
<thead>
<tr>
<th>Table 15 Volume analysis after the ring degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>Calculated volume of the intact ring</td>
</tr>
<tr>
<td>Intact Mg remaining after 6 weeks</td>
</tr>
<tr>
<td>Corroded Mg after 6 weeks</td>
</tr>
<tr>
<td>Total Mg ring remaining after 6 weeks</td>
</tr>
</tbody>
</table>

Fig. 65. Micro CT image of the leftover ring after 6 weeks (a) greyscale imaging for remaining volume calculations, (b) Corroded part of the ring can be seen in white (c) The corrosion product accumulated after pitting corrosion can be seen in a darker grey due to the density differences.
From these Micro CT results following conclusion can be made about this particular device -

- The ACL in the treated knee was mostly healed with mild foreign body response around the sutures.

- The single crystal Mg ring exhibited pitting corrosion (around 41% of the total volume).

- The corrosion product did not seem to affect the health of the underlying ACL ligament tissue made of fibrosis and granulation tissue.
6 Conclusion

The following conclusions can be drawn from this work.

- High quality Mg single crystals upto 2” in length and 6.5 mm in diameter were grown successfully by directional solidification using Bridgman-Stockbarger method.
- Mg single crystal surface needs to be highly oriented in the basal plane orientation in order to achieve superior corrosion behavior in comparison with the polycrystalline Mg. As the growth was carried out without any seed, the crystals could not achieve the desired orientation perfectly but came very close in achieving that.
- Chemical etching using the nitric acid etchant seemed to be the most effective treatment followed by Micro-arc oxidation and DC Anodization in improving the corrosion behavior of the crystal surface. The surface treatments would serve as temporary barrier during the initial period of implantation till the time they need to have sufficient mechanical strength and integrity. Once the purpose of the implant has been served the long term goal of complete resorption in the body would be achieved.
- Mg single crystal substrates show different corrosion behavior depending on whether it is a surface corrosion like in DC Polarization testing or bulk corrosion like in Weight loss measurements \textit{in vitro} and \textit{in vivo}. Even though corrosion resistance offered by the surface orientated in basal plane orientation is superior to other orientations, when implant is made from a single crystal, many other planes of the single crystal would be getting exposed to the corrosive fluid as implant would be 3 dimensional.
- \textit{In vitro} and \textit{in vivo} experiments demonstrating potential use of Mg single crystal as a biodegradable implant material were carried out with the help of collaborators participating in ERC-RMB project.
7 Future Work

- Further work will involve oriented growth of the crystals allowing more control over its corrosion behavior using appropriate seed.

- The etching treatment needs to be further explored in terms of different etching times, concentration and substrate geometries.

- *In vivo* experiments involving implantation of the bone fixation plates and screws in the rabbit model are currently ongoing at University of Pittsburgh under the guidance of Dr. Sfeir. This will shed more light on the effect of high purity Mg single crystal on bone growth, effect of implant degradation and bone healing.

- Collaborative experiments with Dr. Woo on ACL ring made of Mg single crystal coated with a special coating developed using MAO technique at Dr. Yun’s lab would be continued along with the uncoated ACL ring made using Mg single crystal.
References


Appendix

Procedure to grow the crystals

1) Turn on the Argon and Nitrogen gas cylinders and open the appropriate valves so that the gases flow in to the quartz tube using the valve shown in the Fig. 66 (a,b). Set the Mass Flow Controller to the desired flow rate or pressure (Ar – 40 psi). Turn ON the cooling water shown in the Fig. 66 (c). Make sure all the sensors on the open cabinet doors are turned OFF to avoid any alarms.

2) Turn ON the main switch of crystal grower system followed by the battery backup. The PC will boot automatically.

3) Once the PC has booted, double-click on the “CvdWinPrc” program. Enter the appropriate recipe and date file name and then click on OK for the program to open. The Open program has 3 windows 1) GUI for the furnace, 2) Small J5409 process window on the top shows the control options and 3) Graphical representation of the process parameters of the furnace w.r.t Time.

4) Check if the process indicator light on top of the furnace is blue, which indicates it is safe to Unload as seen in Fig. 66 (d).

Fig. 66. Nitrogen, Argon gas flow controller, Water flow controller, Light wand representing various process stages.
5) Press the UNLOAD (Fig. 67) button on the main door panel. Wait for several minutes for the furnace and the quartz tube to unload.

6) Insert the raw material that is slug/s of magnesium in the graphite crucible hole. Put the graphite crucible in the steel crucible holder and close the lid. Put the assembly carefully on top of the quartz rod and press LOAD (Fig. 67) on the controls.

Fig. 67. Controls for loading, unloading, emergency stop and alarm lights on the crystal grower.

7) On the small J5409 process window on top, click on “Abort/Run” and then on “Process” in the drop down options. The turbo pump should kick in at this point. The process is automated. The pumping process can take several hours. The turbo pump evacuates the chamber till a pressure of $10^{-5}$ Torr is reached inside the pump. The chamber at this stage reaches a vacuum of around $6.3 \times 10^{-5}$ Torr. The system automatically turns OFF the pumping and then turns on the argon supply so that the chamber reaches atmospheric pressure but in an inert argon atmosphere. 1 SLPM flow rate is maintained.

8) Thereafter the heating step is activated and the chamber is heated to the preset soaking temperature and held at these temperatures. The system will continue to soak the magnesium until it is manually triggered to go into the next step. The system has to be monitored regularly.
to ensure that adequate soaking is completed. Remote monitoring can be done remotely by using the “Teamviewer” application on the desktop.

9) Once adequate soaking is completed, click on NEXT in the top J5409 process window. The furnace movement is initiated. The nucleation of the single crystal from the liquid melt will happen during this movement. Once the furnace movement is completed the system automatically goes in to the cooling stages. Once sufficient cooling is achieved the ‘Blue’ READY TO UNLOAD light will be turned ON. The sample can now be unloaded just as in during the loading stage i.e. Steps 4 and 5.

10) Once the sample crucibles are removed the furnace can be loaded without the crucible. Close the “CvdWinPrc” program and SHUT DOWN the PC. Once the PC is SHUT DOWN, TURN OFF the battery pack behind the PC monitor and only then TURN OFF the system.

11) Turn OFF the gas cylinders and the water supply.

The whole process can be seen in the flow chart below in Fig. 68

![Fig. 68. Single crystal growth process flow chart.](image-url)