Optimization of Mechanical Properties of Biodegradable Zn-Mg-Cu Alloys for Pediatric Orthopedic Applications

MS Thesis
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COMSATS University Islamabad
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Optimization of Mechanical Properties of Biodegradable Zn-Mg-Cu Alloys for Pediatric Orthopedic Applications

A thesis submitted to
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In partial fulfillment
of the requirement for the degree of

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in
Chemistry

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I Kiran Nayab Laila, CIIT/SP24-R06-011/LHR, hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due to that amount of plagiarism is within an acceptable range. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of HEC.

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It is certified that, Kiran Nayab Laila, CIIT/SP24-R06-011/LHR, has carried out all the work related to this thesis under my supervision at the Department of Chemistry, COMSATS University Islamabad, Lahore Campus and the work fulfill the requirement for award of MS degree.

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Dedication

I dedicate this work of mine to

My Mother Sughran Hameed

A gentle, strong, enthusiastic soul without whom I would not have any existence, taught me the lesson of self-belief, patience, devotion, and hard work and that so much could be done with little.

My Father Abdul Hameed Nasir

For giving me a genuine and truthful livelihood, teaching me the lesson of sheer belief in Allah, being my best friend ever, encouraging and supporting me, letting me dream big by breaking all the stereotypes. I cannot find words to justify my thanks to him for his efforts.

My Guardian Abdul Majeed

In loving memory of my beloved guardian, who 's unwavering support and encouragement shaped the person I am today. Though you are no longer with me, your guiding light continues to illuminate my path. This thesis is a humble tribute to your values and wisdom you installed in me. I dedicated this work to your cherished memory, with heartfelt gratitude and boundless love my papa!

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**Praise to be ALLAH, the Cherisher and Lord
of the World, Most gracious and Most Merciful**

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Abstract

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By

Kiran Nayab Laila

The research for biodegradable metals for pediatric orthopedic applications with suitable mechanical strength is still ongoing. Previous study demonstrates that although Zinc has a suitable corrosion rate but it possesses low mechanical strength which is not suitable for pediatric orthopedic applications. On the other hand, magnesium and copper have a suitable mechanical property and their addition in Zn based alloys make them a potential candidate for Orthopedic applications. This study aims to develop Zinc-based biodegradable alloys using powder metallurgical processing technique and to analyze their properties using different techniques (SEM, EDX, XRD, hardness, UTM and AAS). It was concluded that addition of magnesium has increased the density, compressive strength and microhardness of the Zinc alloys due to small grain size. However, inclusion of copper to Zn-Mg alloys enhanced the density, microhardness and compressive strength further due to formation of rich intermetallic phases. Analysis of AAS revealed the increased concentration of release of Zinc ions and loss of Zn mass in stimulated body fluid (SBF) after degradation of Zn alloys in different time intervals.

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Chapter 1

Introduction

1.1 Overview of Pediatric Orthopedics

Pediatrics orthopedics, the specialize branch of medicine encompassing musculoskeletal treatment of patients which begins with the fetal development and lasting to the skeletal maturity. Pediatric orthopedics is a fundamental concept of understanding the growth and development of joints and muscles in infants, children, adolescents and young adults. Unlike adults, Orthopedics face challenges while dealing with child's bones because they are still remodeling, growing and metabolically active. The faster bone regeneration rate and higher cellular activity in child's bone tissues rather than adults, demanding implants which are quite suitable and matches with their dynamic biological conditions. In orthopedics field, research is still ongoing to resolve a lot of issues faced by medical industry for metallic implantation because of superior mechanical properties which they possess for treatment.

1.2 Biomaterials

Orthopedic Implantation is done through creating a biomaterials device which is capable of providing support to the broken parts of joints or may be used as substitute for fractured parts. However there raise an issue using these orthopedics implantations which associated to joints and bones when the real parts of body have been worn out and they would not be able to operate independently. The infections or broken parts needed to be removed due to various reasons such as scoliosis, bone fracture, spinal stenosis and osteoarthritis. To secure the broken bones different forms of implants such as pins, screws, rods and plates are used [2], [3].

1.3 Background

Musculoskeletal disorders are the worldwide human health issue related to the hips and knee replacements. According to reports, ithin US in 2009, these implantations cost approximately around $42.3 billion. The Food and Drug Administration (FDA) from year 2011 to 2000 gave remarkable approval of 150 new medical orthopedic implant devices. Since 2006, the total sales of hip and knee replacement orthopedic medical devices and trauma products have been increased upto $18.1 billion. Sir John Charley in 1961, pioneered as first total hip replacement arthroplasty using low friction Teflon with a metal implant and acrylic cement for the fixation into native bone. In 1970s, the polyethylene with high molecular weight would be introduced into industry for orthopedics implants[4]. Most of these implantable medical devices are constructed from materials like polymers, stainless steel (SS), ceramics, cobalt and titanium-based alloys. After long term uses, these biomaterials have high strong chances of being failure and additional surgery or recommended revision is required. Due to advancement in the medical field, most of the population traumatized by road accidents and sports injuries live longer life by these implant devices. It is now essential to develop implants without failure and revision surgery with better longevity and biocompatibility [3].

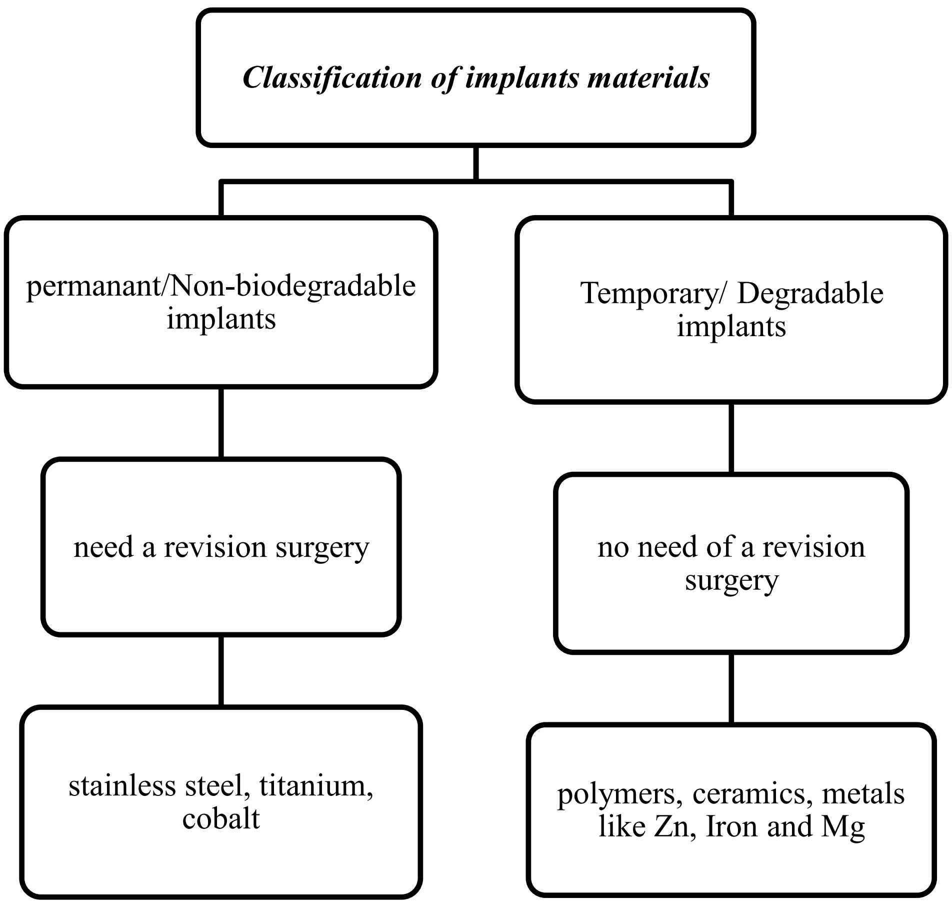
1.4 Advancement of biomedical Materials

Biomedical biomaterials are engineered to deal with biological system for diagnostic and therapeutically purposes for the treatment of human diseases since ancient times. Over the time, different biomedical material has been used which are foreign to human body such as for the suture material hair and cellulose are used and for bone fractures fixing wood or horn proved to be very effective. During 2000BC, the Egyptians used splints and braces to protect and support broken or fractured bones, they also used ivory for replacement of lost teeth. During that time, to replace missing parts of human body copper was used but due to toxic effects of copper ions these implants failed [5].

In modern times, different alloys and metals have brought as a first choice for implantation in human body because of their good mechanical properties, superior strength, lessen the rejection risk and most importantly due to the biological inertness. [6, 7] They would be extremely utilized in different fields, such as orthopedics, drug delivery, cardiovascular devices, and for skin tissue engineering. Polymers, metals and ceramics like biomaterials are preferred over the conventional implantation of orthopedics nowadays. Knowledge of biocompatibility and mechanical properties of materials are the key points for their use in field of orthopedics.

1.5 Classification of Orthopedic implants

Most of the people meet with accidents and joint diseases such as the rheumatoid arthritis, osteoarthritis and post- traumatic arthritis required implants such as the knee and total hip replacements. Orthopedic implants include most of the permanent and temporary fracture fixation components and devices such as different pins, wires, nails and screws. These orthopedic implants must work under various different working conditions in human body under physiological conditions which is essential for optimization and design of these implants material with novel properties and better performances[8].



1.5.1 Permanent/non-degradable Orthopedics implants

“The permanent or non-biodegradable orthopedic implants are devices which are able to serve throughout the life span of patients in human body and they do not deform or break within the human body unless additional surgery is required to remove them because these devices remain very intact and unchanged". Variety of various total joints including shoulder, hip, elbow, finger joints, ankle and knee are used as replacements made of different material such as metals, polymers and ceramics. In recent years, knee joints and hip prostheses have faced clinical acceptance and the rapid development. But these prostheses are very difficult to design because of delicate articulation and the complex transfer of load. The device used for hip replacement is made up of femoral head, stem, acetabular and linear head. It is observed that biomechanics and geometry of knee replacement devices are more complicated as compared to hip devices. The knee replacement devices are composed of femoral component, tibial tray and patellar component.

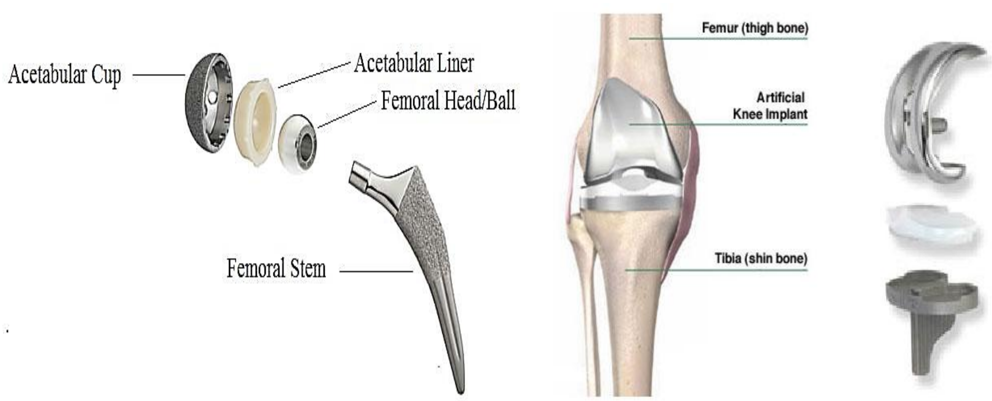


Figure 1. 1 Hip joint replacement (Left) and Knee joint replacement (Right) [1]

1.5.2 Temporary/Degradable Orthopedics Implants

Temporary or biodegradable orthopedic implants are required to fix fractured and broken bones during the healing process. "Degradable implants are those which degrade over the period of time in human body and no additional surgery is required to remove them after healing of broken bones". Biodegradable orthopedic implants are able to serve for the relatively short time just long enough to allow bones heal properly including screws, plates,wires, pins and intramedullary nails [9]. Biodegradable implants have been widely used in orthopedic because of their biocompatibility, biodegradability, intrinsic bio signals and also have low immune response. Biodegradable materials such as polymers and metallic alloys have gained much popularity in orthopedics because of similar young's modulus to the human bone where bone healing process is promoted and implants natural degradation allows slow reduction of strength of implants and the last absorption by the human body. However, these implants still face issues due to poor mechanical strength, rapid degradation, inconsistent purity and difficulty in sterilization process.

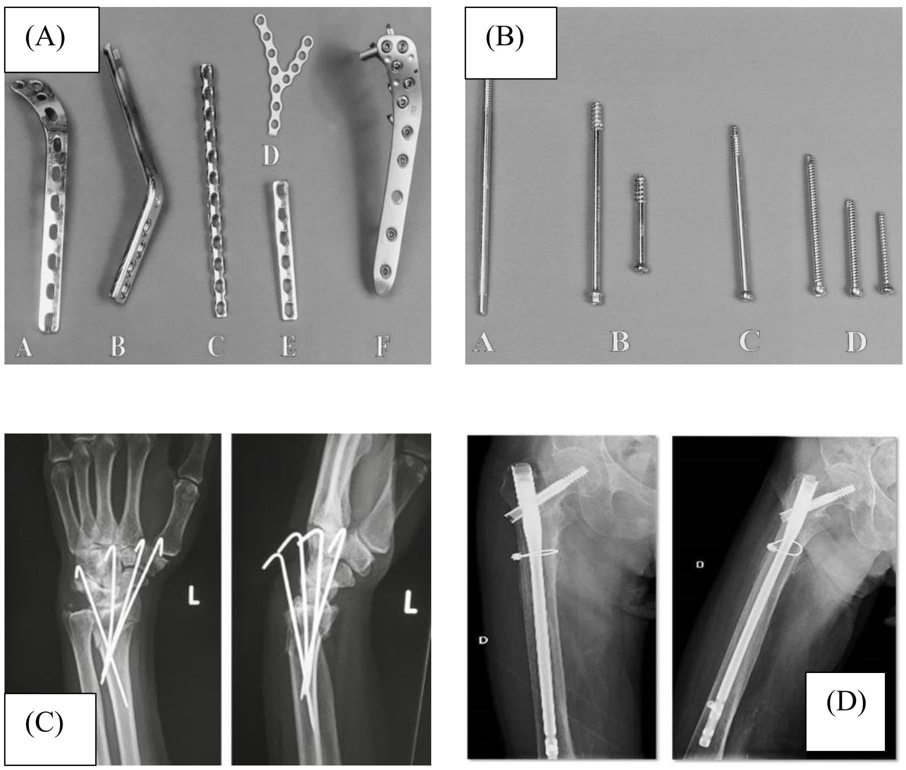


Figure 1. 2 (A) Plates, (B) Pins, (C) Screws, (D) Nails [10]

1.6 Types of non-biodegradable orthopedic implants

There are different types of non-biodegradable implants biomaterials which are being used in orthopedic fields for treatment of fracture or broken bones. These biomaterials include metals, polymers and ceramics. In recent years, metals such as titanium and its alloys, stainless steel and cobalt based alloys have been used as non-biodegradable implant devices. Different types of synthetic and natural polymers and ceramics are used for medical implant devices.[11].

1.6.1 Metals

In pediatric orthopedic applications, metals and its alloys are the first biomaterials to be used in because of their good mechanical properties and superior strength. Different metals have been used in orthopedic till now and detail of each of these metals is listed below.

1.6.2 Stainless steel and its alloys

Stainless steel are iron-based alloys used for bone fixation plates, contains a significant amount of chromium up-to 11-30wt% and minimum level of nickel. Mechanical properties, corrosion resistance, biocompatibility and cost effectiveness of these versatile materials made it exceptional as compared to other metals [12]. These stainless-steel based implants are best choice for temporary devices such as fixation screws and bone plates. Corrosion resistance of stainless steel has been improved by alloying it with Ni, Mo, Cr and nitrogen by different mechanisms. Cr reacts with O to form layer of Cr-rich oxide (Cr2O3) surface film which is protective and adhesive that have ability of self-healing process while Ni causes formation of Ni oxide film on steel surface which is protective. One major disadvantage of stainless steel is that it causes release of toxic Cr^{3+} and Ni^{2+} ions which have negative effects on human body. The wear resistance and fatigue strength of stainless steel are also very poor leading to implants failure[13, 14]

1.6.3 Cobalt based alloys

Cobalt based alloys are referred to the alloys of Co-Cr. Corrosion resistance would be enhanced due to formation of oxide layer of Cr2O3 in human body which make it resistance to degradation. The major strength of these Co-Cr based alloys are their high corrosion resistance and good wear resistance. They are hard, strong and fatigue resistance. They have been used in total joint replacement prostheses due to their high abrasion resistance. Co-Cr alloys are considered to be a good biocompatible material but them arise some issue regarding the cytotoxicity of its component material such as Nickel and chromium. The release of nickel from surface of implants causes allergic reactions in human body. Another drawback of these alloys in orthopedic applications is that their surface treatment often change the properties of material and high Young's modulus causes the stress shielding effect,[5] [15]. But as compared to stainless steel these alloys are very costly and have limited share in medical industry.

1.6.4 Titanium based alloys

Titanium alloys have wide range of applications in pediatric orthopedics because of its good mechanical properties, corrosion resistance, yield strength, fatigue strength and moderate elastic modulus. Based on microstructure, these Ti-based alloys are categorized into different groups in which most important phases are α and β due to their good strength and their mechanical properties can be change by addition of chemicals. These alloys due to formation of protective, stable and strongly adherent layer of oxides on its surfaces allow them to possess excellent corrosion resistance. Addition of V, Al, Zr, Nb, Ta and Mo would be enhanced properties of biomedical T-based alloys [16].

As compared to cobalt and stainless-steel alloys, Ti-based alloys have half of the elastic modulus which is 110GPa and they are prone to the stress shielding effect because of higher elastic modulus than that of human bone. They have good biocompatibility and corrosion resistance [8].They have low flexural rigidity and are relatively lighter in weight. The major limitations of Titanium alloys are their relative softness, poor abrasion resistance, relatively poor wear and frictional properties; low shear strength, relatively low elastic modulus, and poor resistance to the erosion of pure titanium [17].

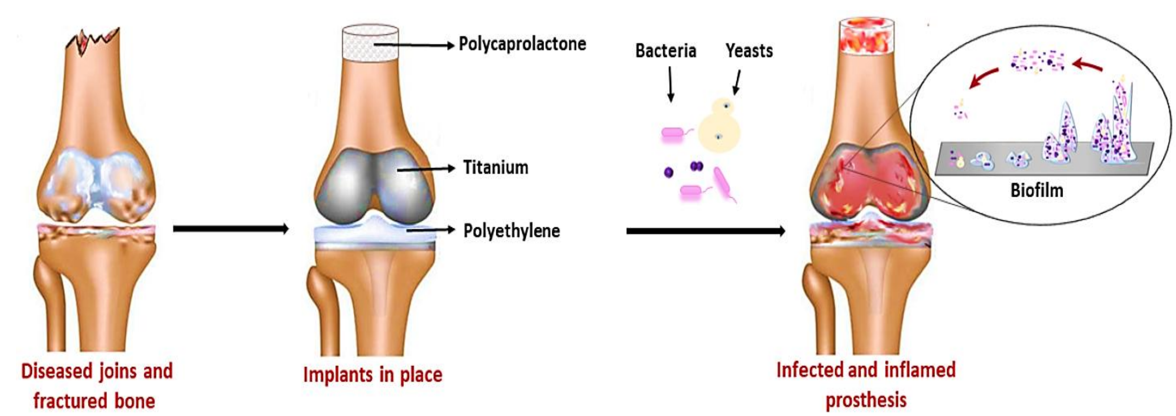


Figure 1. 3 non-biodegradable orthopedic implant materials [18]

1.6.5 Polymers

Non-degradable synthetic or natural polymers have wide range of applications in medical field such as orthopedic implants, heart valves, drug delivery system, bone cements, tissue engineering scaffolds and in vascular grafts. The use of polymers in orthopedics has been increasing steadily because of good biocompatibility, ease of processing, robustness, biological stability and their excellent mechanical properties during study of in-vivo applications [19]. As compared to ceramics and d metals, polymers have gained much popularity due to its good properties in biomedical field. Most of the synthetic non-degradable polymers are biologically inactive. The risks of failure of these implants are high due to issues arising from polymers surfaces, despite their biological inertness and mechanical properties. These issues caused by poor integration and infection with the surrounding tissues or bone resorption would be caused by the stress shielding effect [20].

1.6.5.1 Polyethylene (PE)

Polyethylene, a versatile biomedical polymer are classified as high-density polyethylene (HDPE), low –density polyethylene (LDPE) and ultra-high molecular weight polyethylene UHMWPE based on the molecular weight. Polyethylene has gained much attention as biomaterial in medical field because of good mechanical strength, chemical inertness, biostability and limited tissue reaction. PE has specific property of undergone melting and solidification at optimum temperature in a reversible manner without being degradation.[21]

PE has been widely used in orthopedics due to molding and quick shaping of material into desire shapes and sizes, also shows semi-crystalline behavior leading to crystallization. UHMWPE elastic modulus is closer to the bone that's why in worldwide UHMWPE implants have been used for bone joint replacement surgeries. One major disadvantage of using these implants is their difference in elastic modulus than natural bone which often leads to stress shielding effect on bone. As a result of this reduction of mechanical load on bone, its lead to bone loss around the implant due to bone-implant interaction.[22]

1.6.5.2 PMMA

Poly (methyl methacrylate) PMMA is a polyacrylate, extensively utilized in orthopedics as a nonmetallic implant material that possesses different properties such as biocompatibility, stiffness, biological inertness, thermo-plasticity and hydrophobicity. PMMA is a standard implant biomaterial in worldwide for intraocular lens when it is in contact with vascular tissues due to bio inertness, UV light resistance, nondegradability, smoothness retention on surface and transparency with refractive index.[23] Bone cement based on PMMA used for bone implant fixation and osteoporotic bone due to its strong instant fixing property. The main limitation of using these implants is the toxic nature of methyl methacrylate, exothermic reaction of polymerization, brittleness, less fracture toughness, poor adhesion and wears resistance to the bone tissues. The low wear resistance of polymer releases the wear particles during compression which stimulate chronic inflammatory response.[5, 24].

1.6.6 Ceramics

Ceramics materials have been extensively utilized in orthopedic field due its excellent property such as wear resistance and biocompatibility which reduces the risk of side effects from the body and decrease osteolysis and wear debris. Ceramics as compared to other materials has low coefficient of friction that reduces tear and wear resistance and inflammation risks which is especially helpful in mobile joints where constant friction is unavoidable [23]. They are resistant to body fluid due to nature of chemical stability which prevent them from corrosion and keep their prosthesis structure intact for long time.

The main limitation of this ceramic material is their brittleness which leads to fractures under intense mechanical stress and high impacts. This aspect restricts its use where prosthesis has to support high bearing load and where the patients have very active lifestyle. This fragility of ceramics caused postoperative complications like in case of fracturing and cracking there is need for prosthesis replacement. In addition, the high implantation and production costs of these ceramics materials due to the advanced machining technologies make them less accessible implants as compared to other materials [25].

1.7 Types of Biodegradable orthopedic implants

In orthopedic field, different type of biodegradable implants materials has been used over the long period of time to treat fractured or broken bones. The extensively utilized biodegradable materials include metals, polymers and ceramics. There have been significant research and the exploration of biodegradable orthopedic metallic implants such as those composed of zinc (Zn) and its alloys, magnesium (Mg) and its alloys, iron (Fe) and its alloys [19]. These metallic based implants have gained interest because of their ability to naturally degrade and proven to be promising candidates used for orthopedic applications. The detail of these biodegradable implant's materials has been given below:

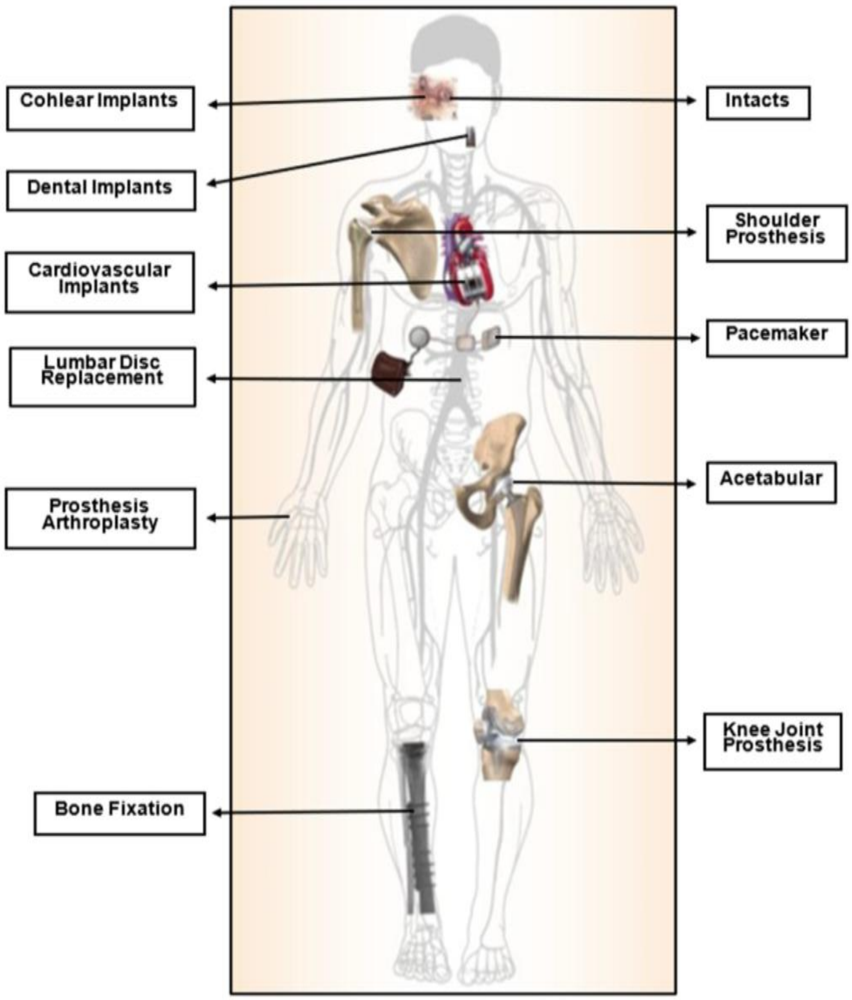


Figure 1. 4 Biometallic devices utilized in human body [26]

1.7.1 Degradable polymers

In orthopedic implants, the resorbable polymer materials have been widely utilized because of their good mechanical strength, plasticity, biocompatibility and elasticity. They have ability to degrade gradually with absorption and excretion of degradation products by human body. Polymer structure is able to control the rate of degradation. These biodegradable polymers are classified as natural such as chitin, collagen, cellulose and synthetic polymers such as polylactic acid (PLA), polyglycolic acid (PGA) and polylactic-co-glycolic acid (PLGA) [27]. These polymers have been chosen based on required properties such as chemical, mechanical and physical properties. Polymers considered to be very effective in bone repair applications in which issues such as inflammation, bone loss and corrosion are treated due to elastic modulus, tensile strength and non-corrosion properties of polymers. But these polymers have to experience the loss of mechanical strength due to its degradation rate when implantation time increases [28].

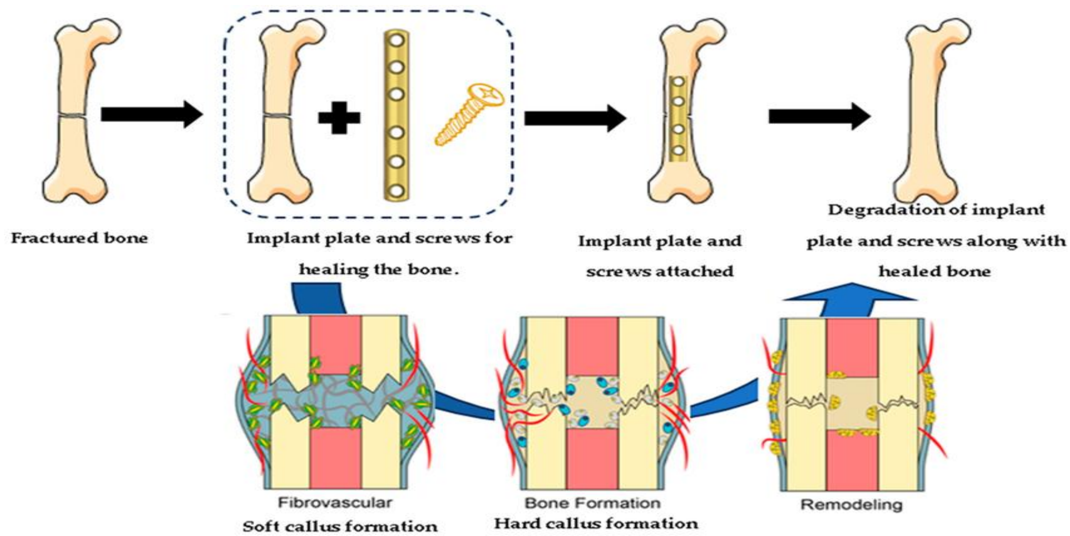


Figure 1. 5 Biodegradable device implantation [29]

The most commonly used polyester for orthopedic applications is the copolymers of PGA and PLA. The pioneering biodegradable polymer PGA used for orthopedic fixation specifically in nails, screws and plates. PGA elastic modulus is almost similar to human bone such as 12.8 GPa and its exhibits very high crystalline structure but it experiences a very short degradation time almost from 6 to 12 months. This drawback of PGA to degrade rapidly causes the loss of mechanical strength in vivo conditions approximately in 4 to 7 weeks after the implantation is done. Also PGA implantation leads to side effects such as swelling, sinus wound formation, and fluid accumulation due to high presence of glycolic acid [30] [31].

PLA, biodegradable aliphatic thermoplastic polyesters possess excellent mechanical properties, high rigidity, excellent processability, transparency, glossy appearance and young's modulus of elasticity which is almost 4.8 GPa. Slow degradation rate, brittleness and poor toughness make its limited to be used in orthopedic for bone fixation. Some of novel composites and self-reinforced materials have been added such as (HA) hydroxyapatite, to enhance the mechanical strength and rate of degradation of Oste implants. This binder helped to improve ,mechanical strength , reduced the rate of degradation and able to provide durable mechanical integrity of implants.[32] [33].

1.7.2 Metals

Metallic biomaterial devices used in orthopedic implantations possess properties such as strength, hardness, ductility, corrosion resistant, fracture toughness and biocompatibility which is essential for the load bearing components like fracture fixation devices and total joint prostheses. These resorbable metallic implants are able to degrade in vivo, stimulate host response and then completely dissolve once the healing process done. Here three different type of degradable alloys are listed below:

1.7.2.1 Mg and its alloys

Mg-based metal alloys are advance generation of biodegradable metallic biomaterials with good property of osseointegration. Mg is an essential element of human body and able to support enzymatic reactions, heart and neurological functions, digestion and bone growth. An adult human body contains Mg in bones and muscles upto 30 grams while the recommended daily allowance of human body is 400mg. magnesium deficiency causes heart and vascular problems. The process of making biodegradable Mg-based alloys is a very complicated because it combines both medical and engineering requirements for the material. Low elasticity similar to bones distinguished it from other metals which able to protect stress shielding negative effect in bone structure [34].

Mg-based alloys have gained much attention in medical orthopedic applications because they are lightweight material, its density 1.75-2.1 g/cm^3 closer to bone, have a good mechanical properties and biodegradable. Its elastic modulus is 45GPa which is close to bone (3-20GPa) and less shielding effect which does not have any adverse effect on human body. Its alloys also possess high damping capacity, having the ability to absorb energy from any of the metals used for the load applications. Another advantage of Mg is it fracture toughness, and high machinability with dimensional accuracy that complex shape are easy to obtain that are needed for medical applications. The good biocompatibility of Mg and its alloys make them attractive in in-vivo conditions because mass gain occurs when Mg reacts with human body constituents[35, 36].

The major concern of using Mg-based alloys in biomedical implants applications is that they can corrode rapidly during healing process in physiological environment. This issue mainly arises because of low standard electrode potential of Mg which is -2.37V at 25C^{o}. the corrosion rate is too high that ranging from 0.3-2mm per year in SBF solution. The rapid degradation of Mg-based BMs causes excessive evolution of hydrogen gas (H_2) at the surrounding tissue and implant interface. This hydrogen gas evolution causes embolism. The suitable rate of degradation of Mg based alloys permits desirable healing process and surface treatment is performed to increase the corrosion resistance [37] [38].

In the field of orthopedic implants researchers are trying to find out alternative material that can biodegrade and able to potentially serve as potential implants. The use of Mg based alloys as metals biodegradable are facing some challenges and scientists have been exploring other opinions to overcome these issues. Iron due to its remarkable properties are emerging as new material in orthopedic implantation devices [39].

1.7.2.2 Iron and its alloys

Iron is an essential element of the human body and it plays has many vital functions and roles in the human body such as storage, transport, molecular oxygen activation and reduction of dinitrogen. The average intake of iron in adults is 12-18 mg/day and approximate amount of 10% is extracted by the digestive tract. Especially most of part of iron is used to produce hemoglobins and liver stores in human body in the form of the haemosiderin and ferritin.[40, 41]

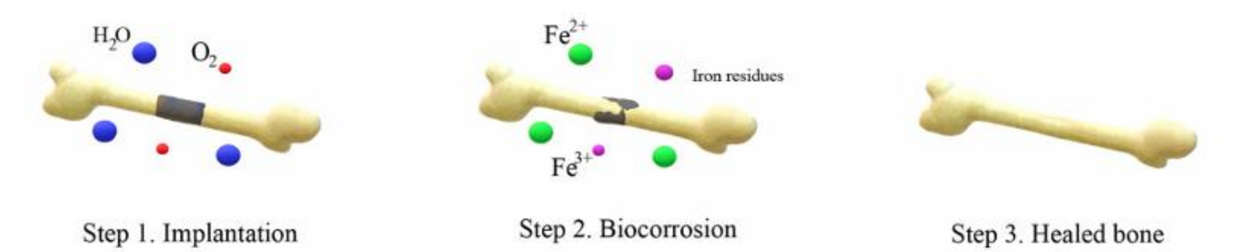
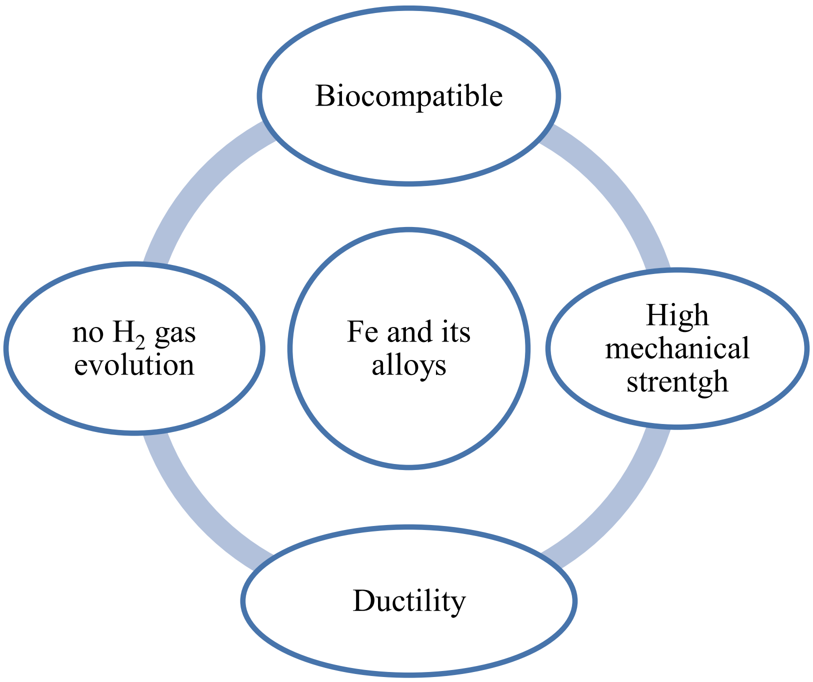


Figure 1. 6 Mechanism of iron-based alloys [42]

Iron and iron-based alloys are considered to be a good biomaterial for the temporary replacement of bones of human or as osteosynthesis material and they are considered to be first biodegradable metals. Pure iron has high elastic modulus (211.4 GPa) as compared to other materials such as pure Mg (41GPa). They are extensively used in pediatric orthopedics because of their ductility, high mechanical strength and formability which allow them to be used as excellent source of stents with special shapes like foils or foams. Biocompatibility of iron and iron-based alloys are outstanding to be used in orthopedic applications. There is no H_2 gas evolution during process of degradation of these iron based alloys [43].



Unfortunately, their arise an issue while using pure iron in orthopedics field is their low rate of corrosion so they can hardly be called as biodegradable and they degrade too slowly in the human body. Their young modulus is higher than that of human bone which cause problem during healing process of bones. Other complication is their low corrosion rate such as 0.1mm/yer [44] .

1.7.2.3 Zinc and its alloys

Zinc is the most second abundant element of the human body even after Fe and plays a essential role in human health. The daily intake of Zinc in human body is 15mg/day with varying concentration in different organ is present like 11% of zinc is presents in skin and liver, 85% found in muscles and bones and the remaining concentration is present in other tissues. Zn present plays very essential roles such as in bone metabolism, enzymes regulations, and growth of organisms. Zinc deficiency causes weakness of bones and its presence enhance the bone promoting effect. Zn as biodegradable material perform many physiological functions while their excessive intake have a significant effects on various organs as compared to insufficient intake of Zinc [45] [46].

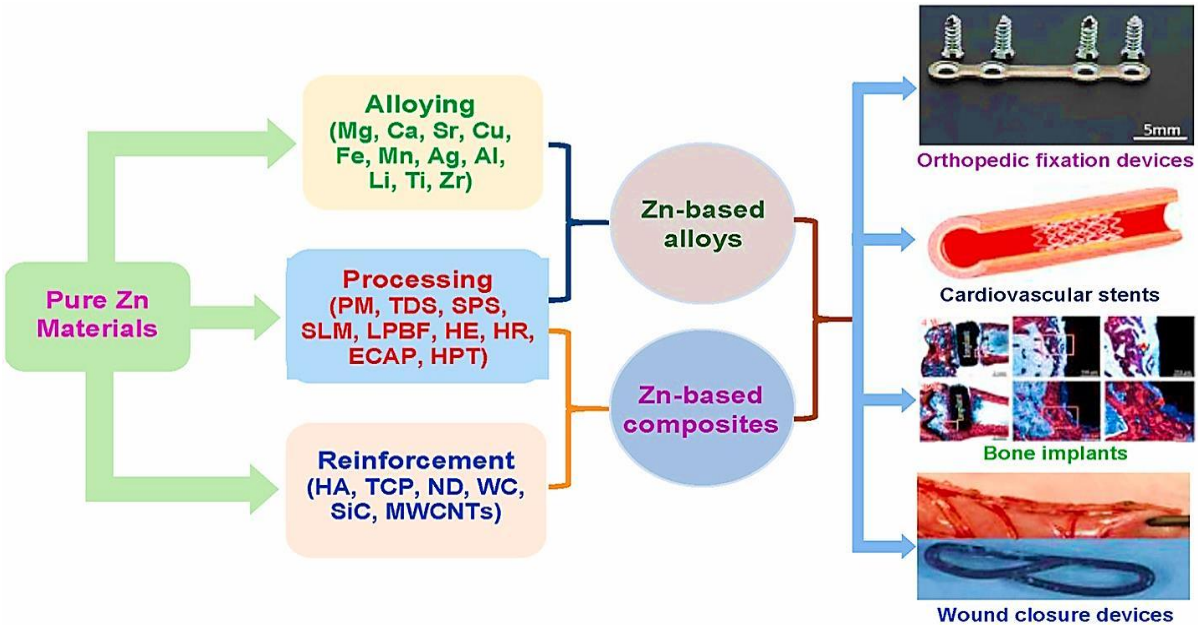
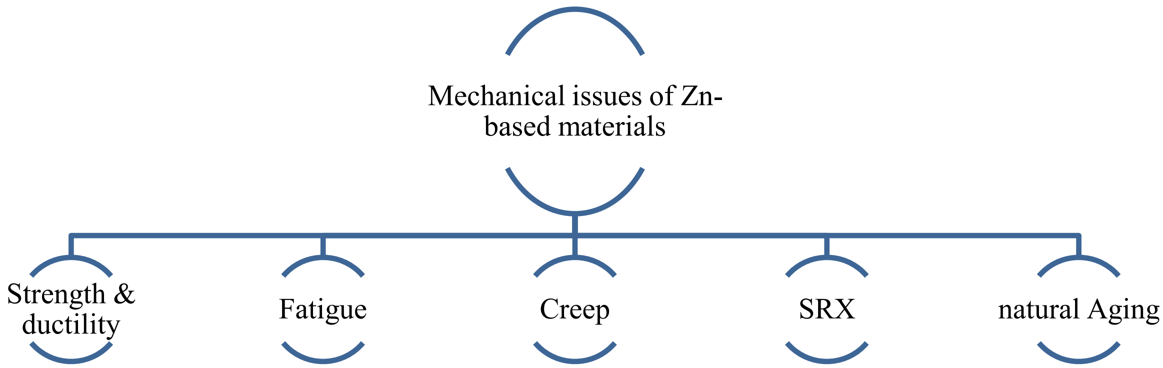


Figure 1. 7 applications of Zn biodegradable material [47]

Zn based biodegradable materials have gained so much focused for the applications of orthopedic because of their good combination of biocompatibility and moderate degradability. Their corrosion rate is between the biomaterial such as magnesium and iron. There is no creation of hydrogen gas during degradation process of Zn based alloys and they have a very low melting point. [47]The corrosion potential of zinc is -0.763V much higher than that of magnesium and low as compared to iron. In a system containing both magnesium and zinc the higher Mg reducing nature make it to lose electron and Zn on other hand is ready to accept these electrons. So in a system where zinc and copper present , zinc is able to lose the electrons allows copper to gain electrons [48] [41].

The disadvantage of using zn based alloys in orthopedic is their low mechanical strength i.e YS= 29.3MPa and ϵ of 1.2% while the modulus of elasticity is almost 94GPa. They also have relatively the lower creep resistance, high susceptibility, low temperature recrystallization low and fatigue strength which restricted its use in orthopedic applications and lead to the failure of biomedical devices during storage at room temperature (RT) [49]. In recent years, a lot of research has been done to fabricate Zn-based biodegradable alloys with improved biocompatibility, biocorrosion and high mechanical properties. The Zn alloys mechanical properties can be improved by altering their microstructure by alloying it with other elements like Cu and Mg [50].

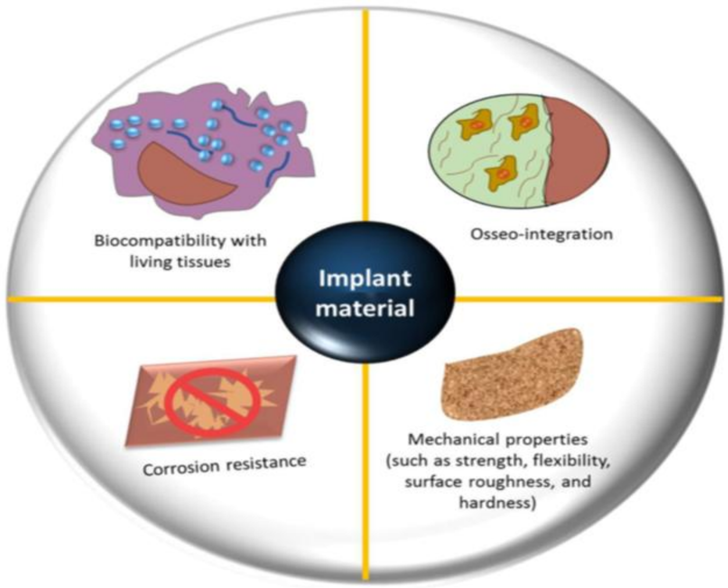


1.8 Room for research

The slow rate of deterioration of magnesium and iron, the zinc alloys has become an excellent choice to be used in orthopedic devices as they have ability to reduce the risks of implant failure in human body and proved to be helpful for bone healing process. However, the challenge faced by Zinc alloys in orthopedic devices is their poor mechanical properties as compared to other alloys. Therefore the choices of materials are considered to be very important in the field of orthopedics biodegradable implants as they have ability to directly impact the functionality and durability of the implants [51].

1.9 Requirements of orthopedics bioimplants

The basic requirements for biomaterials implant in orthopedics are the manufacturing and clinical properties of those materials. For the clinical criteria, the materials used for implant must have specific property not to be rejected by the human body nor it causes any harmful impacts on body cells. As far for the manufacturing criteria the material must have access for fabrication of configuration at optimum and affordable prices. [52, 53]. The conventional fabrications processes faced challenges to fulfill the bioimplants strict requirements related to complex structure, precision and novel materials. However, ongoing development in processing technologies discovered the manufacturing of very sophisticated bioimplants, and most of these technologies are immature and tentative. Researchers have focused their attention to the evaluation and measurements of implanted biocomponents due to increasingly demand of these implants into human body and also, they would be able to analyze the causes of these implants' failure. For suitable implants in orthopedics these multi-functional evaluation and the characterization technologies are essential [6] [54].



1.9.1 Mechanical properties

The requirements of mechanical properties for orthopedic implant materials are considered to be a crucial factor related to specifics working conditions and applications. The important mechanical properties required for implantations are the yield strength, the young's modulus, fracture toughness, ultimate tensile strength, elongation and resistance. The chances of implants failure and bone resorption increase, when young's modulus of material is the higher than that of bones of human because the stress transfer will be prevented to the adjacent. So the preferable implant materials are those who's young;s modulus is similar exactly to human bone [55, 56].

The fatigue strength is also an important factor to consider for the orthopedic implantation from point of view of the cyclic load sitting especially in the joint replacement of knees, ankles and hips. Additionally the wear particles releases during this process have ability to harm the body by entering into the surrounding tissues. [57]So the implant must be able to withstand stress without being degradable. These particles are then engulfed by macrophages, triggering the inflammation around the implant. Furthermore, implant fracture toughness would be sure to resist the crack propagation under the impact of load and also to improve manufacturability the certain elongation amount is required [58].

1.9.2 Biocompatibility

Biocompatibility is one of the most important feature s of the biodegradable biomaterials which are used in orthopedic applications. It is basically the ability of biomaterials to perform different desired functions in response to host in specific applications without causing any systematic or undesirable local effects on beneficiary or recipient of that host. It means that the any material or leach out products from it does not causes any cell death, inflammation, chronic or other impairment of cellular functions. [6]Materials consist of different properties such as the bioactive, biodegradable, bioinert and bioresorbable to obtain specific desired functions of the bioimplant in the body. The term bio manufacturing basically refers to the combined effect of life sciences and basic engineering to form product which is compatible to improved quality of life sciences [59].

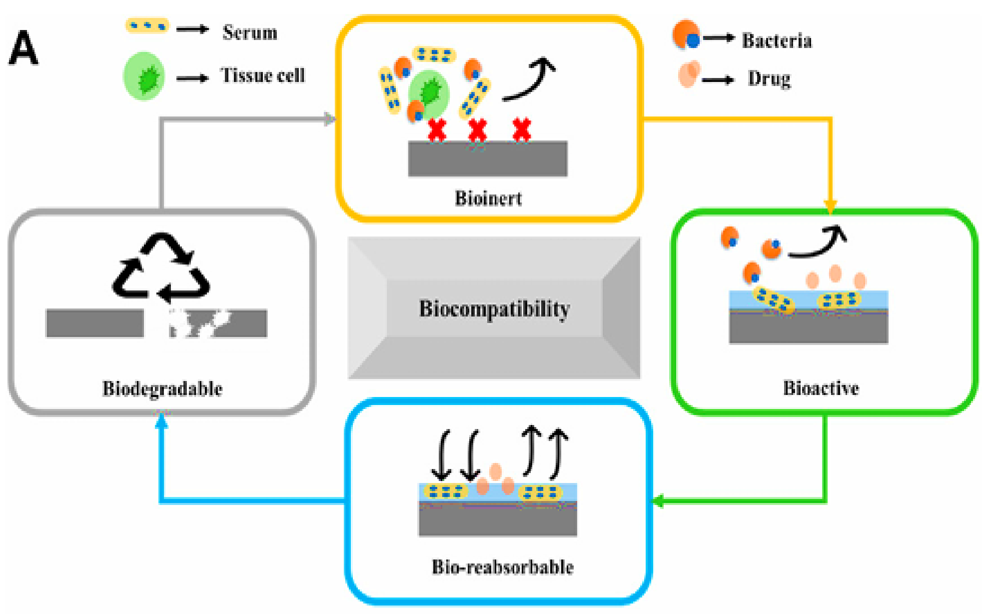


Figure 1. 8 diagrammatic representation of Biocompatible behavior [60]

Bioinert materials have ability to lower the foreign body reaction and immune reaction in the implanted area. On the other hand, the bioactive materials are manufactured to improve the cell behavior and the biological response [61]. The material potential to degrade without causing any toxic effects in the physiological environment is known as the bioresorbable material. So it is important to choose non-toxic materials for the fabrication of implant because excessive ions release causes inflammation at the site [8, 62].

1.9.3 Osseointegration

Osseointegration in orthopedic implantation is the direct functional and structural connection between the human bone and the surface of the load bearing implant. For permanent orthopedic implants, the implant ability to associated with the surrounding host bone, is another essential requirement. Insufficient osseointegration is lead to the formation of fibrous tissue and the loosening of the prostheses. [63] Many factors such as surface roughness, chemical composition, design, load conditions and the surface chemistry of implant are so essential for good osseointegration of implants. Osteolysis prevention is done through the surface integration with the adjacent bone. Sometimes, bond bonding's are not essential or sometimes there are required for the temporary short term devices because after healing process they would be removed [64].

1.9.4 Corrosion resistance

Corrosion is one of the important requirements for the implantation in orthopedics and the implants are design according to the body environments. The human body shows a very aggressive environment due to the (SBF) human body fluid which consists of different cations like the sodium (Na), calcium (Ca), potassium (K) and magnesium (Mg) ions and also the anions such aas the phosphate, Chloride ions, bicarbonate ions, protein, amino acids and the dissolved oxygen. The normal human body pH is normally 7.2-7.4, if this value decreased to the 3 then the infection would occur around the implantation after surgery and injury. Corrosion of implant materials would be accelerated by the acidification in the physiological environment.[65, 66] Some of the released degradation products proved to be toxic to human body such as the metallic Ni, Co and Cr ions.

Therefore, for the orthopedic implantation of biomedical materials the corrosion property is one of the essential requirements. For the biodegradable prosthetic implants, the degradation process has ability to reduce the structural integrity of the implants as a result of this premature failure and it needed the revision surgery. So the fabrication of implant materials with outstanding corrosion resistance is important to obtain expected long-term of that implant in human body. The biomaterials possess a controllable rates of degradation, and have a excellent potential as the temporary orthopedic implants due to their ability to perform suitable functions during the process of healing stage and then after healing completion they are not needed[67, 68].

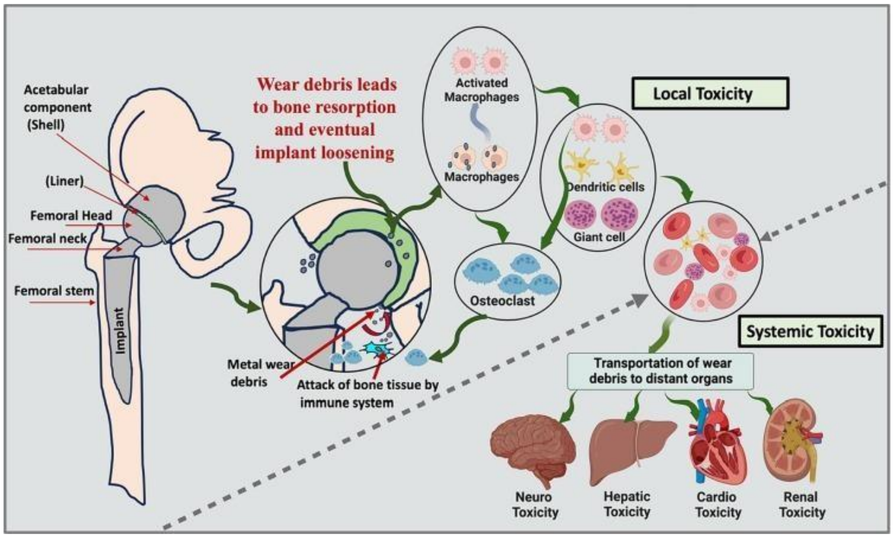


Figure 1.9 effects of wear debris [52]

1.10 Processing techniques in orthopedic

Selection of suitable manufacturing technique is very important in orthopedic biomedical implantation to obtain the desirable mechanical integrity and the desired grain size. The microstructure, corrosion rate and mechanical strength of the biodegradable metals highly dependent on the processing routes. Various fabrication techniques have been evolved to improve uniformity, refine the grain structure and tailor the degradation behavior. Here's the detailed discussion of different routes used for the manufacturing of various bioimplants for orthopedic applications. The most widely used techniques are powder metallurgy (PM), Casting, severe plastic deformation (SPD) and selective laser melting (SLM) [69].

1.10.1 Casting techniques

Casting is one of essential and conventional fabrication techniques used for the metallic alloys in orthopedic applications. In this technique, different metals and alloying elements are melted together and then poured into molds under different controlled conditions to solidify these materials. [70].Several alloys have been manufactured by this method. During the solidification, the composition control and cooling rate plays very significant role in examining the resulting grain size, microstructure, and intermetallic phase's distribution. They have a significant impact on alloy's corrosion and mechanical properties [71].

1.10.2 Severe plastic deformation (SPD)

SPD is a processing technology of thermo-mechanical material to achieve the alloys and metals with the outstanding properties to be used in different medical fields. one of the significant features of SPD is extensive plastic strains that is high deformation level applied to the material without causing the change in its overall shape. SPD has gained popularity over the years because of producing the nanostructured (NS) bulk materials and ultrafine grained (UFG) with high mechanical and impressive physical properties [72]. A variety of different SPD methods are investigated and produced such as ECAP, HPT, equal channel forward extrusion, friction stir processing and planar twist extrusion [73].

It is observed that in Zn based materials processed by SPD the exceptional grain refinement is obtained which enhanced the corrosion resistance and mechanical properties of them. However, the impact of severe plastic deformation techniques (SPDTs) on the tensile properties of Zn based alloys have not been determined until. The reason behind is the size of SPD processed samples are very small and pure Zn is soft at high strains because of dynamic recrystallizations. The research was carried out to see the impact of ECAP processing on Zn based alloys. The Zn-3Mg alloy was synthesized by ECAP, led to the grain refinement (GR) where the size of grain reduced from 48 the μm to 1.8 μm, and resulting a remarkable increase in ultimate tensile strength σ_{UTS} from 85 MPa to 220MPa and 1.3% to 6.3% ε increases, however the CR reduced from 0.3 to 0.24 mm/y. ECAP and HPT methods used by several groups of researchers for preparation of Zinc based alloys. [41, 47].

1.10.3 Selective Laser Melting (SLM)

Selective Laser Melting (SLM) is the revolutionary the additive manufacturing technology the enable the rapid production of metal parts directly from the metal powder. It was first proposed by the Fraunhofer Institute in the 1990s. SLM has the ability to allows intricate designs without the need for molds, thereby it would be able for reducing both production time and costs. [74].

SLM has gained the popularity to boasts or improve the superior mechanical performance comparable to traditional methods like forging, while achieving high-density and excellent surface smoothness in fabricated parts. Key aspects of SLM include its flexibility in design, improved material utilization, and advancements in processing parameters. The paper discusses common materials used, challenges faced by SLM, and the future prospects of this technology in innovative manufacturing.[75].

SLM technology works best on principles of using low temperature solid forming and high temperature melting of the metal, and to melt the powder metal the high-strength laser beam is being used which finally becomes cools and forms. The other advantage of using SLM is density of metal which exceeded up to 99% and the mechanical properties are equally important to the traditional process. While the poor surface roughness, the poor resolution and the residual internal stress are the major drawbacks of using SLM technology [76].

1.10.4 Powder Metallurgy (PM)

In the field of medical device manufacturing, powder metallurgy (PM) presents a compelling alternative to traditional methods for creating metallic biomaterials. Given their favorable properties such as the mechanical strength, ductility, and the biocompatibility, metals like titanium, stainless steel, cobalt-chromium alloys, and its alloys would dominate over 70% of implant medical devices, especially it was used in load-bearing applications. However, conventional manufacturing techniques such as the forging, casting, and milling are the material intensive and often they are extensive post processing techniques. In addition, powder metallurgy (PM) would be able to cost effective mass production of the complex parts with minimal secondary processing, allowing for adjustments in mechanical properties, surface characteristics, and with the porosity [77].

This adaptability is essential for increasing implant attachment inside host tissues and addressing concerns such as stress shielding. Optimizing the porous structures to support osseointegration, osteoinduction, and mechanical stability is one of the current focus areas. Other challenges are enhancing the ductility and fatigue strength of PM-manufactured components, which could lead to contamination issues that may cause embrittlement. Thus, initial powder purity is essential especially for delicate alloys such as nickel-titanium [78].

While PM has the potential to manufacture customized ferrous alloys and biodegradable implants, its focus has recently turned to additive manufacturing (AM) because of it's ability to produce advanced three-dimensional porous structures. Ongoing research works to enhance flexibility in implant design to satisfy particular mechanical and geometrical criteria, however AM methods are still constrained by material selection. Innovative advancements in customized medical implants could be made possible by the merging of PM and AM techniques [35].

Powder metallurgy is selected in this research work for manufacturing of alloys as PM has ability to synthesize the customized alloys. According to the requirements the porosity and dimensions of the alloys would be designed, because in orthopedics the implant porosity is essential in determining the mechanical strength, ductility and degradation behavior of the alloys. Moreover, this process as compared to melting is less expensive, and with efficient use of the material it causes minimal wastage of the material. The labor cost is also very low because of high degree of automation which improves the final product uniformity. So, the use of dies and molds with different dimensions causes the manufacturing of implants with desired features.

1.11 Selection of alloying elements

It has been understood from literature review that mechanical properties of Zinc based alloys have been improved by incorporation of other metals such as magnesium. The addition of Magnesium into the Zinc alloys causes the improvement of mechanical strength with formation of intermetallic phases such as Zn_2Mg_{11}. Also, magnesium is good material because of its biocompatibility which makes it the best choice to be used in Zn alloys.

The copper is selective as one of the essential elements for the Zinc alloying, because it possesses unique properties. In blood, it is present in trace amount approximately in range of 1.1 to 1.5 µg/ml. The incorporation of copper due to formation of phases such as $CuZn_4$ causes the enhancement of hardness of implant material. Copper also has ability to possess antibacterial property that’s why it is best choice for combating bacterial infections in body. It can inhibit the growth of bacterial around the implantation site.[79, 80]

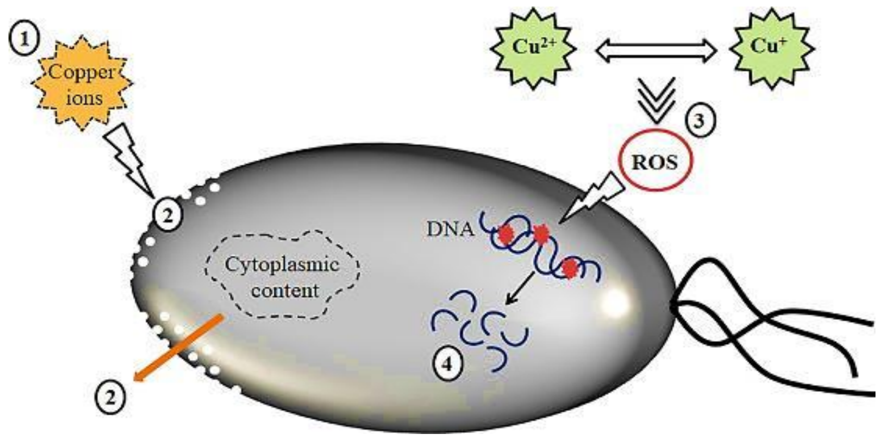


Figure 1.10 Antimicrobial nature of Copper [81]

1.12 Selection of methodology

PM is selected for the synthesis of alloys in this research work, as powder metallurgy is useful in the preparation of customized alloys such as their properties would be easily manipulated.

The porosity and dimensions such as length and width would be designed according to desire that make this technique different from others. In pediatric orthopedics applications, implant porosity is very essential factor in analyzing its activity like effective to the penetration of bacterial in terms of its degradation behavior and strength. The density of material will be enhanced from the compaction of desired powders [82]

Moreover, the powder metallurgical process is very less expensive than the melting because the further processing like the wrought is not recommended to make the alloy even more stable. This is associated to the efficient use of the materials with the minimal waste. Furthermore, the high degree of the automation in powder metallurgy can reduces the labor costs and improved the uniformity of desired final product. Additionally, this technique is enables the production of the intricate shapes that unattainable with the older methods. The use of the molds and dies in this process will facilitates the synthesis of complex shapes, and allowing for the manufacturing of the implants with intricate features. [83]

Chapter 2

Literature Review

The objective of this chapter is to present the comprehensive review of background knowledge and scholarly literature essential for the field that is being investigated. This chapter provides essential ideas that are necessary for this study a wall as recent research about manufacturing and characterization of the biodegradable biomaterials implants that are composed of especially zinc, magnesium and copper elements for their application in medical field as an implant device. Also, this chapter analyzes applicable commercial applications that are associated with these topics. By examining the recent current academic studies and the commercial patent, this research work will provide a firm groundwork of the relevant material to address the originality and importance of the conclusions of the inquiry.

Zinc is a chemical element of periodic table with Z=30, its molar mass is 65.39g/mol and a density of 7.14 g/cm^3. Its melting temperature is in range of 419.5 °C, and it shows the +2 as its oxidation state. After iron, aluminum and copper it is the one of most used metals in the world. As compared to other metals such as magnesium, it is less reactive because it has ability to loses two of its electrons and the remaining 18 electronic shells making it more stable as compared to other. it possesses closed-packed hexagonal crystal structure while the transformation of α-Zn to β-Zn is possible at 13.2 °C. Since 2016 the production of Zinc in worldwide is almost 14 million metric tons. For engineering purposes and medical field Zinc and its mixtures are applied in a wide range of configurations as a structural element. Nearly half of the total global zinc consumption is applied as coatings for safeguarding the components of steel against corrosion [26].

Zinc used for the production of zinc-based alloys worldwide and its approximate consumption is up to 15% that used in biomedical field for different applications. These zinc-based alloys would be synthesized by high fluidity and low melting points that help them to be used for foundry applications. They are synthesized by high pressure die-casting hot chamber where they can be casted to thickness as low as approximately 0.13mm. The zinc alloys fabricated by die-casting possesses the good mechanical properties which allow them to be used in variety of functional applications. Zinc alloys can also be synthesized by different methods such as gravity, cold chamber die-casting and sand casting, slush casting and spin casting depending upon the alloying elements and purposes.

Research was carried out to fabricate biodegradable biomaterials that are used in medical field without causing any harmful impact to human body. This concept of using biodegradable biomaterial reduces the limitations of the traditional non-biodegradable implants such as stents used in coronary vessels causes' permanent tissue irritation. So the purpose of this research was to synthesize stent that is made of the material which does not cause any harmful effects to human body and obtaining the best biocompatibility. The materials used for synthesizing these alloys are Zinc, magnesium, zirconium, tantalum and zirconium that possess the good mechanical properties and also enhance the bioresorability. The addition of soluble components such as iron, manganese, potassium, sodium, calcium, and lithium enables the uniform corrosion, further improving the safety and effectiveness of the stent [84].

Zinc-based alloys due to their remarkable mechanical properties were used in implantation of cardiovascular stents because they have moderate corrosion rate as compared to magnesium which shows rapid rate of degradation which is not suitable to implantation. Their mechanical properties were negatively be affected by the presence of intermetallic phases that are present in the zinc-based alloy. This effect was resolved by the extrusion, insertion and homogenization of other suitable metals. For the purpose of stents usage, the optimal rate for alloys degradation was 9.41 ± 1.34 μm per year would be acceptable that is showing their potential to be used in medical applications. The elongation of extruded alloys, the (YS) and ultimate tensile strength are observed $51 \pm 2\%$, 250 ± 10 MPa, and the 270 ± 10 MPa respectively. The present research shows that slow degradation rate, excellent strength, good biocompatibility an ductility was indicated as using extruded Zn-Cu alloys [85].

Powder metallurgical technique is used to synthesize the zinc-based alloys. The ball milling process with low speed would be used for the uniform and unique dispersion of initial powders. After process of extrusion the finer grains would be results from the use of slow speed ball milling. Very small size grains are produce using high speed solicitation and in grain boundary there is continuous distribution of secondary phases. In this study the better corrosion resistance would be achieved by using low amount of zinc in alloy if they are treated in PBS solution [86].

Melt casting process would also be carried out for the synthesis of Zn-3Cu-xMg based alloy for orthopedic applications. The intermetallic phase i.e., Mg_2Zn_{11} that are formed in this alloy would be overcome by the concentration of magnesium and its concentrations has direct impact on these phases. The in vitro corrosion rate and biocompatibility would be enhanced by using these alloys. The high yield strength would be achieved by these intermetallic phases but there is also a high rate of degradation which made it not suitable for the implantation in field of biomedical [87].

In this study Krystynova and her team synthesized the zinc alloys using powder metallurgical technique with using different ratios of powder of particle sizes. Cold pressing was used to increase the binding between atoms and capable of improving the mechanical integrity. OM was used to analyze microstructure of prepared material or alloys and Vickers microhardness testing was used to analyzed mechanical properties of alloy. It was observed that the particle size has prominent impact on compacts mechanical properties. The toughness and strength of zinc powder Zn150 was greater than zinc powder in range of Zn7.5. These findings in this study showed that selection of appropriate powder size for alloy preparation using metallurgical processing technique is necessary [88].

Zn magnesium alloys were synthesized by Xiao and their team for permanent orthopedic implantation in the load bearing applications. They studied in vivo and in vitro degradation in their research with controlled amount of pure zinc. The process followed by extrusion melts the alloys at temperature of 500°C. The research showed that the ultimate tensile strength and elongation would be improved to 225MPa and 26% by addition of magnesium in these alloys respectively. The degradation rate is these synthesized alloys are near about zinc alloy. In vivo study analysis showed that these alloys are non-toxic to cells and they do not have any harmful impact on living organisms [89].

The alloy of Zn-3Mg-1Ti was synthesized by the treatment of ultrasonic of Zn-Mg alloy melting using the ultrasonic radiation rod of Ti. The mechanical properties, degradation property, microstructure, phase structure, and the in vitro cytotoxicity were examined by systematically. The fabricated Zn-3Mg-1Ti alloy is basically composed of the Zn, TiZn16 and Mg2Zn11. The mechanical properties of Zn-3Mg-1Ti alloy would be enhanced having the grain refinement and due to reinforcement of second phase. In addition, the Zn-3Mg1Ti alloy would also shows minimal cytotoxicity as compared to Zn-1Ti alloy and pure Zn. Electrochemical tests showed that the alloys of Zn-3Mg-1Ti has an appropriate degradation rate in Hank's solution [90].

In this study conducted by Kalowole M and colleagues synthesized Zn-xMg alloys using powder metallurgical technique. This process involved milling the alloys of Zn-xMg at 350 rpm for four hours while using the zinc stearate and silicon oil based lubricant slurry. The pellets would be delubricated after compressing powder at 300 MPa for about three minutes and then these pellets were sintered for 3 hours. The studied showed that mechanical properties of alloys of Zn-xMg based such as their hardness (93%), strength (111%) and elastic modulus (93%) using this techniques [91].

Biodegradable zinc (Zn) based biomaterials synthesized to be used for applications of orthopedic because of their suitable biodegradability. The pure Zinc possesses the poor mechanical property and has reduced bio functionality that restricted its application to be used in biomedical field. Research was carried out to synthesize the Zn based alloys especially Zn-Mg-Cu to improve the the zinc matrix mechanical strength and allows the alloys with excellent antibacterial activity. The addition of Copper (Cu) to the Zn-3Mg-Cu alloys has been studied to investigate the effects on biocompatibility, corrosion behavior and antibacterial activity. In vitro immersion test showed that the Zn-3Mg-1Cu showed the increase in rate of corrosion of 0.0504 mm y^{-1}. The MC3T3-E1cells relative cell availability was over the 70%, the co-culture with the 2-fold diluted extracts of the Zn-3Mg-xCu alloy for 3 days, which is indicating the acceptable cytotoxicity. The Zn-3Mg matrix antibacterial activity would be improved by Cu addition and Zn-3Mg-1Cu alloy also demonstrated the highest inhibition zone diameter (IZD) values in range of 6.0 mm and 10.4 mm against the E. coli, and S.aureus respectively. So, it was proved that the Zn-3Mg-1Cu based Zn alloys are the best and suitable biodegradable orthopedic biomaterial with favorable degradation behavior, the substantial antibacterial activity and the satisfying biocompatibility.

Research was also conducted for improving the mechanical properties of Zinc alloys by adding the other metal like silver from 2 to 7%. The method used by researchers was casting technique which is followed by the extrusion and homogenization to synthesize the alloys of Zinc and silver. The results exhibited that by enhancing the silver content from 2 to 7% generally enhanced the mechanical properties of the alloys even without effecting its ductility. Specifically, the alloy of Zn-7Ag demonstrated the (UTS) ultimate tensile strength = 287 MPa and YS = 236 MPa because of the precipitation of $AgZn_3$ during the process of extrusion. However, it was observed that high level $AgZn_3$ precipitation would have also increased the cell formation micro-galvanic and also the corrosion behavior of the alloys would be improved [21].

the research was carried out, to understand the impact of ECAP process on zinc alloys. Melt casting process was used to synthesize the Zn-0.5Cu and then they were subjected to the process of annealing at temperature of 400ºC for 4 hours for the experiment. After four hours, the pellet would obtain the required plasticity. The results from these reactions demonstrated a well-known reduction in the size of microstructure ranging from 0.56 mm to 0.001 mm. additionally; it was observed that the maximum elongation of 510% was achieved at a $0.0001 s^{-1}$ strain rate. It was observed that the elongation reduces with decreased in the strain rate $0.0001\ s^{-1}$. These results shows that ECAP has the ability to enhance the zinc alloys mechanical strength [92].

A study was conducted on synthesizing the alloys of zinc magnesium in which magnesium was added ass alloying element (Zn-0.05%Mg). The melting process was used to synthesize alloys at a temperature of 500°C which is followed by extrusion. Their research demonstrated that the inclusion of magnesium to the alloys sufficiently enhanced the UTS and the elongation fracture values to the 225MPa and 26% respectively. The degradation rate of these Zn-Mg alloys was observed to be closely to that of zinc alloy (0.15mm/y). Moreover, the in vivo studies were also be conducted on these Zn alloys proved that they are non-toxic to human body cells and do not cause any harm to the living organisms [89].

Powder metallurgy technique was used by researchers to develope a alloys zinc-magnesium in which concentration of magnesium varied such as (Zn-1Mg, Zn-6Mg, and Zn-16Mg). The powders were milled using ball milling machine at 800 rpm/min for approximately 2 hours, while also the stearic acid was used to prevent the agglomeration of powders. The SPS technique was used to perform the compaction process under an atmosphere of argon. The sintering was done by setting the temperature 300 ºC, with a heating rate of 10 ºC/sec and with 19.1 MPa pressure. The use of SPS technique demonstrated the synthesis of Zn alloys with ultrafine microstructures, which is ranging from 100-500 nanometers. The formation of intermetallic phases such as the Zn_2Mg_{11}

would have contributed to the high compressive strength of 327 MPa obtained and hardness of 86HV1 would be observed [93].

In the study, the ECAP process was used to enhance the properties of alloys of Zn-Mg for applications of orthopedic. It was observed that the size of grain of alloys reduced ranging from 48 µm to 1.8 µm, which was related to formation of the dislocations. In addition, the study showed that the process of ECAP also decreased the degradation rate from the 0.0075 mpy to 0.006 mpy. This decrease was related to the fine grain structure, which would be able to provides some active points for degradation [94].

A scientific study was conducted to synthesize the alloys of zinc using the powder metallurgical processing by utilizing different powders with the different particle sizes. Cold pressing has been performed to increase the binding between the atoms of powders and it would improve the mechanical integrity. Significantly, the mechanical strength and toughness of the Zn150 powder was greater as compared to the Zn7.5 powder. The toughness was observed 148 MPa for Zn150, while it was decreased to the half for Zn7.5 alloys. These results showed the importance of selecting suitable powder size during the powder metallurgical processing for the synthesis of zinc alloys [88].

In a study conducted by the researchers, powder metallurgical processing was used to fabricate the alloys of Zn-Fe. During the compaction process, a 500 MPa pressure was applied, and for two hours sintering was carried out at 320°C, which is followed by extrusion. It was understood that the grain size was decreased because of extrusion. The degradation behavior was observed to be alleviated after extrusion because of an increase in the surface energy on grains. Cell viability tests was performed and it was observed that cells exposed to the 12.5% and 25% extract solutions that were compatible with the cells, but the exposure to the extract solution of 100% showed up to 40% of the cell cytotoxicity [95].

A group of researchers studied out to understand the mechanical properties of Zn-xCa alloys, with varying calcium concentrations such as (x = 0.5, 1, 2, and 3%). They observed that strength and hardness of these Zinc alloys enhanced, as the calcium concentration increased, which is surpassing that of pure zinc. Moreover, the alloys would also be exhibited the higher levels of corrosion, which negating the improvement in performance of mechanical behavior. The most suitable option was the Zn-2Ca alloy, which showed better results in terms of mechanical properties and degradation [96].

In this work, high-strength alloys of aluminum were synthesized by cold isostatic pressing, the hot extrusion, sintering, and the heat treatment using the Al-Zn-Mg-Cu powders containing the 0.15 and 0.33 weight percent oxygen. The transmission electron microscopy (TEM), Scanning electron microscopy (SEM), high-temperature tensile tests and electron backscatter diffraction (EBSD), were performed to check the microstructural and mechanical characteristics at increased temperatures of 250, 350, and 450 °C. The fabricated Al-Zn-Mg-Cu alloys with 0.15 weight percent of oxygen had the tensile strengths of 185, 46, and 18 MPa at the temperature of 250, 350, and 450 °C, respectively, according to the results. Tensile strengths at the estimated temperature enhanced to 205, 68, and 25 MPa, respectively, when the oxygen level of the Al-Zn-Mg-Cu alloy reached 0.33 weight percent. The superior performance at optimum temperatures could be described to a significant nano y-Al2O3 amount to produce by the increased oxygen which causes double obstruction to the dislocation motion and the grain boundary migration, which is leading even at high temperatures in tiny grains [97].

A researchers developed the alloys of Zn-xNi in which concentration of nickel varied such as (where x = 0, 5, 10, 15, 20) utilizing the non-conventional method for their potential use in the biomedical field applications. The alloys were fabricated by mechanical alloying at a 200-rpm speed for approximately 4 hours. Subsequently, the Zinc and nickel powders were compacted at pressure of300 MPa and sintered for 60 minutes at 375℃ under the atmosphere of nitrogen. It was observed that the intermetallic phases were then only activated after the process of sintering because of the low milling time. It was observed that the inclusion of nickel proceeds to a enhancement of intermetallic phases, while concurrently it would be decreasing the density of these alloys. Among the various alloys, Zn-5Ni showed the highest densification at the 90.3% [11].

The research was conducted to observe the mechanical and microstructure characteristics of zinc and zinc alloys with Ag, Cu, and Mn additions (0.5 atomic percent) using the equal channel angular pressing (ECAP). For every material, four ECAP Route BC passes were carried out at room temperature. The characteristics of the examined materials following ECAP were contrasted with those of their coarse-grained counterparts produced by the process of indirect hot extrusion at 300°C. The alloy with the Mn addition showed the strongest strengthening effect. Following ECAP, the mean grain diameter in materials is less than 3.2 μm for alloys and equal to 20 μm for pure zinc.

All fine-grained materials showed an increase in plasticity that was dependent on strain rate; the Zn-Cu alloy showed a maximum elongation of 510% following ECAP. Following ECAP, grain refining did not improve the alloys' yield or ultimate tensile strength. Tensile characteristics following ECAP were 20–60% lower in all examined materials than in the hot extruded samples. The alterations in the primary deformation mechanisms were taken into consideration based on the tensile characteristics, texture analysis and microstructure. It was shown that the primary parameters influencing twinning, non-slip and slip, deformation mechanisms, which lead to significant variations in observable mechanical characteristics, are the crystallographic grain size and texture [98].

A study conducted on alloy Zn60Zr40 that was fabricated using a process which is called SLM that was supported by the mechanical alloying. During this study, it was observed that the mechanical alloying was resulted in the induction of transformation of amorphous in these zinc alloys. This was because of the atomic sizes difference and due to the negative heat of mixing. The amorphization phenomenon enhanced with an increase in the time of milling. On the other side, SLM showed in the restriction of the atomic diffusion of these amorphous powders [74].

A study conducted on Zinc-based metals that are useful for the biodegradable medical implants, but synthesizing pure zinc alloys with laser powder bed fusion (L-PBF) process has been difficult. Because boiling point of zinc is a low, it can evaporate quickly during the laser melting, that has effects on quality of printed parts. Previous studies that were used showed that they had very small processing windows and the poor results. In this research, a superficially designed gas flow system was used to decrease the evaporation of zinc. Simulations would have helped to understand that how the gas moves and they interact with fumes of evaporation. By enhancing the gas flow and then also adjusting the laser energy, the researchers then produced zinc parts with the very high density of approximately 99.90%. The roughness of surface was around to be 10 μm, and then sandblasting enhanced it to 4.83 μm. The study then explains that how gas flow and the laser settings impacts the quality of parts. This method would also help in printing the other metals which evaporate easily, like aluminum and the magnesium alloys [99].

The researchers studied a zinc-based alloy composed of Zn-1Mg-xSr to explore its potential for biomedical applications. They synthesized the Zn-Mg-Sr alloy using the gravity casting and then performed many tests to understand its mechanical properties and the biocompatibility. The findings that are obtained exhibited that the Zn-Mg-0.1Sr alloy had significantly better mechanical strength such as ultimate tensile strength, yield strength, and the hardness than pure Zn. Moreover, its blood compatibility that tested in vitro and the elongation were slightly lower. Even so, the alloy still meets the essential requirements for use as a biomedical implant [100].

In-depth study was conducted on the alloying Zn with Mg, Ca and Sr. They manufactured the alloys from process of rolling and extrusion after preparing it from simple casting. It was observed that the mechanical properties of the Zn-Mg-Sr was sufficiently better than the pure zinc and the other alloys. The alloys proved that the enhanced cytocompatibility and the effective resistance to deformations and dislocations, making them useable for different industrial applications [101].

The study conducted on utilized an induction of furnace to produce the Zn90-Mg8.5Ca1.5 alloys and understand its biocompatibility. The research provedd that the addition of Ca and Mg significantly impacts degradation behavior of the Zn alloys. Zn90Mg8.5-Ca1.5 was corroded uniformly in stimulated body fluid (SBF), as compare to pure zinc that displayed the localized corrosion holes or pits. This research showed the potential of the alloying to control the degradation behavior of zinc alloys, which make them more suitable for applications of biomedical [102].

A study was carried out to produce a Zn-3Mg-1Ti alloy by adding titanium (Ti) to molten Zn-3Mg. The results showed that the alloy became less plastic as the grain size decreased. Its corrosion rate was found to be 78.5 μm/year, and further the tests confirmed that the alloy is suitable for biomedical implants due to its good biocompatibility. Inside the alloy, the TiZn6 phase acted as a sacrificial anode, protecting the zinc and reducing the amount of zinc ions released into surrounding cells. Cytotoxicity tests also confirmed that the alloy is safe and does not cause harmful effects on living cells [90].

A study conducted to produce a Zn-Cu-Ti alloy using the process melt casting. The microstructure analysis proved that CuZn5 phases were mainly located along the boundaries of grain. After hot rolling process, the mechanical properties enhanced significantly, with the yield strength (YS) increasing by 2.7 times and the (UTS) ultimate tensile strength increasing by 2.4 times. The alloy exhibited a rate of corrosion of 0.029 mm per year after the 30 days of testing, indicating good stability. It also showed better wear resistance in the cast form compared to extruded samples. In biocompatibility tests, the alloy's extract at a 12.5% concentration showed no toxic effects on cells, suggesting its safety for potential biomedical use [103].

A study conducted to compare the mechanical properties of alloy of Zn-0.5Al-0.5Mg-xBi and Zn-0.5Al-0.5Mg. The research proved that the coupling presence between the zinc matrix and Mg_3Bi_2 resulted in a decrease in the degradation behavior of the quaternary alloy as compared to the ternary alloy. In addition, the cytotoxicity test showed that a high concentration of bismuth has a toxic impact on cell growth, but despite this, the alloy was found to be biocompatible [104].

The study conducted to examine the properties of alloy of Zn-Al-Cu-Li manufactured through casting process. The process resulted in the formation of many phases that is including the LiZn4, rich zinc η and CuZn4 phase that improved the mechanical integrity of the implant. The Zn-2Al-4Cu-0.6Li alloy showed impressive results among the different compositions. It demonstrated an ultimate tensile strength (UTS) 535 MPa and a strain Ɛ = 37%, that is similar to the commercially available (Ti) titanium alloys. In addition, the moderate rate of degradation is 8.5 µm/year, which controlled by making it more suitable for the applications of implant [105].

A study was conducted to produce the properties of the Zn-1Mg and Zn-1Mg0.5Ca alloys for applications of biomedical. These alloys were manufactured by using the process of die-casting at the temperature of 600 ºC with the pressure of 180 tons. The Microstructure analysis would have revealed that the binary alloy proved the good corrosion resistance because of the presence of intermetallic phases the Zn_2Mg_{11} phase. On the other hand, the ternary alloy would be developed by micro galvanic pits because of the $CaZn_{13}$ phase. In addition, the cytotoxicity test would be indicated that the presence of metal like calcium (Ca) makes it to non-toxic and suitable for the use as an implant material [106].

Powder metallurgy (PM) was also be utilized to produce the alloy of Zn-1Mg-0.8Mn-0.8Ti alloy.

During the milling the toluene was used. The powders were then mixed at 350 rpm for the 16 hours and then compaction was also be carried out at pressure of 400 MPa. The pellets that produce were sintered at temperature of 375ºC for two hours. The sintered disks that produce were then dipped in solution of MWCNT for 4 hours and subsequently it placed in a furnace for 3 hours and 20 minutes at 95ºC. The results would be indicated that the inslusion of 1% Mg, Ti and 0.8% Mn significantly enhanced the CS of the alloys. The CS values achieved were 218 MPa, 215 MPa, and 177 MPa, for the respective alloys. Zn-1Mg-0.8Mn showed the most highest properties which is required for bioimplant applications [7].

Chapter 3

Materials and Methodology

Materials

3.1 Chemical required:

Zinc (Sigma Aldrich, Assay ≥ 99.9%), Magnesium (Duksan, Assay ≥ 99.9%), Copper, Zn Stearate (Sigma Aldrich) and silicon oil for die lubrication, distilled water, 100% and 70% Ethanol and chemicals for SBS (stimulated body fluid). These SBS chemicals include NaCl (8.035g), KCl (0.225g), $NaHCO_3$ (0.355g), $MgCl_2$. H_2O (0.311g), $K_2HPO_3.3H_2O$ (0.231g) ,1M HCl (4—50mL), Na_2SO_4 (0.292g), $CaCl_2$(0.292g), Tris Base (6.118g), Diamond suspension, acrylic powder.

Table 3. 1 chemical composition of used Metallic Powders

Sr No	**Metallic Powders**	**Density g/cm^3**	**APS (µm)**	**% Assay**	**MP (°C)**
1	Zinc	7.133	44	≥ 99.9	>300
2	Magnesium	1.74	-	High grade purity	648
3	Copper	8.94	74	99.8	1083.4

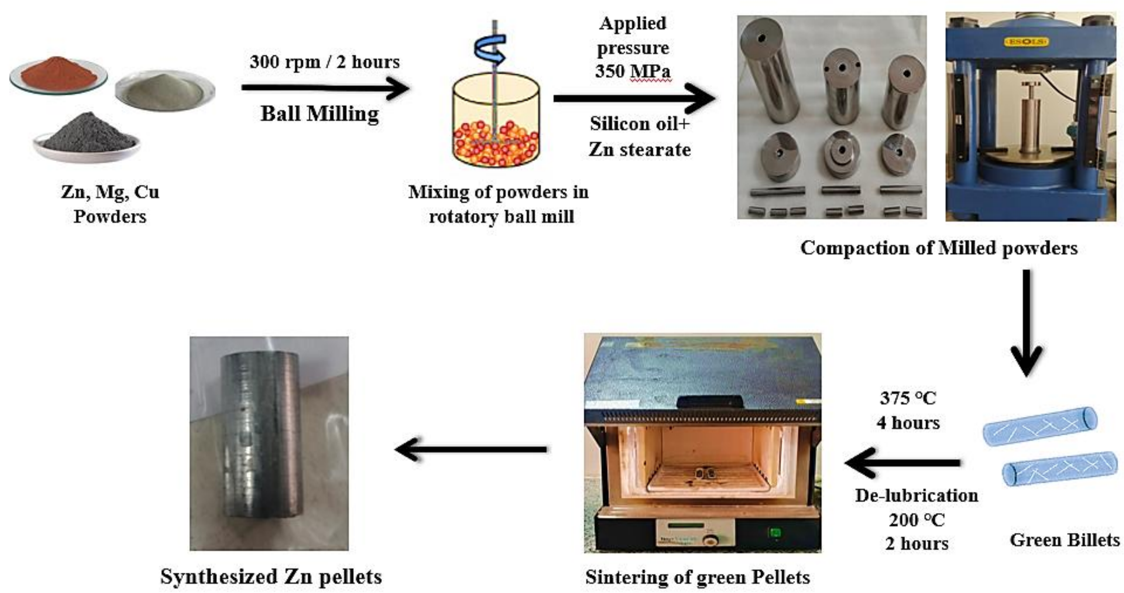
3.2 Instrument and Glassware Required

Ball milling, Laboratory compaction press, Furnace (Vulcan Electric Furnace), Grinder and

Polisher, Diamond cutter/ Micra-cut 152(Metkon), Vernier Caliper, Weighing balance, Hot plate(Corning PC-4200), pH meter, Incubator, Sonicator (WiseClean), Grit paper/ sands paper (320, 100, 1500,3000), polishing pad, Pipette (10 mL), Foroceps, Spatula, Beakers (250mL, 500mL, 1000mL), measuring cylinder (50mL, 100mL, 250mL), Magnetic stirrers, Falcons (50mL, 15mL).

3.3 Methodology:

The methodology of synthesizing the pellets is involved three major steps. The detail of each step is mention below:



3.3.1 Mechanical alloying of Metal Powders:

For the preparation of Zn-Mg and Zn-Mg-xCu (x=0.5, 0.1,1,2,3) alloys from powders of Zinc, Magnesium and Copper the accurate weight of each powder is required. A weighing machine was used with accuracy of 0.001g to measure the required weight. The percentage compositions of each metal vary that are listed in table 3.2.

Table 3. 2 Zn, Mg and Cu percentage Composition

Sr#	Zinc (weight %)	Magnesium (Weight %)	Copper (Weight %)
1	97.5	2	0.5
2	97.1	2	0.1
3	97	2	1
4	96	2	2
4	95	2	3

An accurate mass of 11.20 grams was carefully weighed using an electronic balance in which concentration of each metal of zinc, Magnesium and Copper varied to make pellets of d=10mm and height h=20mm.

Sr#	Zinc (Mass in grams)	Magnesium (Mass in grams)	Copper (Mass in grams)
1	10.92	0.224	0.056
2	10.8752	0.224	0.0112
3	10.864	0.224	0.112
4	10.752	0.224	0.224
4	10.64	0.224	0.336

After weighing accurate mass, the powders were placed into an aluminum ball mill jar for proper mixing. The ball to powder ratio (BPR) was 10:1 utilized. Different balls sizes such as 40% large balls, 35% medium balls and 25% small balls are used for good mixing and grinding of powders. The powders were then mixed homogenously with the help of rotatory ball milling for two hours running at speed of 300 rpm. The direction of rotation of rotatory ball mill was changed every 10 minutes between anticlockwise and clockwise direction. During the ball milling process did not any additives were added into the powders to prevent agglomeration and ensure final product purity.

3.3.2 Compaction of powders

The walls of die meticulously lubricated before the compaction process with the fine slurry of silicon oil and zinc stearate and they were mixed in a precise ratio of 1:1. This lubrication of dies ensures that powders were efficiently and smoothly compressed. Using applied pressure of 350 MPa for 5 minutes, a green compacted pellets with a h=20mm and d= 10mm was produced by addition of milled powders to laboratory compaction press. The compressed pellets were then ejected upward slowly by applying pressure of 100 MPa. Afterwards, in zip-lock bags green sintered pellets stored and then these bags were put in glass vials to avoid any contamination.

Figure 3. 1 different dies used for compaction

3.3.3 Sintering

The sintering of green compacted pellets was done by using a Vulcan furnace. The lubricant that was applied during compaction on walls of dies need to be removed before sintering. To do this the compacted billets were placed in crucible and then put in Vulcan furnace. The Vulcan furnace was heated for 2 hours at temperature of 200ºC, with the heating rate of 20 ºC per minutes. The samples after delubrication were sintered for four hours at 350ºC temperature with gradually increasing temperature at the rate of 20ºC per minutes. After that the samples were set to cool down manually and then placed in desiccator.[91]

Figure 3. 2 Vulcan furnace with green pellets

Table 3. 3 Different parameters for Alloys synthesis

Composition	Mechanical alloying	Compaction	Sintering
Pure zinc	The optimized ball milling parameters were used for example 300rpm for 2 hours	Optimized parameters were applied for 5 minutes with applied pressure 350MPa	Optimized sintering parameters were used for 4 hours at 350 ºC with 20ºC per minutes

Zn-2Mg-xCu (x=0.5,0.1,1,2,3)	The optimized ball milling parameters were used for example 300rpm for 2 hours	Optimized parameters were applied for 5 minutes with applied pressure 350MPa	Optimized sintering parameters were used for 4 hours at 350 ºC with 20ºC per minutes

3.3.4 Samples preparation

The sintered pellets were then cut in disk shape using Diamond Micracut 151 (Kemet International) with the thickness of 1.5 mm and diameter 10 mm. These samples were then grinded using grinder with 320-grit paper until a smooth surface was revealed. After grinding till 1500-grit paper the final surface area was fixed to area of 1.25cm^2. Finally, the pellets after cutting were thoroughly cleaned while using distilled water and Ethanol (DW & C_2H_5OH) to ensure the complete removal of any contaminants on surface of discs.

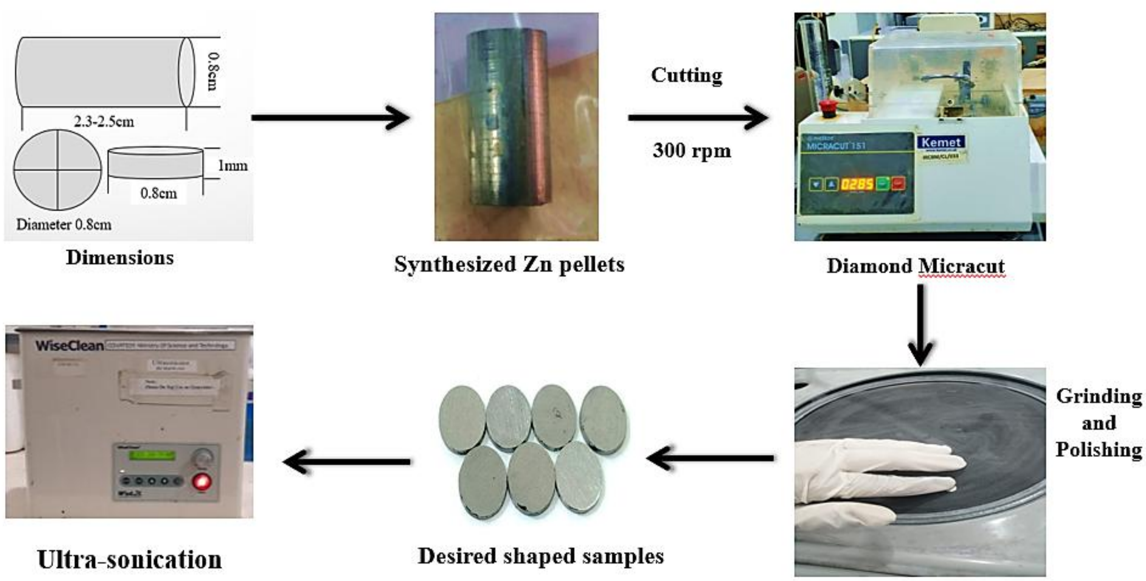


Figure 3. 3 Diamond Micracut , grinder and polisher and samples Disk

3.3.5 Green and sintered Density

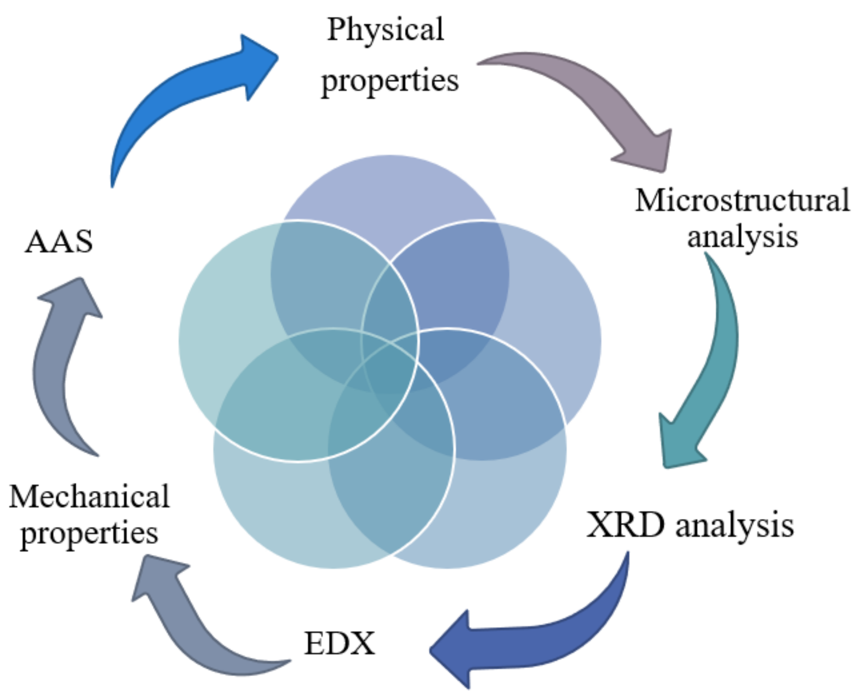
The average green and sintered density of all the pellets of Zn and Zn-2Mg-xCu were measured using the standard ASTM. Weight of each pellets were measured in grams using the electronic weighing balance . with the help of Vernier Caliper the radius (r) and Volume (V) of each pellets were measured. After that the green and sintered density of each pellets were measured by usng the following equation. Procedure were repeated by three times and then average were observed for the graphical representation.

$$\rho = \frac{W}{V}$$

Figure 3. 4 Measuring dimensions using Vernier Caliper

3.4 Characterization

When Zn based alloys are synthesized, the next step is to do a characterization of these synthesized alloys to observe their characteristics.



3.4.1 EDX:

EDS is required in order to analyze in detail, the surface features of Zinc, This technique give information or in-depth analysis of behavior of the electrons as they are directed towards the flat surface. The samples were prepared by cutting the disc into diameter (d) = 10mm and height (h)=1.5mm and then polishing these discs using polisher pad. For EDS and Maping of samples the discs were mounted using acrylic powder by ECO-press machine. After that the polishing of mounted samples were done using diamond suspension of 3 and 6 Micron. The analysis of samples was conducted using a Vega3-XMU Tuscan SEM. A voltage of 20 KeV was applied to the samples, and images were captured for further study.

Figure 3. 5 (a) ECOPRESS for sample mounting, (b) Mounted samples

3.4.2 SEM

The microstructure of the prepared Zinc alloys was analyzed using Scanning electron Microscopy (SEM). This technique used to analyze the electron behavior as they are directed towards the surface flat surface. An SEM technique known as Vega3-XMU Tuscan SEM are used. A voltage of 20 keV was basically applied on sample surface and the images were captured for studying microstructure of samples[107].

Figure 3. 6 SEM Instrumentation

3.4.3 XRD

Samples of Zinc, Mg and Cu in powder form after ball milling are basically characterized by utilizing the rapid and non-destructive spectroscopic technique which is known as PXRD. Each particle of powders behaved like the single crystalline in the powdered samples and they oriented randomly. By using the powder X-ray diffractometer, different peaks are scattered. Because of presence of d-spacing ‘s they provide diffractograms in the crystal. These peaks intensities of each powder help to give the basic information about the morphology and structure of powdered sample. The samples are analyzed with the help of crystallographic elements by using PXRD. To analyze the sample purity the PXRD would also be applied

3.4.4 Mechanical Properties

Mechanical testing method performed by using Ultimate Tensile Strength (UTTM) to check the compressive strength at room temperature. The samples compressive strength were analyzed in accordance with the ASTM E9-09 standard procedure with the strain rate of 10^{-3} s^{-1}. The dimensions of sample were in diameter (d)=10 mm and height (h)= 5 mm. The test for each sample was performed in doublet.

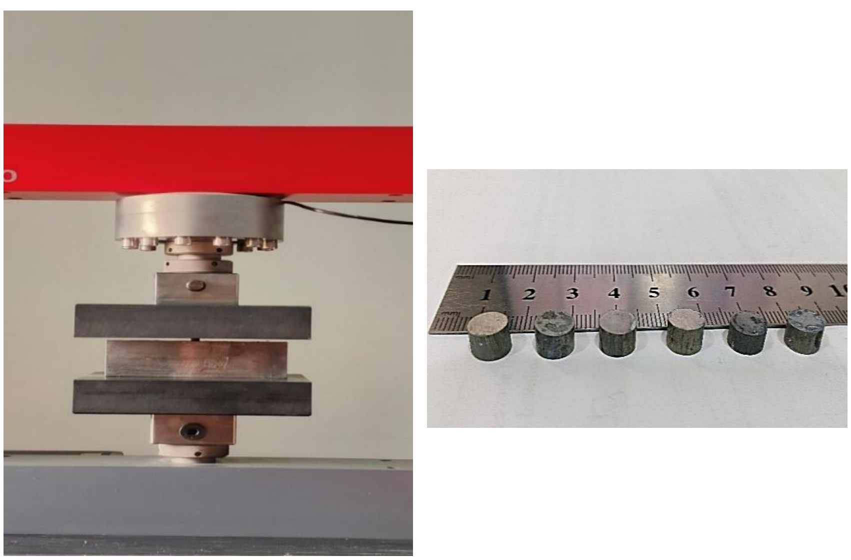


Figure 3. 7 UTM machine for Mechanical testing

3.4.5 Microhardness

The Vickers test basically utilized to examine the resistance of material to plastic deformation. The testing of Zn and Zn-2Mg-xCu has been done by Vicker's hardness which was performed by Vicker's Microhardness tester, No HVS1000 accordance with standard of ASTM-E384-17 [108].

Figure 3. 8 disc samples for microhardness testing

The samples were placed on stage of micro hardener. The 1.98N force applied for time of 10 sec for measuring the microhardness. On each samples the diamond-shaped indentation was presses against the material, and it will leaves an indentation on samples surface. Then, the hardness would be calculated from these indents' length [108].

Average of these indents was calculated using the following equation.

$$\boldsymbol{HV = 1.854\frac{P}{D^2}}$$

Here "D" is the average of all the sample indents and "P" is the applied force.

3.4.6 Atomic adsorption spectroscopy (AAS)

Atomic adsorption spectroscopy (AAS) is a technique used to determine the concentration of metal ions in a liquid solution. We used this technique to analyze the concentration of release of Zinc ions, after degradation of Zn samples in Stimulated Body Fluid (SBF) in different time intervals 1, 3, 7 and 14 days. For AAS analysis, standard solution of 20 ppm was made using Zn salt such as $ZnCl_2$. Further dilution of different (0.5ppm,1,2,3,4,5,6,7,8,9,10ppm) known concentration was done from standard solution for analysis of AAS. These dilutions were run on AAS to check the absorbance of known concentration on different wavelength. These readings were measured as values of known solutions. After that, the solutions of SBF containing release of Zn ions on different days 1,3,7,and 14 were run on AAS to check the release of ions in stimulated body fluid. The readings were measured from AAS instruments known as contrAA 800D.

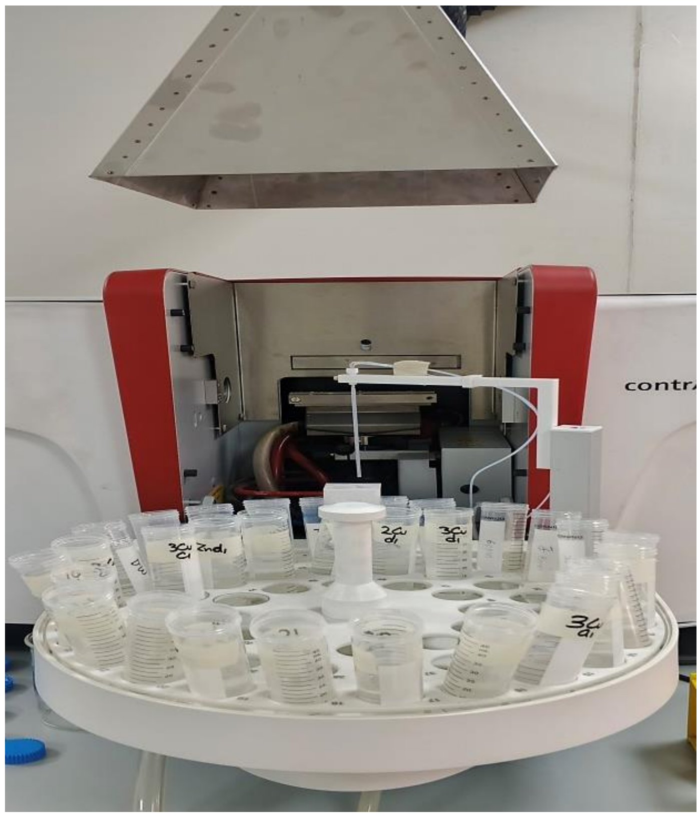


Figure 3. 9 AAS instrumentation

Chapter 4

Results and Discussions

4.1 Physical Properties of Zn-Mg alloys

Density measurements were carried out in determining the physical properties of Zn-Mg alloys before and after the sintering process. It was observed that density of green pellets increases significantly after sintering of alloys. The pre-sintered density that was calculated for pure Zn was 5.73 g/cm^3, while the post sintering density of same pure Zn pellets was increased to the 5.74 g/cm^{3}as it was shown in figure. The increase in density suggests that sintering of green pellets lead to stronger and dense material structure.

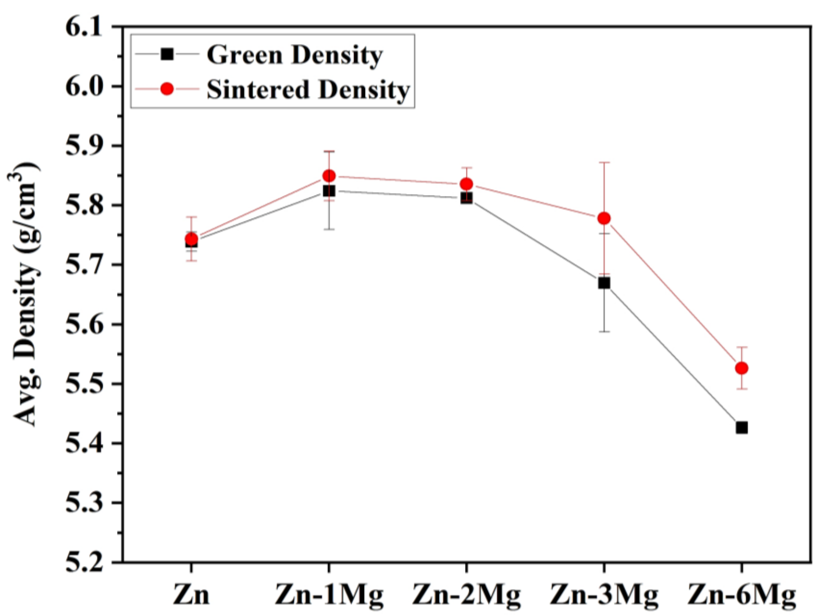


Figure 4. 1 Average sintered and green densities of Zn-Mg alloys

In powder metallurgy, sintering is one of the most important factors because it caused the particles of material to fuse together when they were heated at high temperature. also, during sintering, the adjacent grains of metal share their molecules which leads to “neck” formation between the grains. As a result, denser and stronger material is formed that is resistant to tear and wear. This material has increased density, reducing the porosity that is left after compaction in alloys and enhancing mechanical properties of metals. So Zn shows a relatively higher density also due to the higher atomic weight of Zn atoms.

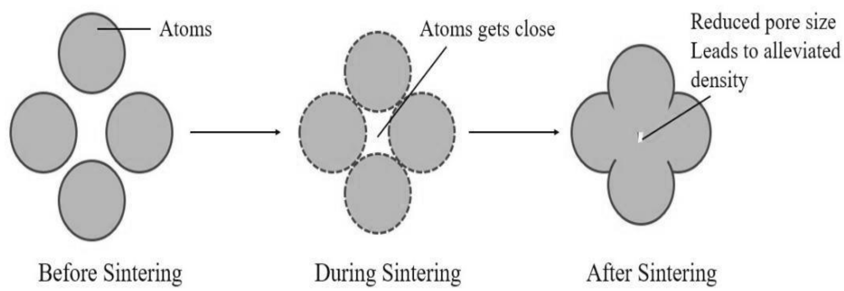


Figure 4. 2 process involved during sintering

However, it is observed that the addition of Magnesium (Mg) into Zn alloys caused the pre-sintered and post sintered density to decrease. The decreased in density due to addition of Mg is because of much lower density of Mg (1.73 g/cm^3) as compared to Zn (7.14 g/cm^3). Also when Mg is added it caused heavier atom of Zn to be replaced by lighter atoms of Mg in matrix as a result overall mass per unit volume decreased. However the density of Zn-6Mg is lowest among all other because when we increase Mg content it forms stable oxide layers (MgO) due to high chemical reactivity nature. These oxides layers inhibited the atomic diffusion, reduced neck formation between grains, particles rearrangement became difficult, non-uniform packing occurs, the pores are not eliminated completely, micro-voids created due to high vapor pressure of Mg as a result overall porosity increased which caused density to be decreased.

However the density of Zn-1Mg and Zn-2Mg is higher than Pure Zn. Because during sintering, Mg atoms easily diffused into the Zn lattice in these alloys, as atomic radius of Mg is comparable to Zn, resulting formation of lattice defects. These deformations caused internal energy to be increased at grain boundaries which provide a site for formation of intermetallic phases. These intermetallic phases increased the density of alloys because these phases have higher mechanical strength as compared to pure matrix of Zn alloys.

4.2 physical properties of Zn-Mg-Cu alloys

The density measurements taken for Zn-Mg-Cu alloys before and after sintering shows a remarkable increase in density of alloys as shows in fig. For example the green density of Zn-2Mg-0.5Cu was found to be 5.53 g/cm^3 while the sintered density of same alloy increased to be 5.83g/cm^3. This confirms that sintering process leads to a denser material structure. The sintered pellets show a higher density of Zn-Mg-Cu alloys as compared to the green pellets as shown in figure

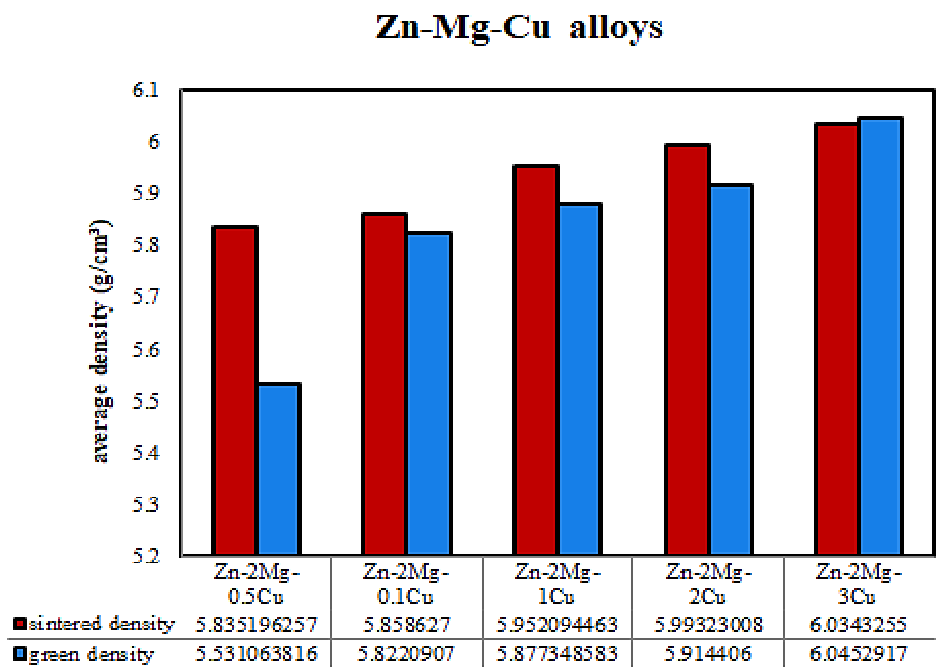


Figure 4. 3 sintered and green density of Zn-Mg-Cu alloys

Addition of copper in Zn-Mg alloys play a significant strengthening and compensating role in enhancing the density of alloys. The density of Cu is higher such as 8.96 g/cm^3 as compared to zinc and Magnesium density, which leads to increase in average atomic mass of Zn alloys system. Copper acts as sintering activator in increasing overall density of alloys by enhancing the solid-state diffusion and by improving the formation of “neck” growth between particles of Zn. Cu addition promotes the localized pathways of diffusion and also helps in rearrangements of particles. As a result the particles bonding in Zn matrix increases, pore volume decreased, densification efficiency of alloys increased which caused overall increase in density of Zn-Mg alloys.

The copper addition also plays a role in reducing the negative influence of oxide layers (MgO) produced by incorporation of magnesium. Copper has ability to increase the interfacial bonding between the particles and it would stabilize the microstructure which results in decreasing porosity and increasing the density of Zn-Mg-Cu alloys.

So, it was confirmed that the density of Zn alloys increases significantly by adding the alloying elements such as copper metals. According to the study conducted by Hu et al., that density of Zn-Mg alloys improved by adding zinc upto 30%.

4.3 SEM of Zn-Mg-Cu alloys

The SEM analysis of Zn, Zn-Mg and Zn-Mg-Cu alloys shows the presence of intermetallic phases. In the figure 4.4, the BSE images of pure Zinc and Zn-2Mg alloys are shown in which a black zones and white matrix are observed. The BSE image of pure Zn shows a uniform and smooth microstructure in which Zn matrix is clear with few second phases, and grain boundaries are not even prominent. These indications show a ductile and soft material with low mechanical strength. While BSE image of Zn-2Mg shows presence of dark rich Mg-intermetallic phases, in which microstructure became heterogeneous. Addition of Mg is lead to a secondary intermetallic phase. This confirms that the mechanical strength of alloys improved but structure became less uniform.

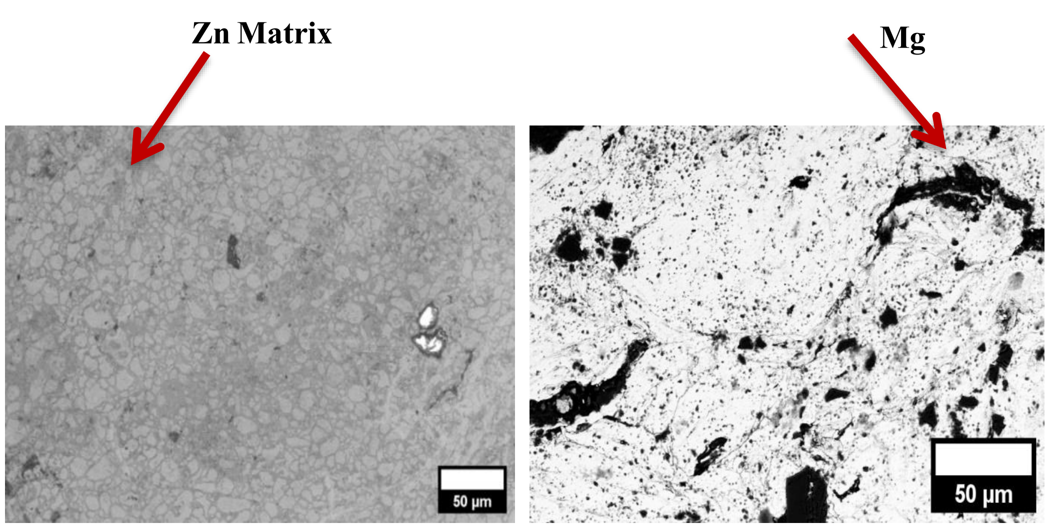


Figure 4. 4 BSE image of Pure Zn (left) and Zn-2Mg (Right)

In BSE image of Zn-2Mg-0.5Cu and Zn-2Mg-1Cu it is clear that with addition of copper grain boundaries in alloys became visible. Copper acts as grain refiner, a more refined and compacted microstructure would be observed and the intermetallic phases are distributed more uniformly within the matrix of Zinc metal. This shows the further enhancement in the mechanical strength of Zn based alloys.

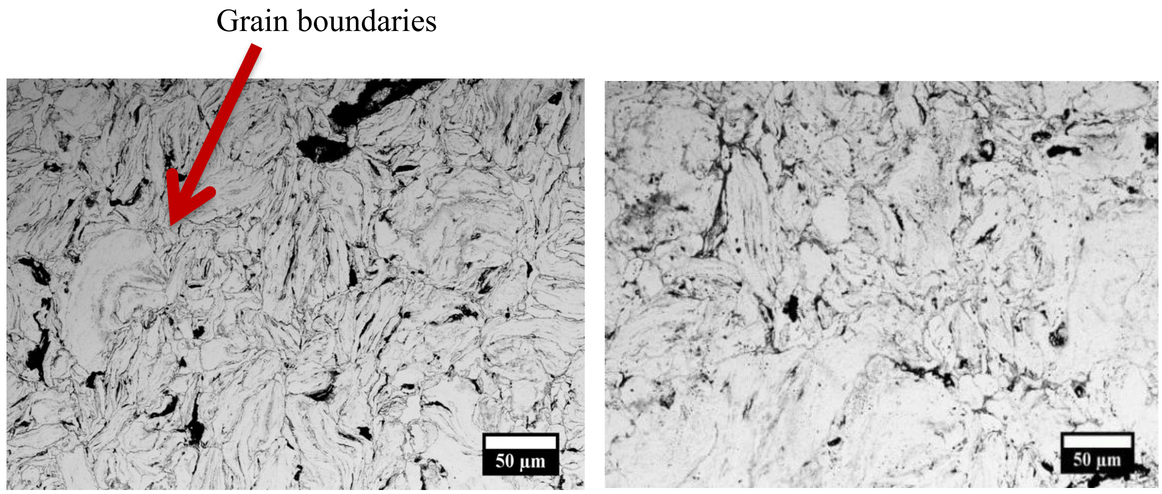


Figure 4. 5 BSE image of Zn-2Mg-0.5Cu (left) and Zn-2Mg-1Cu (Right)

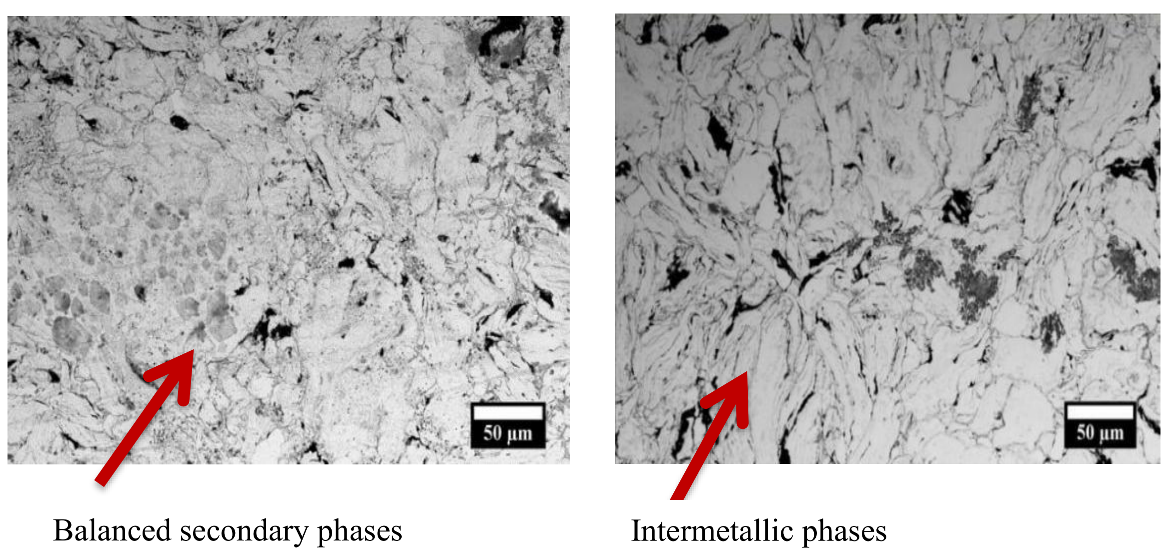


Figure 4. 6 BSE image of Zn-2Mg-2Cu (Left) and Zn-2Mg-3Cu (Right)

While figure 4.6 shows microstructure of Zn-2Mg-2Cu and Zn-2Mg-3Cu in which intermetallic phases are prominent, and balanced distributing of secondary phases are observed. So, its confirm from microstructure analysis of alloys that Mg addition increase strength of Zn alloys and Cu inclusion will be able to promote the grain refinement.

4.4 XRD analysis of Zn-Mg-Cu Alloys

The crystallographic structure and phase composition of the Zn-Mg-Cu alloys were identified using the X-ray diffraction (XRD) analysis. The bottom peaks are corresponding to the pure Zn because all major diffraction peaks matched to the standard Zn (JCPDS card). It shows that pure Zn consists of only single Zn matrix phase and there are no other secondary phases are present. However, the XRD analysis indicated the presence of primary Zn phases and also intermetallic phases of Mg and Cu such as Zn_2Mg_{11}, and Cu_5Zn_8, which confirms presence of successful alloying elements such as copper and magnesium in matrix of zinc. The diffraction peaks corresponding to phase of Zn were identified at the 2θ values of approximately 36.3°, 39.0°, 72°, 82° and 87° which match well with the standard hexagonal close-packed (hcp) structure of zinc. the peak at 43.3° is refer to intermetallic phase $Cu_5Zn_8$of copper. The additional peak was also be found at 58° which is basically the peak of intermetallic phase of magnesium Zn_2Mg_{11}.

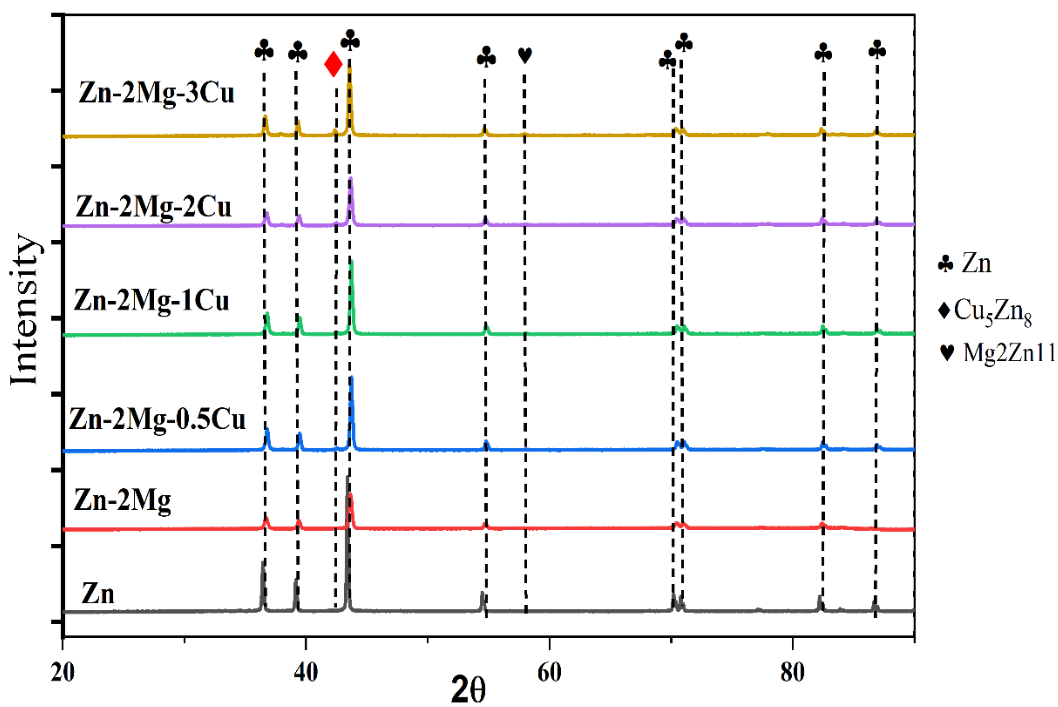


Figure 4. 7 XRD peak analysis of Zn-Mg-Cu Alloys

So the XRD patterns confirm the Zn matrix presence along with intermetallic phases of Mg_2Zn_{11} and Cu_5Zn_8. The increasing and emergence intensity of the Mg_2Zn_{11} peaks have verified the formation of Mg-induced phase, while the growth and appearance of Cu_5Zn_8 peaks with the increasing content of Cu confirm the formation of Cu-driven intermetallic phases. The intensity and sharpness of the peaks suggested a high degree of crystallinity in the Zn-Mg-Cu alloys

4.5 EDX (Energy Dispersive X-rays) of Zn-Mg-Cu alloys

EDX analysis is used to identify the presence of element in materials and understand their distribution within the microstructure. In the EDX image of Zn-2Mg-1Cu, it was cleared that the grey region represents the matrix of Zn that is base phase of the alloy. However the elongated and dark region corresponding to secondary intermetallic phases such as phases of Mg_2Zn_{11} that's show the Mg reacts with Zn to form strengthening phases in Zn matrix.

The mapping of Mg shows that the brighter region are Mg rich areas in which Mg is not distributed uniformly but it is localized in specific region. These specified regions are basically phases of Mg rich interemetallic in Zn matrix. However, mapping of copper shows that Cu is uniformly distributed across the scanned area and here signals of Cu are weaks. These is no such formation of Cu rich clusters instead of that Cu is completely dissolved in matrix of Zn.

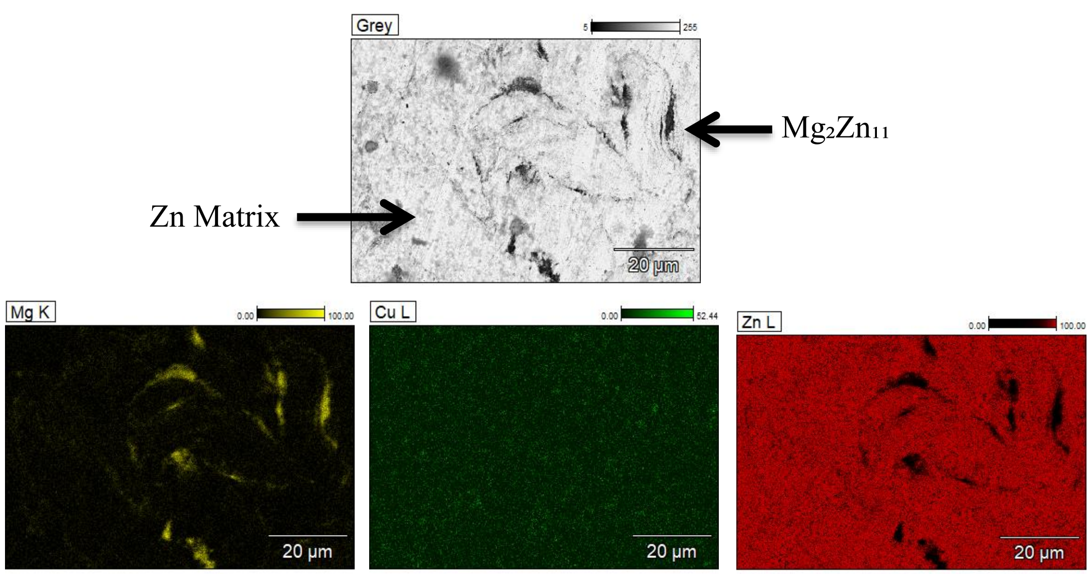


Figure 4. 8 EDX analysis of Zn-2Mg-1Cu alloys

In figure 25, the EDX analysis of Zn-2Mg-3Cu are shown which indicates the presence of elements in Zn alloys. The grey region represents matrix of Zinc in which dark or irregular region is formed due to secondary intermetallic phases. These rich regions are phases of copper in Zn matrix. The mapping of Mg showed weak signals in which Mg is not concentrated in the Cu-rich phases. This suggests Mg does not even participate in rich phases of Cu.

However, mapping of Cu showed rich intermetallic phases of Cu in which copper is not uniformly distributed but they are localized to a specified region. These specified regions are actually Cu_5Zn_8 rich intermetallic phases

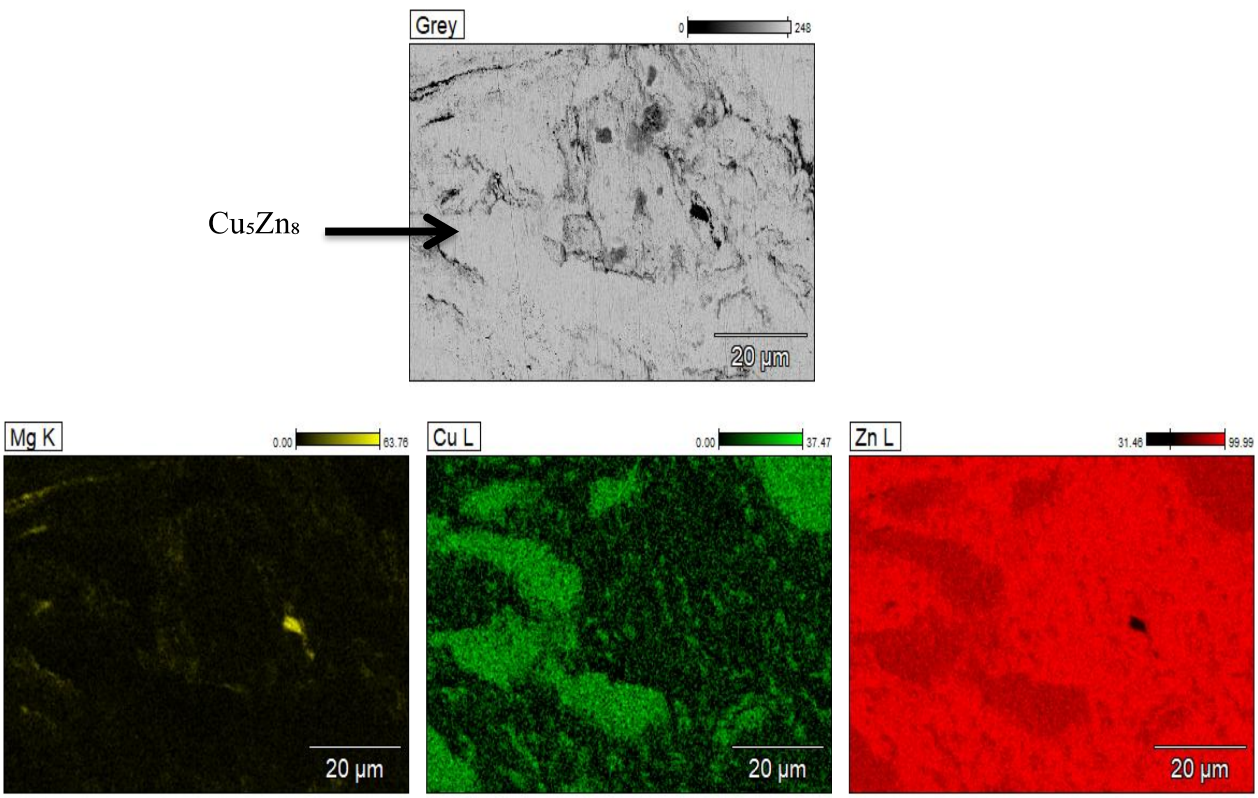


Figure 4. 9 EDX analysis of Zn-2Mg-3Cu alloys

4.6 Mechanical properties of Zn-Mg-Cu alloys

In this section mechanical properties of Zn-Mg and Zn-Mg-Cu alloys were discussed that how compressive strength of Zn alloys increased with addition of alloying elements such as Magnesium and Copper.

4.6.1 Compressive strength of Zn-Mg alloys

Mechanical properties of Zn alloys showed the effect of compressive strength and strain with increasing %wt of Mg in Zn-xMg alloys (x=1, 2, 3, 6) in this figure. It was observed from figure 4.10, that weight fraction of concentration of Mg in Zinc has significant influenced on the mechanical strength of Zinc alloys. The compressive strength increased with increasing % wt of Mg in Zn alloys upto 2 %wt. however it was observed that Mg concentration beyond 2 %wt caused the compressive strength to be declined.

The increased in strength from 99.76 MPa of pure Zn to 210.2 MPa of Zn-2Mg is due to solid solution strengthening of Zn matrix. The Mg atoms dissolved into Zn matrix and replaced heavier atom of Zn with Mg as a result atomic size mismatched occur. This leads to lattice distortion and dislocation movement became hindered which increased resistance to deformation as a result compressive strength improved.

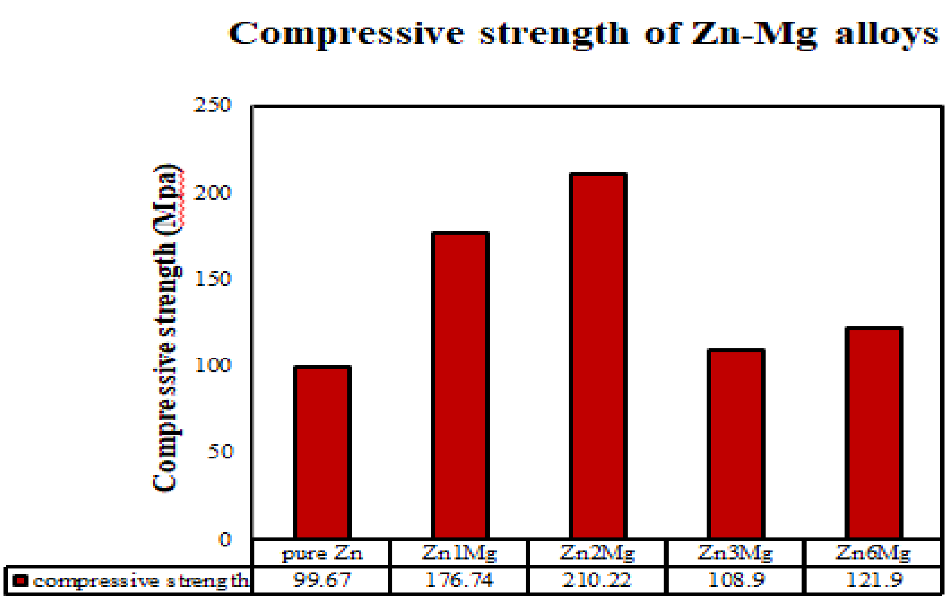


Figure 4. 10 compressive Strength of Zn-xMg alloys

However, the sharp decline in compressive strength from 210 MPa of Zn-2Mg to 121 MPa of Zn-6Mg is due to higher concentration of Mg upto 6 %wt occur. Because excess Mg concentration forms Mg- rich intermetallic phases which are hard but brittle and easily cracked under applied load. Also, Mg oxidation reduced the metallurgical bonding, porosity between particles increased which leads to premature failure of alloys. So the excessive %wt of Mg significantly reduced mechanical strength of alloys.

4.6.2 Strain of Zn-Mg alloys

This graph illustrates the strain of Zn-Mg alloys that how much material is able to bear load when stress is applied before undergoes deformation. Pure Zn has less strain of 6.17% at compaction pressure of 350 MPa. The addition of Mg into Zn increased strain upto a certain concentration and with higher Mg concentration there is sharp decline in strain. However, it was observed Zn-1Mg has maximum strain of 36.9% because small Mg addition improves the dislocation mobility and uniform deformation which results in higher ductility. So, a balanced strength and ductility combination is obtained.

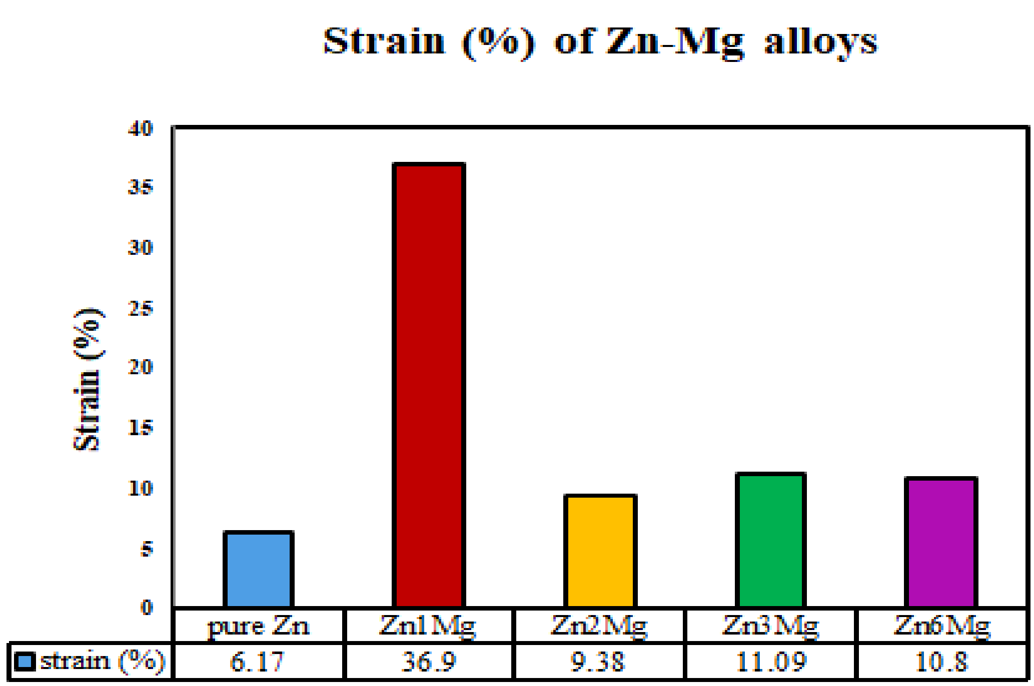


Figure 4. 11 strain % of Zn-Mg alloys

Howeverr, higher Mg concentration increases more brittle phases formation which limits plastic deformation, pores not fully eliminated which initiate cracks and reduced strain before fracture. As a result, both strength and strain decreased with higher %Wt of Mg due to poor densification.

4.6.3 Compressive strength of Zn-Mg-Cu alloys

This graph clearly illustrates the increased in compressive strength of Zn alloys with addition of Cu. The compressive strength increased from 150MPa of Pure Zn to 400MPa of Zn-2Mg-3Cu. It was observed that increasing the %wt of Cu in Zn-Mg alloys significantly improved the overall compressive strength. this is due to copper has higher density and Cu atoms dissolved into Zn matrix which leads to formations of Cu rich precipitates. These precipitates pins dislocation, resist plastic deformation which increased mechanical strength of alloys.

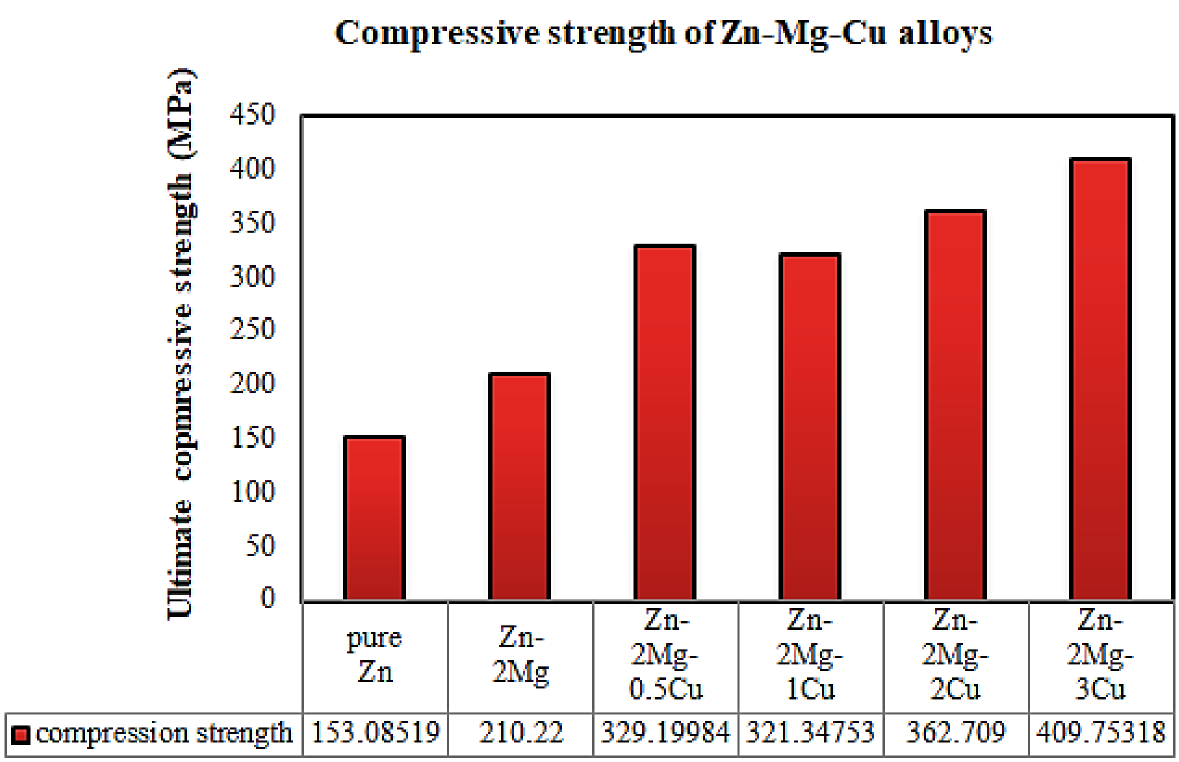


Figure 4. 12 compressive strength of Zn-Mg-Cu alloys

4.6.4 Strain % of Zn-Mg-Cu alloys

This graph showed that increase in strain % of Zn-Mg-Cu alloys with increasing the %wt of Cu concentration in Zn alloys. Pure Zn shows a strain of 6.17% which increased with addition of copper concentration from Zn-2Mg-0.5Cu of 34.4% to Zn-2Mg-3Cu of 41.77%. Cu addition enhances the densification; pores are eliminated completely which delayed the crack initiation. Cu also stabilize the microstructure and allows the sustained plastic flow under compaction. So overall, strength and ductility of alloys improved with inclusion of copper atoms.

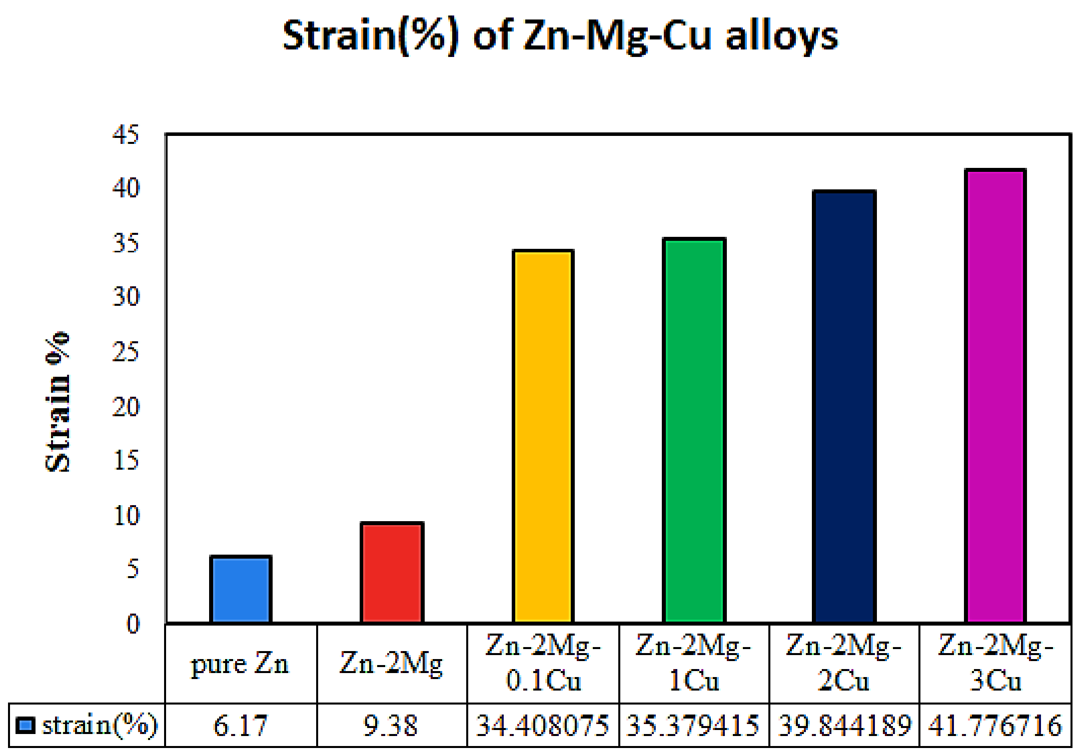


Figure 4. 13 strain % of Zzn-Mg-Cu alloys

4.7 Micro-hardness of Zn-Mg-Cu Alloys

This graph clear illustrates the microhardness of Zn-Mg-Cu alloys to understand the resistance of Zn-Mg-Cu alloys to the plastic deformation. Micro-hardness basically reflected the strengthening of surface and microstructure. Pure Zn has the lowest hardness of 39 HV because of its soft nature, large grains and low resistance to dislocation movement. However addition of Mg into Zn improved the hardness of alloys. Notably, Zn-2Mg has the highest microhardness of 43.3 HV as compared to pure Zn due to solid-solution strengthening and grain boundaries refinement. Mg addition leads to formation of secondary intermetallic phases of Mg_2Zn_{11} in matrix of Zn. It was also observed that inclusion of Cu into Zn-Mg alloys significantly enhanced the hardness with increasing concentration of copper upto 3 %Wt. micro-hardness increased from 47 HV of Zn-2Mg-0.5Cu to 76.6 HV of Zn-2Mg-3Cu alloys. Copper addition has strong impact on hardness of alloys as compared to Mg. Cu atoms caused distortion of Zn lattice , hindered dislocation movement and also precipitates of Cu rich phases are formed and these precipitates acted as strong obstacle to dislocation. As a result microhardness of Zn-Mg-Cu alloys improved to undergo plastic deformation.

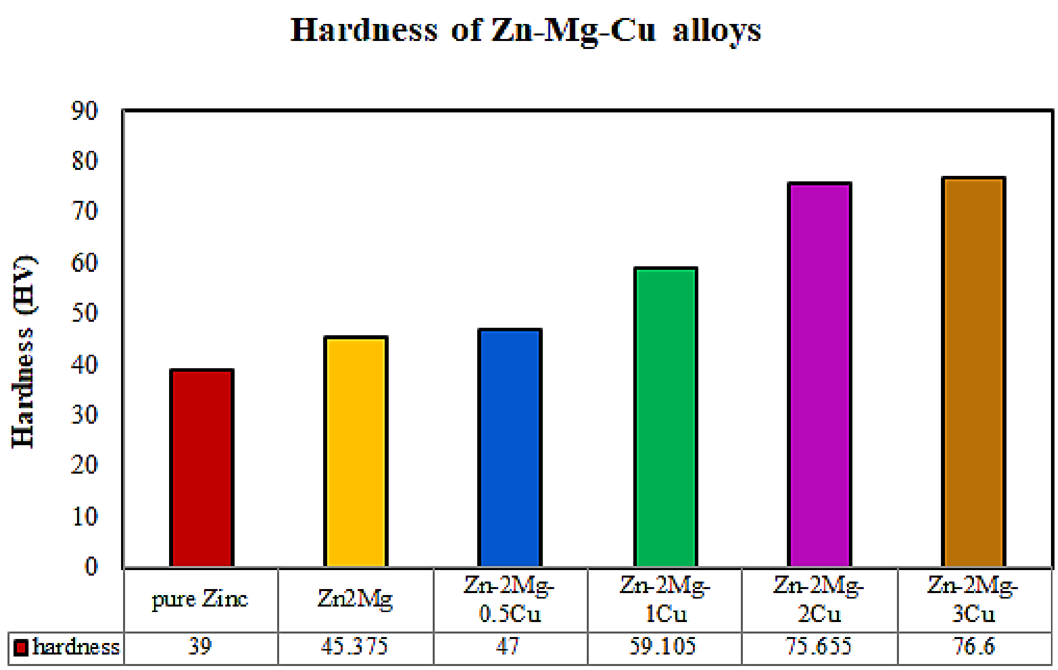


Figure 4. 14 Microhardness of Zn-Mg-Cu alloys

4.8 Mechanical Strength Mechanism

This mechanism clearly explains the concept of how mechanical strength is improved with addition of Mg and Cu atoms in Zn alloys. Pure Zn has large grains and weak grain boundaries. Cracks will easily propagate along the grain boundaries which make pure Zn to shows low strength and brittle behavior. Addition of Mg into Zn matrix caused hard Mg-rich intermetallic phases to be formed, grain boundaries to be stronger as a result crack propagation will be blocked. Strength improved initially due to hard phase formation and grain boundary strengthening.

However, inclusion of Cu causes lattice distortion to occur which restricts dislocation movement and increase the resistance to deformation. Cu also forms intermetallic phases or precipitates. Mg and Cu both prevent grain boundaries to grow during sintering and they pinned these boundaries. These hard phases transfer the stress from soft Zn matrix which leads to uniform distribution of load that’s prevent from early failure. In this way the mechanical strength of Zn-Mg-Cu alloys improved.

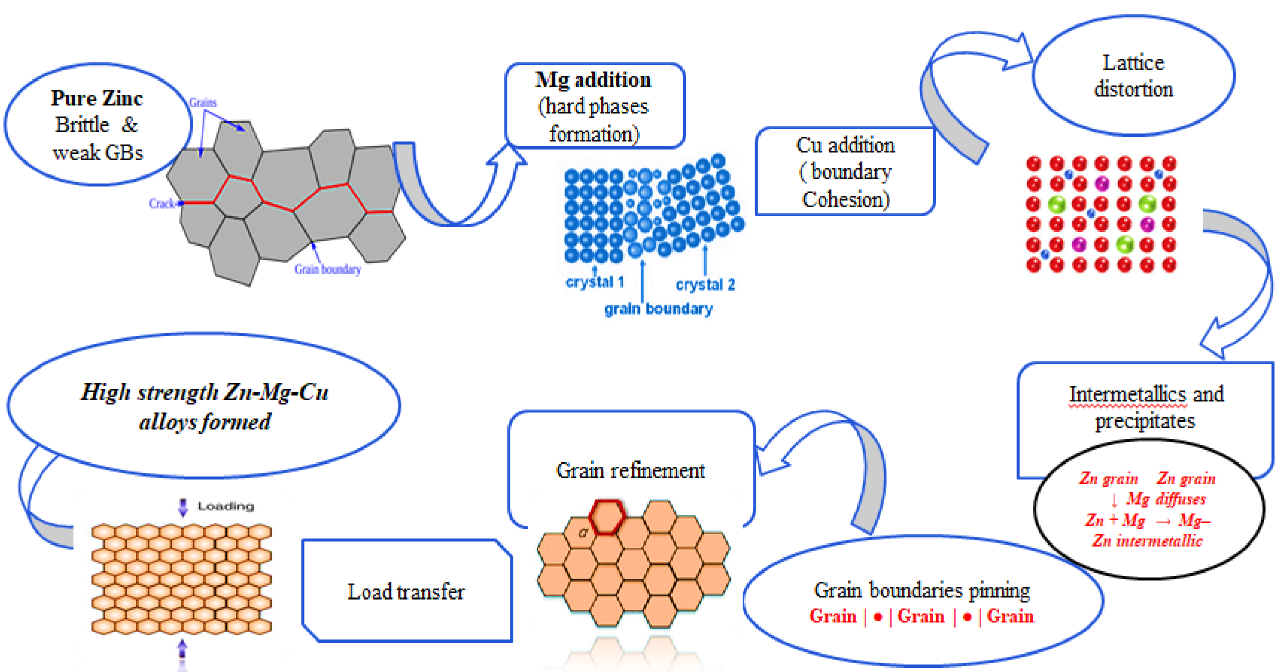


Figure 4. 15 Mechanical strength mechanism of Zn-Mg-Cu alloys

4.9 Atomic adsorption spectroscopy (AAS) via degradation extract

The graph clearly explains degradation rate of Zn-Mg-xCu (x0.5,1,2,3) alloys in submerging SBF for the fourteen days (1, 3, 7, 14). It was observed that adding copper to Zn-2Mg alloys increased the degradation values. A noticeable increase of weight loss of Zn alloys has been observed as the time interval increases. The weight loss increases with higher concentration of copper. Among all of the alloys, the highest degradation rate was observed for Zn-2Mg-3Cu. On day 1, weight loss of Zn-2Mg-3Cu was about to 0.3 mg/cm^2 and increased ton day 14 upto 1.4 mg/cm^2 while for pure Zn it was about 0.1 mg/cm^2 and improved to 0.6 mg/cm^2. This degradation study was conducted by our passout MS scholar in her thesis research.

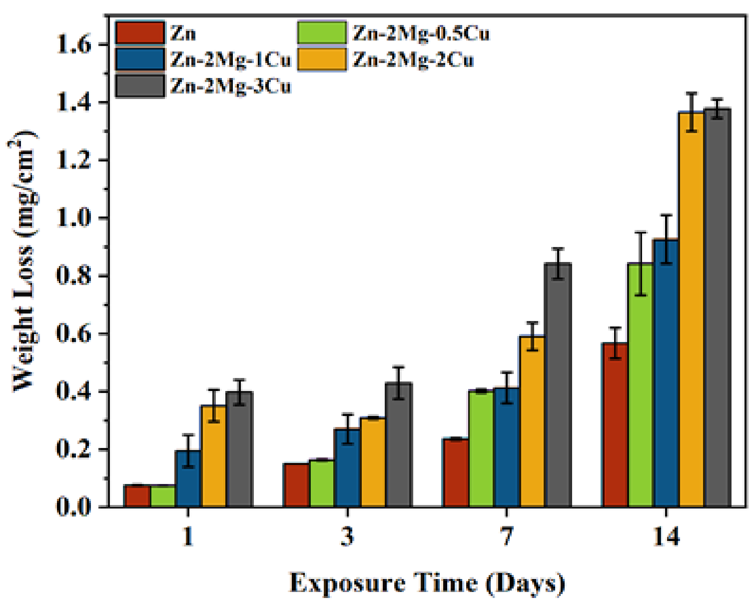


Figure 4. 16 Degradation study of Zn-Mg-Cu alloys

AAS analysis showed the release of Zn ions into solution of Stimulated Body Fluid (SBF) after emerging samples of Zn alloys for fourteen days. The material degrades and released metal ions such as especially Zn^{2+} into the solution. This figure represents concentration of zinc ions released (mg/L) measured from degradation extracts by atomic absorption spectroscopy after immersion in SBF for 1, 3, 7 and 14 days. For all composition of Zn and Zn-Mg-Cu alloys the Zn ions concentration increased with immersion time that showed a time-dependent degradation behavior.

Pure Zn showed low and more gradual ion release which reflects slow and more stable degradation behavior.

However addition of copper and Mg showed significantly higher released of Zn ions concentration especially with having higher content of copper such as Zn-2Mg-3Cu after immersion of 14 days. The increased released of Zn ions in Cu containing alloys is due to micro-galvanic coupling between the Zn matrix and Cu-rich intermetallic phases. This galvanic coupling would promote the localized corrosion, leading to increased dissolution of ions of Zn into the solution of SBF. However, a slight fluctuation is observed in Zn concentration for some alloys at intermediate immersion times. These results showed copper content plays a role in controlling the ion release and the excessive Cu concentration would be result in uncontrolled Zn ion liberation that is undesirable for most of the orthopedic implant applications.

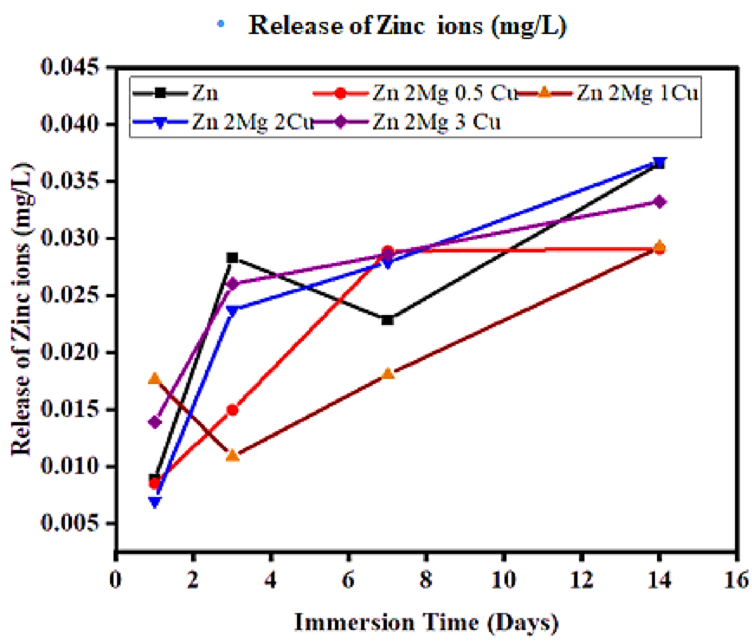


Figure 4. 17 release of Zn ions (mg/L) of Zn-Mg-Cu alloys

This graph clearly illustrates the rate of Zn mass loss (mg/day) at different immersion intervals. At the day 1, all samples of Zn and Zn-Mg-Cu alloys demonstrated a lower loss of Zn mass that indicating the initial dissolution. However, Zn mass loss increased significantly as the immersion time increases to 1, 3, 7 and 14 days that's confirmed the degradation became more pronounced with long exposure to SBF.

It is confirmed that lowest mass loss observed for pure Zn at all the time intervals that exhibits slow degradation behavior. A moderate increase in Zn mass loss observed for Zn-2Mg-0.5Cu and Zn-2Mg-1Cu that suggests a more uniform and controlled degradation rate. However, the highest mass loss was observed for Zn-2Mg-2Cu and Zn-2Mg-3Cu especially at the longer immersion intervals. So the highest Zn mass loss was observed in higher Copper content alloys which indicating an accelerated rate of dissolution that can be linked to the intensified galvanic corrosion occurred due to Cu-rich phases. Although on alloys surface over the time corrosion products formed, and these layers are insufficient to fully suppress the Zn dissolution with higher content of Cu.

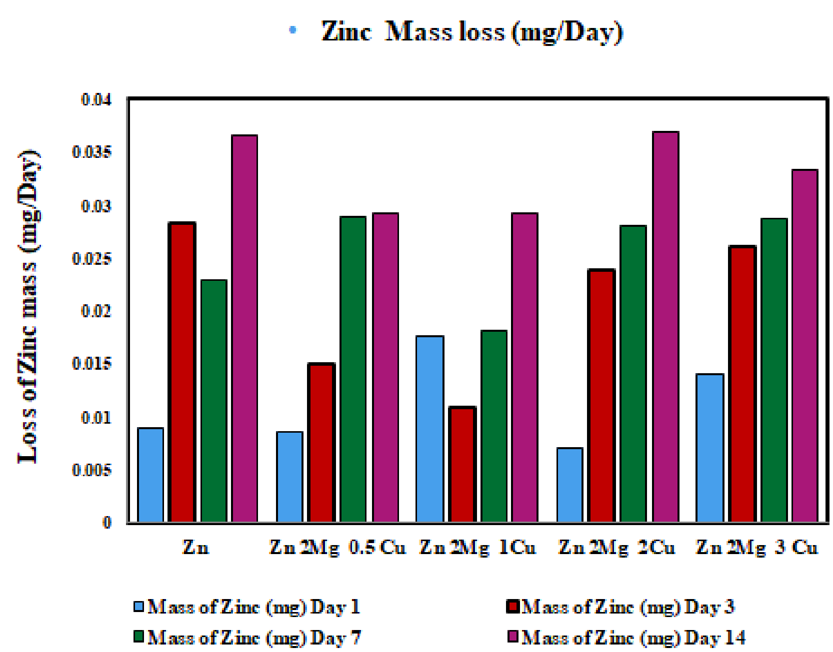


Figure 4. 18 Zn mass loss (mg/day) of Zn-Mg-Cu alloys

Chapter 5

Conclusion

Zinc alloys were synthesized using powder metallurgical processing techniques for their potential used in pediatric Orthopedic applications. Density measurements showed that addition of copper to the zinc alloys enhanced the overall density of zinc alloys from Zn 5.73 g/cm^3 to Zn-2Mg-3Cu of 6.04 g/cm^3 which is effective for hardness of implant to be used in orthopedic applications. SEM images indicating that addition of Mg and Cu leads to formation of intermetallic phases and reduction of grain size. XRD analysis confirmed the formation of these Mg and Cu rich secondary phases of Mg_2Zn_{11} and Cu_5Zn_8 in Zn alloys which plays role in strengthening of alloys. EDX images showed the elemental distribution within the microstructure of alloys that Cu and Mg are localized to a specified region of Zn matrix. Mechanical properties demonstrated that compressive strength and strain % of Zn alloys enhanced from pure Zn of 99.97 MPa to Zn-2Mg-3Cu of 409 MPa and 6.17% to 41.7% respectively which is quite suitable for implants to be used in orthopedic applications. The AAS analysis showed the optimum released of Zn ions into the SBF solution in different time intervals. It is concluded that addition of Cu and Mg to zinc alloys significantly improved the mechanical properties of alloys and their inclusion did not have any toxic effects on human body.

Chapter 6

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