BORON NITRIDE INCORPORATED WITH HYDROXYAPATITE COATING ON PURE MAGNESIUM FOR BIOMEDICAL APPLICATION

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DECLARATION

I, Hamza Khan, bearing registration number 110-FET/MSME/F-22 and enrolled as a student of MS Mechanical Engineering in the academic session 2022-2025, confirm that the research study entitled "Boron nitride incorporated with hydroxyapatite coating on pure magnesium for biomedical application" is entirely my work. This research has not been submitted for evaluation elsewhere. Whenever external sources were used, they were duly cited and acknowledged.

Signature of Student: __________________________

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Certificate of Approval

It is with this certification that **HAMZA KHAN**, Registration No. **110-FET/MSME/F22**, has completed the thesis titled **"BORON NITRIDE INCORPORATED WITH HYDROXYAPATITE COATING ON PURE MAGNESIUM FOR BIOMEDICAL APPLICATION"** for the degree of MS (Mechanical Engineering) and that the work submitted is of sufficient scope and quality.

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DEDICATION

This thesis is dedicated to my parents, who have made this journey possible with their constant love, support, and sacrifices. Their unending support and well wishes have been my unwavering source of courage. To my distinguished mentors, Dr. Sajjad Ahmad and Dr. Sakhi Jan, whose advice and support have been crucial to my development as a researcher. And to Dr. Wasim Akhr, this work would not have been possible without their cooperation and encouragement. This work is dedicated to each of you with sincere gratitude and testimonial to your belief in me.

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I want to express my heartfelt gratitude to my parents, whose unwavering support and sacrifices have been the foundation of my journey. They have worked tirelessly to provide for my education and have always kept me in their prayers, for which I am eternally thankful.

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Thank you all for being an integral part of this journey.

(Hamza Khan)

ABSTRACT

Magnesium, with its biocompatibility, mechanical properties, and degradability, is a potential biomaterial in orthopedic and cardiovascular applications. However, the rapid degradation of magnesium in physiological environments still poses a big challenge, mainly because it has been shown to release hydrogen gas and lose mechanical integrity. The purpose of this study is to enhance the corrosion resistance and overall performance of pure magnesium with a composite coating layer of Hydroxyapatite (HA) and Boron Nitride (BN) and thus produce material that could be applied for biomedical applications, specifically for implants, and its optimized degradation rate concerning humanized healing.

The composite coating was prepared using an electrophoretic deposition technique comprising HA + BN, resulting in good uniformity and adhesion. HA comprises calcium phosphate with excellent biocompatibility and osteoconductive properties for active bone growth.

Intensive characterization was conducted on coated magnesium samples to assess the coated Mg sample's structural, mechanical, and biological properties. Scanning electron microscopy (SEM), X-ray diffractive spectroscopy (XRD), and Energy disperse spectroscopy (EDS) were employed to analyze the morphology and composition of the coating. Electrochemical tests, such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), were carried out to evaluate the corrosion behavior. Additionally, in vitro studies with simulated body fluid (SBF) were carried out to simulate physiological conditions and assess the degradation rate and bioactivity of the coated samples. Preliminary results of corrosion resistance show the improvement after HA-BN composite coating on Mg, which suggests the degradation rate was slower, less hydrogen evolution occurred, and greater calcium phosphate deposition, the factor that has more importance for the integration process into bone tissue. The coated Mg also maintains the mechanical integrity of the substrate even after the elongated exposure to the time line. The findings outline a new approach to mitigate the restrictions of

magnesium-based biomaterials through the use of combined benefits of HA and BN. The results contribute to the blossoming field of bioactive coatings, emphasizing the further development potential of tailored magnesium implants. Future work will include in vivo testing and optimization of the coating process for scalability and reproducibility for clinical application.

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CHAPTER 1

INTRODUCTION

The choice of materials for fixation or replacement can impact the outcome of any medical surgery. Biomaterials are synthetic materials used in medicine to replace and cure damaged or diseased tissue in various body areas [1]. Biomaterials greatly enhance the health and well-being of people. Strains, sprains, dislocations, and fractures are just a few of the unpleasant problems that can occur in the human body. A fracture occurs when an excessive external force acts on the bone, larger than the osseous tissue's strength. Age, gender, bone strength, and general health all significantly affect an individual's fracture risk [2]. Every year, a large number of people suffer from bone fractures or degenerative bone diseases, and to effectively treat these injuries and conditions, a specific type of treatment is required. For curing degenerative bone conditions, typically, bone replacement is needed. To treat such cases, permanent implant materials such as hip joints and knee joints are used, which are then present inside a human body for a lifetime. For this purpose, most biomaterials are synthesized from inert materials such as titanium, stainless steel cobalt chrome alloy. When treating a fracture, metallic pins, screws, and plates may be surgically inserted to support the injured bone tissue externally as it heals. The purpose of this kind of orthopedic implant is to offer short-term support to stop the damaged bone from shifting while it heals [3].

Stainless steel and cobalt chrome molybdenum (CoCrMo) are two substitutes that are currently used in orthopedic surgery, although there is ongoing discussion over the potential harm that these materials can do to the body [4]. After the tissue heals, a revision surgery is required to remove these temporary implants. This results in discomfort for the patient, a large financial burden on the health care system, and the possibility of further damage to the repaired bone. A perfect temporary orthopedic implant would give the required mechanical strength right after insertion, but as the patient healed, it would progressively deteriorate and be replaced by new bone tissue. This would mean that a revision surgery would not be necessary. In addition, the implant must generate non-toxic breakdown products and break down gradually enough to preserve its mechanical strength until the bone tissue has sufficiently recovered to offer load-bearing support [5].

1.1 Biodegradable implant materials for orthopedic purposes

Orthopedic implant materials that are made from biodegradable materials are intended to dissolve and be absorbed by the body over time, preventing the need for revision surgery to remove the implant. These substances are essential for promoting bone regrowth and repair while reducing long-term complications compared with permanent non-degradable implants [6]. With the use of degradable implant materials, the need for revision prostheses will be eliminated despite losing their mechanical properties before the healing of fractured bone [7]. Currently, huge amounts of materials are discovered that are used as degradable materials, including polymer, but regardless of their mechanical properties and integration with natural bone, they are different because polymer does not provide sufficient support to fracture bone [8].

1.2 Magnesium for Orthopedic Biodegradable Implants

Physician Edward C. Huse 1878 successfully stopped bleeding of vessels in three patients by the use of a magnesium wire as a ligature, and other sentiments recommended using it as a surgical suture [9]. However, the issue that persisted with the use of Mg as orthopedic implants was the fast degradation rate, which makes it unsafe for the use of orthopedic implants. Because Mg corrosion rate had not been well controlled, numerous medical professionals thus decided to utilize alternative metallic elements with superior corrosion resistance, such as titanium and stainless steel alloys. As a result, research into magnesium's potential as a biomaterial was put on hold for the time being [9].

1.3 Magnesium implants biocompatibility with human anatomy

A material's biocompatibility is a crucial component of a successful implantation. Williams defines biocompatibility as a material's ability to perform with an appropriate host response in a specific application. It denotes that the substance must be safe, non-toxic, and unable to provoke an immune response in live tissue[10]. The human body's natural corrosion processes have an impact on the biocompatibility of metallic biomaterials. When metallic biomaterials corrode, harmful metal ions, including nickel, chromium, cobalt, and others, are released into the body. These ions can trigger immunological responses that aren't wanted, such as tissue damage, inflammation, and cell death [11].

Mg exhibits superior biocompatibility when compared to other metallic biomaterials. It is the body's fourth most abundant inorganic element. The typical adult human body weighs 70 kg and has 21–28 g of Mg in it.

1.4 Comparing the Mechanical and Physical Characteristics of Magnesium with Natural Bone

Mg is a lightweight metal with great potential for orthopedic implants and other biological applications. It is a prime candidate for bone repair and regeneration since its mechanical and physical characteristics are similar to natural bone. This is one of the main causes of interest in the material. Determining how these attributes compare to natural bone is essential to determining whether Mg is appropriate for use in medicinal applications [12].

Table 1. Relative density of different implant materials

Materials	Relative density
Magnesium's	1.74 g/cm³
titanium's	4.43 g/cm³
stainless steel's	7.9 g/cm³
cortical bone	1.8–2.1 g/cm³,

Mg's 1.74 g/cm³ density is relatively low compared to titanium's 4.43 g/cm³ and stainless steels 7.9 g/cm³. This is because cortical bone has a density of 1.8–2.1 g/cm³, which minimizes the danger of bone resorption and weakening [13]. Additionally, Mg has the same order of magnitude of elastic modulus and compressive yield strength as natural bone. Because of these resemblances to natural bone, the stress-shielding effect should be lessened or avoided, promoting bone tissue remodeling and stimulation.

1.5 Research Problem

Nowadays, researchers are focusing on the Mg implants that have the properties of degradation within the human body. The major problem that persists with the Mg implant is the degradation before the healing of the broken bone. There is a need for bio-compatible non-toxic coating to passive the degradation time of the implant. Despite that, HA coating reduced the fast degradation of pure Mg, but further investigation is required to reduce premature degradation and antibacterial properties simultaneously. The degradation rate needs to decrease further to enhance bone healing. For this purpose, BN is proposed to be mixed with HA due to its excellent anti-corrosive properties.

1.6 Aims and Objectives of Research

The objectives of this research are to investigate h-BN incorporated with HA composite coating on pure Mg via EPD.

1.7 Significance of the research

The significance of the research is to develop a biodegradable implant and overcome the limitations associated with biodegradable implants. Developing advanced and biocompatible implant materials to terminate the revision surgery and financial hurdles.

CHAPTER # 2

LITERATURE REVIEW

In recent years, tremendous progress has been made in the field of biomedical engineering, especially in the creation of novel implant materials. Because of its special combination of mechanical and biocompatibility qualities that closely match cortical bone, pure Mg has emerged among these as a potential candidate. In conventional metallic implants, stress shielding effects can cause bone loss and implant failure [14]. However, a major obstacle to pure Mg widespread use as an implant material is that it degradation quickly in physiological environments. This rapid corrosion can weaken the implant's structural integrity before the surrounding tissue has had time to recover, which could result in early implant failure and patient problems [15].

Among coating methods, electrophoretic deposition (EPD) has drawn a lot of interest because of its adaptability, affordability, and capacity to create homogeneous coatings on complex shapes. Developing advanced coatings for Mg implants is a great use for EPD since it can deposit a variety of materials, including ceramics, polymers, and their composites [16].

After a thorough study of the literature, the electrophoretic deposition of hydroxyapatite is the main focus of the researcher due to the potential of hydroxyapatite, a calcium phosphate ceramic that closely resembles the mineral component of natural bone, which encourages Osseo-integration and improves the biocompatibility of implant surfaces [17].

However, boron nitride gains significant focus from the researcher due to its excellent mechanical, chemical, and biocompatible properties in physiological conditions [18].

Researchers have focused on developing protective coatings as well as other surface modification approaches in an attempt to address this important problem. The objective of these coatings is to preserve or improve the biocompatibility of pure Mg implants while simultaneously increasing their resistance to corrosion. Recent developments in coating technology for pure Mg implants are reviewed in this literature review along with their implications for corrosion resistance, biocompatibility, and overall implant performance.

2.1 Electrophoretic deposition coating technique.

These days, scientists are interested in nanoscale composite coatings of biomaterials. The (EPD) process could readily deposit complex compounds and glass/ceramics laminar particles.

EPD is a nanoscale wet deposition method that uses a straightforward apparatus and little time to coat surfaces. Furthermore, any three-dimensional (3D) substrate can be used for deposition; substrate size and shape are not restricted. The morphology and thickness of the coatings could be modified by merely adjusting the applied voltage, time, electrode spacing, and suspension parameters. Solid particles are dispersed throughout a suspension in the solvent during the EPD process. Particles scattered in a liquid medium become charged when direct current (DC) is applied, and they move toward an oppositely charged conductive substrate electrode, where they deposit.

Furthermore, based on charged particles, EPD is divided into two types: cathodic and anodic. The process is known as cathodic electrophoretic depositing (EPD) if particles are positively charged and deposit on the cathode; on the other hand, anodic EPD occurs when particles are negatively charged and deposit on the anode. Any mode of deposition could be achieved by altering the surface charge of the particles. Hamaker uses the correlation between parameters that affect EPD to describe the quantity of particles that are deposited on the substrate.

Hamaker described the first attempt to correlate various influencing parameters with the amount of particles deposited during EPD.

Hamaker's law uses the following formula to relate the deposit yield (w) to the electric field strength (E), electrophoretic mobility (E), electrode surface area (A), and particle mass concentration in the suspension (C) [16].

$$w = \int_{t_1}^{t_2} \mu \cdot E \cdot A \cdot C \cdot dt$$

The above equation emphasizes the direct proportionality between deposit yield and mentioned dependent parameter, underlining their importance in improving the EPD process. Understanding and managing these parameters can result in higher coating uniformity, improved material properties, and more efficient deposition method.

2.2 Magnesium

The mechanical, lightweight, and biocompatibility properties of Mg and Mg-based alloys are similar to those of natural bone. Due to this, it can be used as an osteoconductive and degradable substitute for fractured bone. However, the earlier degradation before the bone healing prevents it from wider use in physiological conditions [19].

2.2.1 Advantages of Mg

Pure Mg is a suitable option for several biomedical applications since it has numerous distinct benefits as a biomaterial.

2.2.2 Biocompatibility

Mg plays a crucial role in numerous physiological processes due to its essential nutrient in the human body. It is the 4th most abundant cation in the human body and is involved in many enzymatic reactions in the human body. Due to the bio-composite's nutrient properties, which significantly reduce the risk of harmful reactions that are associated with other foreign implant materials [20].

2.2.3 Mechanical Characteristics Resembling Natural Bone

Mg has a significant advantage over other materials due to its mechanical properties that resemble natural bone. The elastic modulus of pure Mg is 41-45 GPa is much closer to that of natural bone 10-40 GPa compared to traditional metallic implant materials such as titanium 110-117 GPa or stainless steel 189-205 GPa [21].

This similarity in mechanical properties helps to reduce the risk of stress shielding, a phenomenon where the implant bears a disproportionate amount of the load, leading to bone biological processes and potential implant loosening. Meanwhile, compared to titanium and other metal implant in vivo studies represent improved results [22].

2.2.3 Biodegradability

Pure Mg possesses a special property that allows it to biodegrade in a physiological atmosphere, unlike permanent metallic implants. According to Zheng et al. (2014), this characteristic minimizes patient discomfort and healthcare expenses by obviating the necessity for follow-up procedures to extract temporary implants [23]. When temporary support is needed, such as fracture fixation or cardiovascular stents, the biodegradation of Mg implants might be especially helpful. Better healing outcomes may result from the implant's ability to progressively transfer the load to the repairing tissue as it deteriorates [14].

2.3 Hydroxyapatite

Calcium apatite and a crystal phase of calcium phosphates (CaP) combine to form the mineral compound known as hydroxyapatite (HA), which has a density of 3.16 g/cm^3. Since hydroxyapatite (HA) is similar to the mineral component of natural bone and has excellent biocompatibility, it has been extensively studied as a coating material for Mg implants. Electrophoretic deposition (EPD) has gained significant attention as a surface modification technique for applying hydroxyapatite (HA) coatings onto magnesium (Mg) and its alloys, especially for biomedical applications.

In a recent study, Akram et al. coated pure magnesium with hydroxyapatite using EPD and reported substantial improvement in corrosion resistance and biocompatibility, making it suitable for use as a temporary orthopedic implant[24]. Previously, Saadati et al. applied HA coatings to an Mg–4Zn–4Sn–0.6Ca–0.5Mn alloy using the same EPD technique. Their findings confirmed the effectiveness of the coating in enhancing corrosion resistance and maintaining structural integrity during degradation [25].

Further studies from 2021 onward have continued to validate and expand the potential of EPD-HA coatings on various magnesium alloys. For instance, abu bakar et al. Studied the effect of applied voltage on nano-HA coatings on AZ31 magnesium alloy via EPD. The results indicated that optimized voltage parameters led to uniform coatings with better adhesion and corrosion resistance [26].

A more advanced study by W.qin et al. developed a reinforced nanocomposite coating comprising wollastonite-hydroxyapatite (WS-HA), magnetic nanoparticles (MNPs), and single-walled carbon nanotubes (SWCNTs), which was deposited via EPD onto magnesium substrates. The composite coatings showed excellent corrosion resistance and bioactivity, highlighting their suitability for next-generation orthopedic implants[27].

Moreover, Iulian Antoniac et al. (2021) applied HA coatings to Mg–Zn–Mn alloys using EPD and systematically studied their degradation behavior. The HA-coated alloys exhibited a controlled degradation rate and increased biocompatibility, which are essential for temporary biomedical implants [28].

Collectively, these studies underline the progress made in improving magnesium-based implants through HA coatings applied by EPD. The consistent improvements in corrosion resistance, adhesion, and bioactivity across different magnesium alloys confirm the potential of this technique in the biomedical field.

2.4 Boron Nitride

Boron nitride (BN) is a composite material made of boron & and nitrogen. Various crystal shapes can develop depending on the temperature and pressure.1,2 (hexagonal, rhombohedral, diamond-like cubic, and wurzite), although the hexagonal form is the most stable at ambient temperature [18]. Biomedical engineering currently focuses on the use of boron nitride nanoparticles for neutron capture treatment and bio-implants. One-dimensional BN nanostructures are among these nanostructures, and due to their exceptional and distinctive qualities, such as their tunable surface and bandgap, electronic, optical, mechanical, thermal, and chemical stability characteristics, they are about to be developed as new materials to meet some requirements for various application areas. It has been established that BN Nano-sheets and BN nanotubes (BNNT) are biocompatible. According to one of these experiments, chitosan/BNNT-OH scaffolds markedly improved the adhesion and growth of human dermal fibroblasts without having any harmful effects, looking at samarium 152 doped BNNTs as a Nano-sized -emission source in the realm of nuclear medical therapy [29]. Hexagonal boron nitride (h-BN), which has a lamellar structure resembling graphite, is regarded as one of the most promising solid lubricant materials in engineering. H-BN is desirable not only for its solid lubricating capabilities but also for its strong corrosion resistance low electrical conductivity, and good thermal stability thermal conductivity Recently, research on h-BN's possible biological applications has also started [4]. A 2D nanomaterial known as hexagonal boron nitride (h-BN), often known as "white graphene," has a few boron nitride (BN) layers and a hexagonal honeycomb network of B-N links. Outstanding barrier properties, increased thermal stability, superior mechanical strength, resistance toward oxidation, and chemical inertness in challenging environments are all characteristics of h-BN [30].

The application of composite coatings composed of hydroxyapatite (HA), chitosan, collagen, and hexagonal boron nitride (h-BN) on Ti6Al4V substrates has gained considerable interest for improving the surface properties of biomedical implants, particularly to enhance corrosion resistance, biocompatibility, and mechanical stability.

Ali Tozar et al. conducted a study on optimizing the electrophoretic deposition (EPD) parameters for hydroxyapatite/chitosan/collagen/h-BN coatings on Ti6Al4V. They employed response surface methodology to determine the best deposition conditions, achieving improved coating adhesion and corrosion resistance, which are crucial for implant longevity and compatibility in physiological environments [31].In an earlier study, Tozar and Karahan compared the reinforcing effects of collagen and h-BN in hydroxyapatite/chitosan coatings. Their results showed that while each component improved mechanical strength and corrosion resistance individually, their combination provided a synergistic effect, enhancing the overall performance of the coating system for orthopedic applications [32].

Collectively, these studies emphasize the evolving role of HA/chitosan/collagen/h-BN-based coatings in enhancing the biological and structural performance of Ti6Al4V implants. By improving critical parameters such as corrosion resistance, cell adhesion, and mechanical durability, these coatings are paving the way for more reliable and long-lasting implant solutions in clinical applications.

Chapter 3

METHOD AND MATERIALS

This chapter demonstrates the technique and method adopted to coat HA with BN on pure Mg.

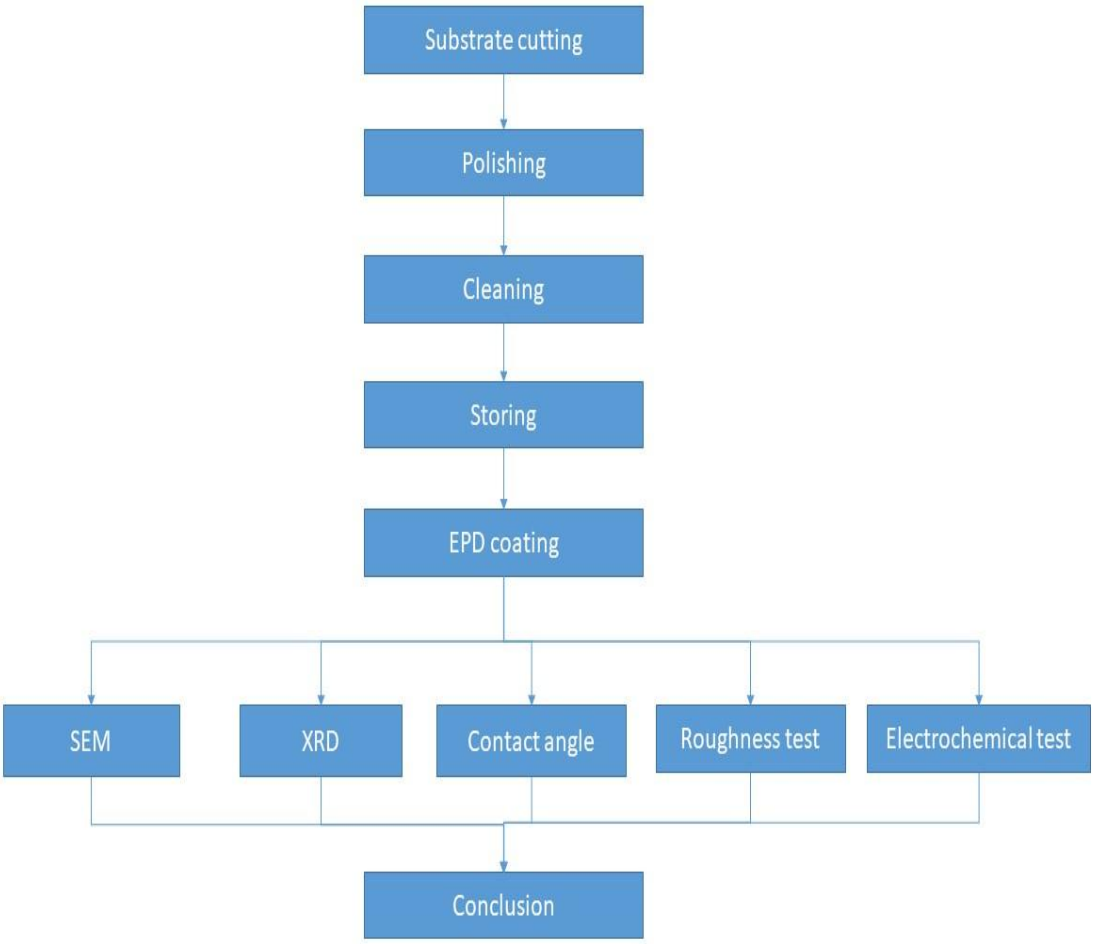


Figure 1. Schematic representation of work plan

Figure. 1 illustrates the sequential steps take place in the preparation, coating, and characterization of a substrate using the Electrophoretic Deposition (EPD) technique.

3.1 Materials

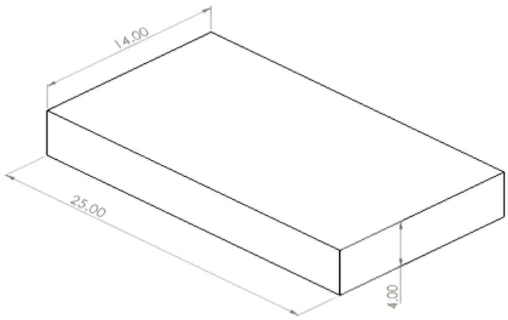
Materials used in this study are pure Mg purchase Henan Yuhang Material Co., Ltd. China, boron nitride particle size < 200nm purchase from Macklin china CAS: 10043-

11-5 hydroxyapatite particles size of <200nm from Merck, medium molecular weight chitosan, and absolute ethanol made in Germany.

3.2 Substrate Preparation

3.2.1 Cutting of Mg substrate

An EDM wire cut machine (model FZC7732/C, manufactured in September 2021, China) was used in the CNC Laboratory at Air University to fabricate Mg substrates from a solid Mg plate.



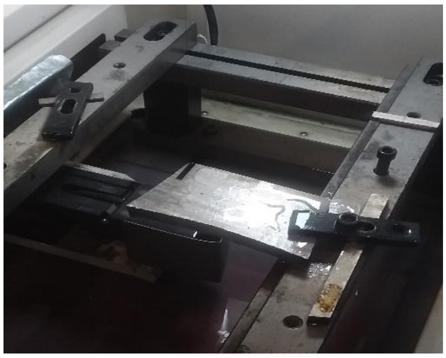


Figure 2: CAD model and EDM wire cut

Figure 2 represents an image that displays the EDM wire cut machine setup used for machining the Mg substrate. The substrate is securely clamped on the working table of the EDM wire cut machine. This setup enabled precision cutting of the soft and reactive Mg material with minimal mechanical stress. The EDM process ensures dimensional accuracy and a fine surface finish, critical for further surface treatment and coating procedures.

The CAD drawings were develop prior to the cut in AutoCAD coupled with wire EDM with the dimensions of length of 25.00 mm, a width of 14.00 mm, and a thickness of 4.00 mm.

3.2.2 Polishing Process

After cutting, the Mg substrate was polished in the International Islamic University lab through a polishing machine to achieve a shiny surface for better electrophoretic deposition.

Figure 3: before and after polishing

Figure 3 illustrates the surface condition of the Mg substrate before and after the polishing process. The sample on the left shows the before state, where the surface appears rough, oxidized, and uneven due to the raw cutting operation carried out during EDM wire cutting.

To achieve a smooth, clean, and mirror-like finish, the substrate was subjected to a systematic polishing process using silicon carbide abrasive papers with progressively finer grit sizes, ranging from 200 grit to 1200 grit. The polishing began with grit 200 to remove larger surface imperfections and scratches. The process continued sequentially through 400, 600, 800, 1000, and finally 1200 grit papers, each stage removing the scratches left by the previous one and progressively refining the surface texture.

The After image on the right clearly shows the polished surface of the Mg sample, which is now bright, smooth, and reflective, indicating a uniform and well-prepared surface. This refined finish is essential for ensuring good bonding and uniform deposition in subsequent surface coating processes.

3.2.3 Storage of polished sample

The polished Mg substrates were then preserved in air-tight sealed containers for preventing form the formation of oxide layer.

3.3 Suspension Preparation

The preparation of the suspension for Electrophoretic Deposition (EPD) begins with the accurate measurement of the coating materials. A clean and dry 50 mL glass beaker is used for the preparation. Initially, 0.5 grams of hydroxyapatite (HA) and 0.125 grams of boron nitride (BN) powders are precisely weighed using a digital balance shown in Figure 4 and transferred into the beaker.

Figure 4 Digital Weight Balance

In the second step, 50 mL of medium molecular weight chitosan solution, previously prepared in a separate flask—is carefully added to the beaker containing the HA and BN powders. This mixture forms the initial suspension required for EPD.

Next, to achieve uniform distribution of the solid particles within the liquid medium, the beaker is placed on a magnetic stirrer. A magnetic stir bar is introduced into the suspension, and the beaker is stirred continuously for approximately 20 minutes. This step is essential to initiate the homogenization of the HA and BN particles in the chitosan matrix.

Following magnetic stirring, the suspension undergoes ultra-sonication to further enhance particle dispersion and break down any residual agglomerates. The beaker containing the stirred mixture is placed in an ultrasonic bath (Model: MAUR EOF 0349) shown in Figure 5 and subjected to 10 minutes of sonication. The ultrasonic waves generate cavitation effects that effectively disintegrate clusters of particles, leading to improved dispersion and overall stability of the suspension.

Figure 5. Ultra sonication

This sequential process of magnetic stirring followed by ultra-sonication ensures the formation of a stable and homogenous suspension. Such a well-prepared suspension is crucial for achieving a uniform, defect-free, and high-quality coating during the electrophoretic deposition process.

Table 2. Quantity of materials in suspension

S.no	Suspension parameter	Quantities
1	Chitosan solution (medium molecular weight)	50ml
2	Hydroxyapatite (HA)	0.50 gram
3	Boron nitride (BN)	0.12gram

3.4 Cleaning Of Substrate Materials

Prior to the electrophoretic deposition (EPD) process, the pure magnesium (Mg) substrate undergoes a critical cleaning step to ensure optimal coating adhesion and surface quality. The substrate is immersed in absolute ethanol for 10 minutes. This cleaning step serves multiple purposes: ethanol, being a volatile and highly effective organic solvent, removes surface contaminants such as oils, grease, dust, and oxides that may have accumulated during handling or machining processes.

3.5 Electrophoretic Deposition

After the achievement of stable suspension of boron nitride with hydroxyapatite, the electrodes were placed in the suspension, connected to a DC power supply with a separation distance of 10mm in between the electrodes. The deposition was done through cathodic deposition in which the substrate pure Mg was connected to the negative terminal of the DC power supply and a counter stainless electrode was connected to the positive terminal of the DC power supply. Show in Figure 6.

Figure 6. Experimental setup for EPD

Electrophoretic setup used in the current study with chitosan base homogenous suspension of boron nitride and hydroxyapatite. Where the positive terminal electrodes were stainless and the counter electrode of pure Mg with a DC power supply.

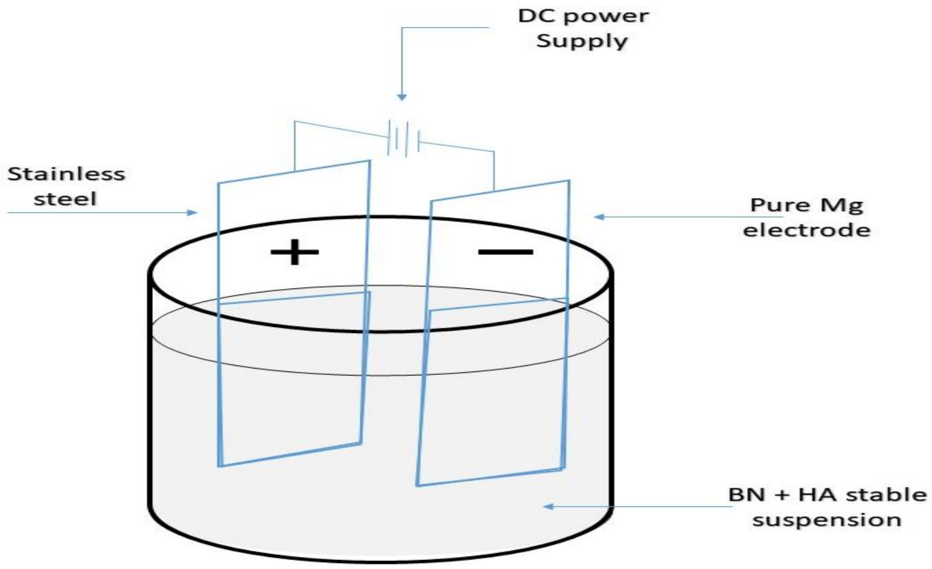


Figure 7. Electrophoretic deposition diagram

For electrophoretic deposition, the parameters for voltage and time were selected from previously conducted experiment that is full design of the experiment approach where the three-level value of time and voltage were selected for the deposition of hydroxyapatite on pure Mg illustrated.

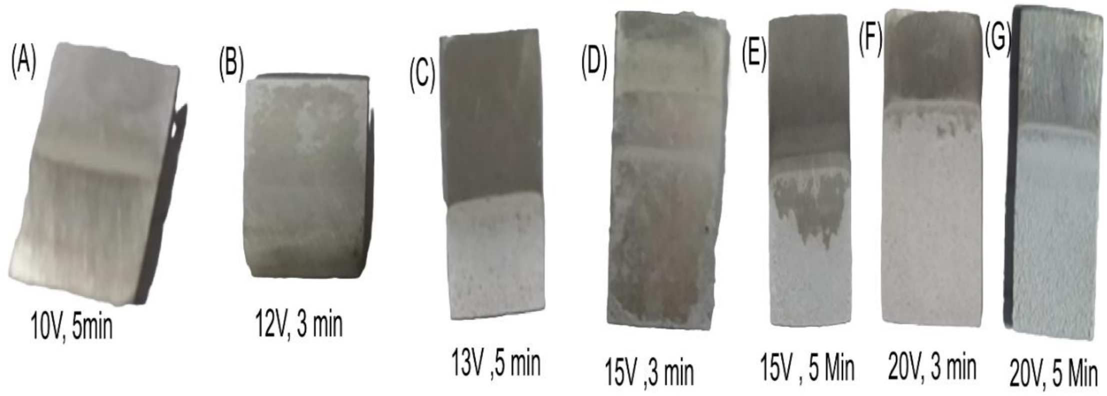


Figure 8. EPD-coated sample

Table 3. Observation varying for different time and voltage of the figure 8

Sample	Voltage (V)	Time (min)	Observation (Visual)
A	10V	5 min	Slight surface change, mostly metallic appearance
B	12V	3 min	Slightly dull surface, early signs of coating
C	13V	5 min	Visible coating begins, a partial matte layer
D	15V	3 min	Uneven coating, the surface starts changing distinctly
E	15V	5 min	More uniform coating layer formation
F	20V	3 min	Stronger matte finish, coating more evident
G	20V	5 min	Dense and complete coating,

Chitosan/h-BN and chitosan/h-BN/TiO_2 composite films were prepared using suspensions with different amounts of h-BN but the same chitosan concentration of 0.5 g/L. To make the chitosan solution, chitosan powder was dissolved in a 1% acetic acid solution. Three types of suspensions were prepared: the first with 1 g/L of h-BN (labeled C-hBN1), the second with 2 g/L of h-BNand the third with 2 g/L of h-BN and 2 g/L of TiO_2 These powders were added to the chitosan solution, which was made using a mixture of water and ethanol, with 17% of the liquid being distilled water. These prepared suspensions were then used to deposit composite coatings onto stainless steel (316L) using the Electrophoretic Deposition (EPD) technique [33].

The hardness and elastic modulus (a measure of stiffness) of the HA/CTS/COL/h-BN bio composite coatings increased as the amount of h-BN was raised up to 5 g/L. However, adding more than 5 g/L caused a slight decrease in these properties. Similarly, the coatings' ability to resist wear (tribological properties) also improved with increasing h-BN content up to 5 g/L. The coefficient of friction (which indicates how easily the surface slides) decreased with the increase in h-BN up to 5 g/L, but slightly rose when the concentration went beyond this level. The corrosion resistance of the coatings followed the same pattern—it improved as h-BN was increased up to 5 g/L and slightly declined after that. Furthermore, biocompatibility tests carried out over 12 weeks of immersion confirmed that the HA/CTS/COL/h-BN coatings are suitable for use in the human body. These results suggest that applying these bio composite coatings on Ti6Al4V implants could improve their performance and compatibility when used in living organisms. Electrochemical testing also indicated the formation of two time constants, which implies the development of a double-layer capacitance on the metal surface due to the penetration of the corrosive environment through pores in the coating. SEM images revealed that the number of pores in the coating decreased as the amount of h-BN in the suspension increased. All the suspensions used in this study contained 1 wt% Nano-hydroxyapatite (HA), with varying amounts of nano-h-BN 0.0, 2.0, 5.0, 10.0, and 25.0 wt%, based on the weight of HA [34].

3.6 CHARACTERIZATION

3.6.1 Surface Morphology

To observe the desperation and morphology of nanoparticles in composite-coated samples. The composition, particle size, and structure of the coating. Field emission scanning electron microscopy (FESEM) was used at the National Center for Physics Islamabad manufactured by Zeiss, integrated with energy-dispersive spectroscopy EDX to measure the elemental composition of coating. In this research, the FESEM of the bare and coated substrate is conducted.

3.6.2 X-ray diffraction spectroscopy (XRD)

The crystallinity of the material is determined by X-ray diffraction spectroscopy. XRD of raw material is conducted at the Air University Physics Department, where the 2θ peaks are plotted using the origin software meanwhile the results from the experimental data correspond to the reference data of CIF data of each material by using VESTA software.

3.6.3 Roughness of coated Mg surface

Surface roughness was measured using a profilometer. Before using a profilometer, the equipment was calibrated with a standard. Then, coated samples were placed on the slab with adhesive tape to grip the sample and leveled with a pitch point for the roughness test. Meanwhile, the tip of the profilometer drew a line of approximately 1 cm to calculate the roughness of the coating. The measurement obtained from the profilometer as an average value to ensure accurate results experiments were conducted serval times.

3.6.4 Contact angle

The hydrophilic and hydrophobic properties of any material can be determined from a contact angle test. To determine the wettability nature of the coating. Using a microliter pipette, simply pour 5 µL of distilled water onto separate locations on the bare Pure Mg substrate and the chitosan + HA + BN coated substrate. After 5 seconds, we used ImageJ software to measure the contact angle of each vertical drop with both a bare and coated surface. We did this by positioning the camera at the same level as each drop.

3.6.5 Electrochemical test

The degradation rate of materials can be measured through electrochemical testing, which measures the corrosion rate of a coated sample of HA with BN in comparison to bare pure Mg. These tests were conducted at the USPCASE NUST laboratory.

A 3.5 g/100 mL sodium chloride (NaCl) solution was prepared by dissolving NaCl in distilled water. The experimental setup was a three-electrode system, which consisted of coated Mg sample (HA + BN) is the working electrode. Graphite as the counter electrode. A silver/silver chloride (Ag/AgCl) electrode acted as the reference electrode.

Electrochemical Tafel (E-Tafel) curves were generated within a range of -3 V to 1 V, where the scan rate was at 0.01 V/sec, with a quiet time of 2 seconds before measurements.

Chapter 4

RESULTS AND DISCUSSION

Subsequently the successful deposition of the HA and BN coating on the pure Mg substrate through Electrophoretic Deposition (EPD) characterization technique is conducted to evaluate the coating's morphology, composition, surface properties, and electrochemical behavior.

Scanning Electron Microscope with energy-dispersive X-ray spectroscopy

1. Raw Materials

Boron Nitride

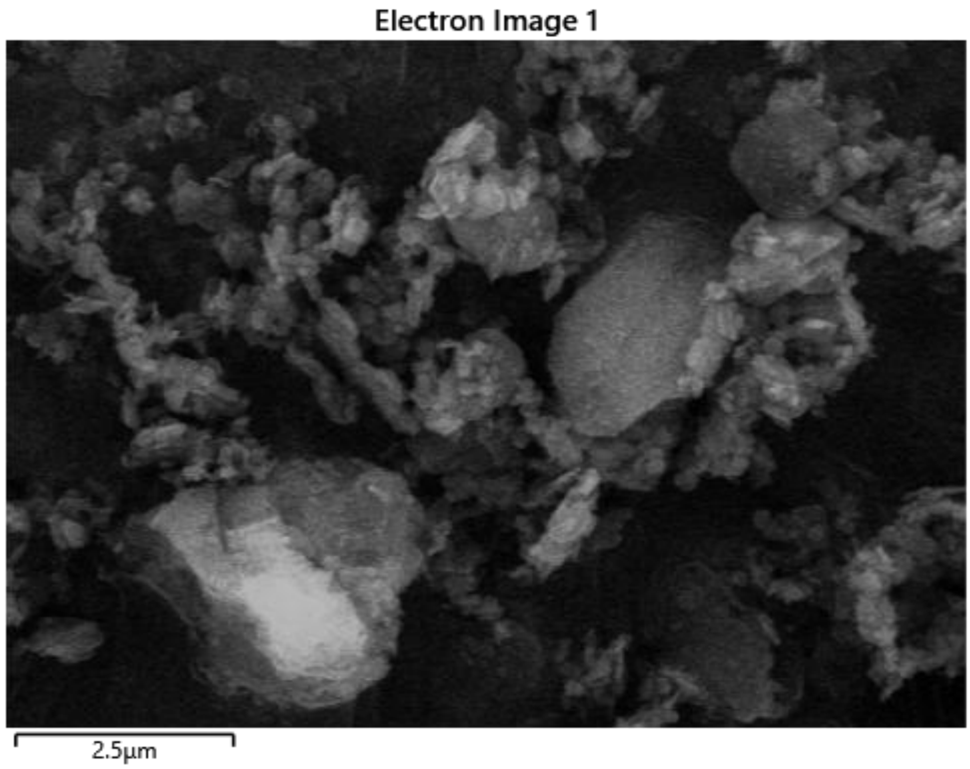


Figure 9. SEM of Boron nitride

Fig 9 demonstrates an SEM image of the raw material of boron nitride with a magnification of 2.5 micrometers from where the surface morphology and structure of materials can be determined.

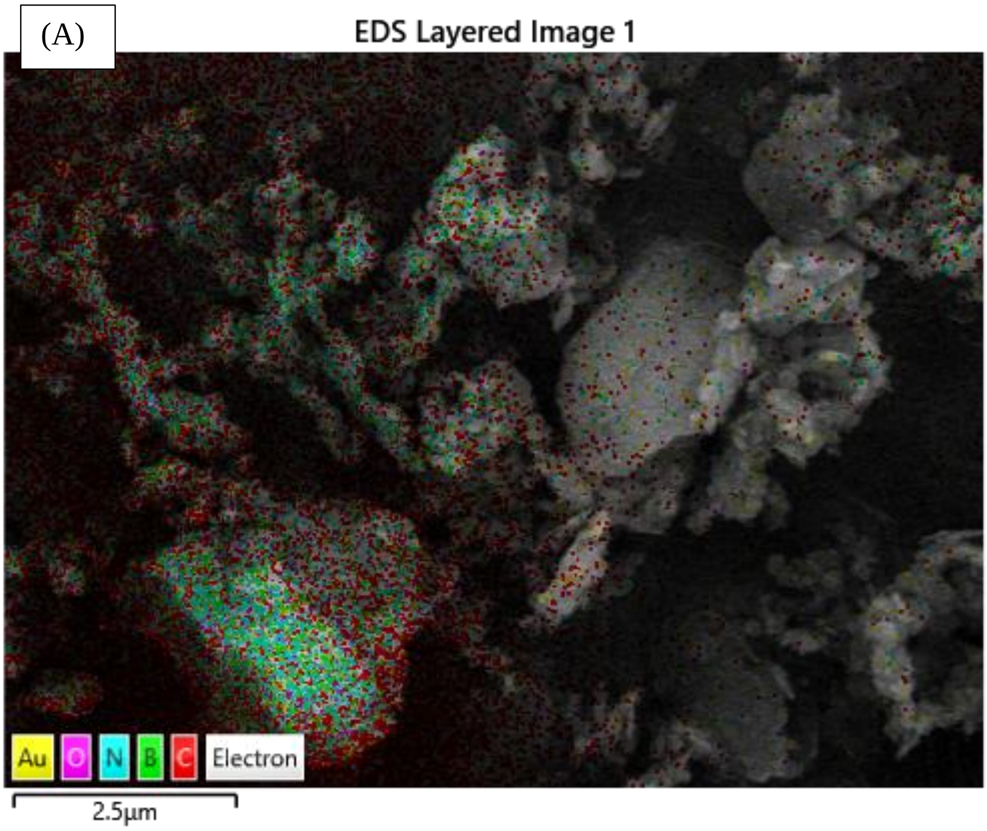
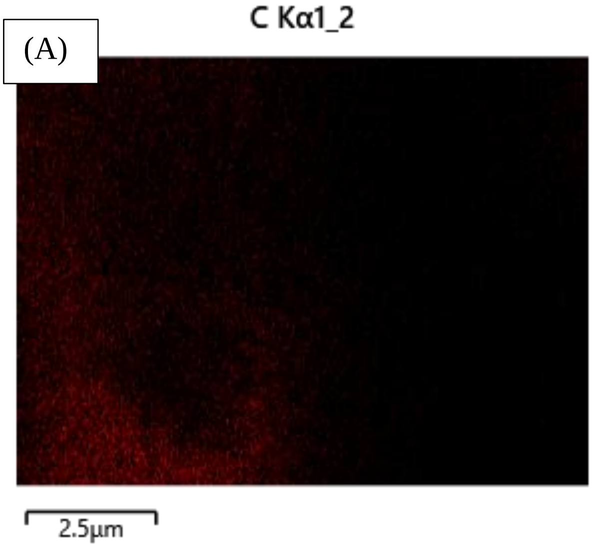


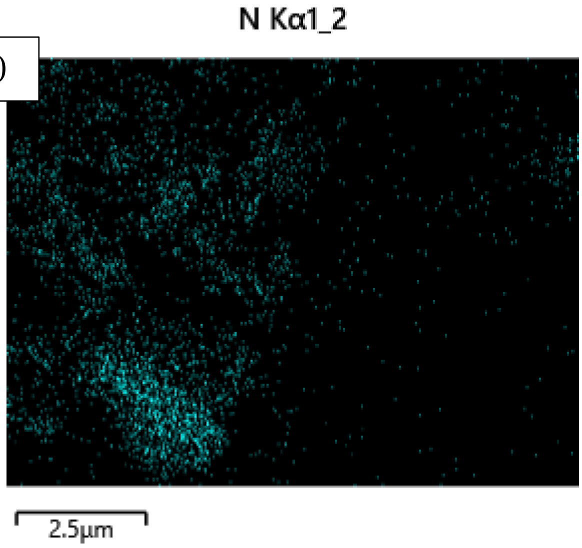
Figure 10. SEM of BN with elemental distribution

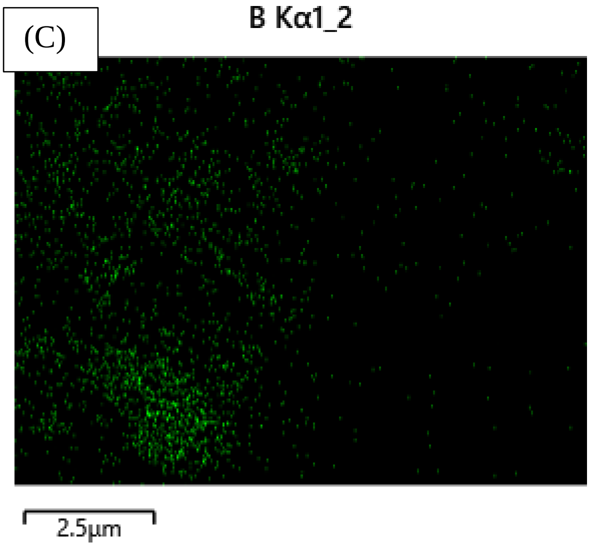
Fig 10 represents the energy-dispersive X-ray spectroscopy of the boron nitride with the elemental mapping of each element present in the observed materials.

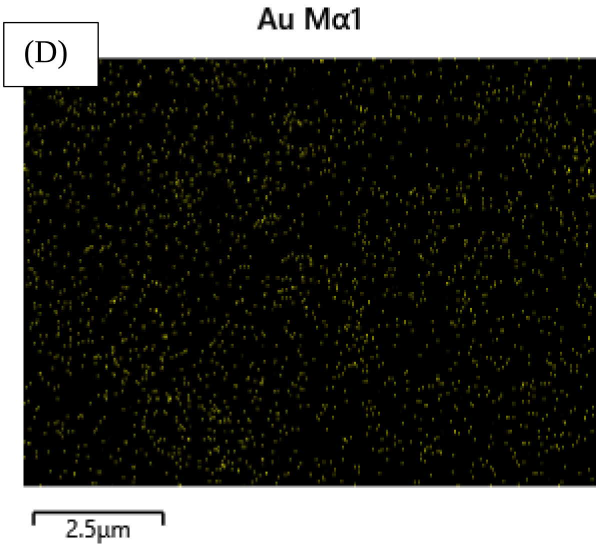
(A)

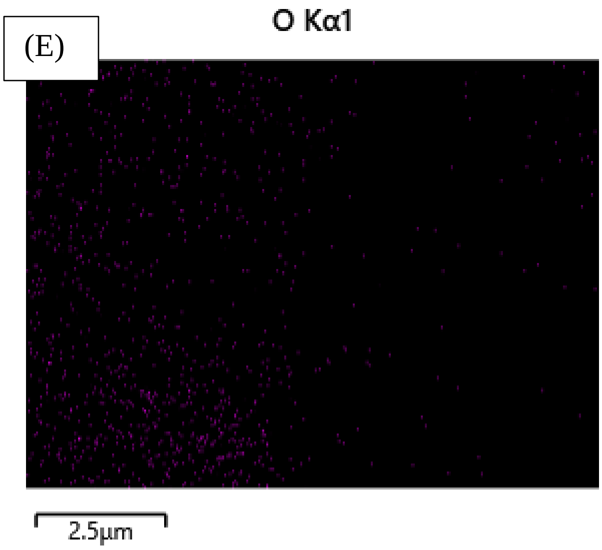


(B)




(C)
B Kα1_2
2.5µm


(D)
Au Mα1
2.5µm


(E)
O Kα1
2.5µm

The above image with each label represent the atomic distribution in sample under the observation of SEM where A is carbon, B represent nitrogen atom, C represent boron atom, D represent gold, and E represent oxygen atom. The presence of gold and carbon and oxygen is due the gold spurting to lower high charge conductivity.

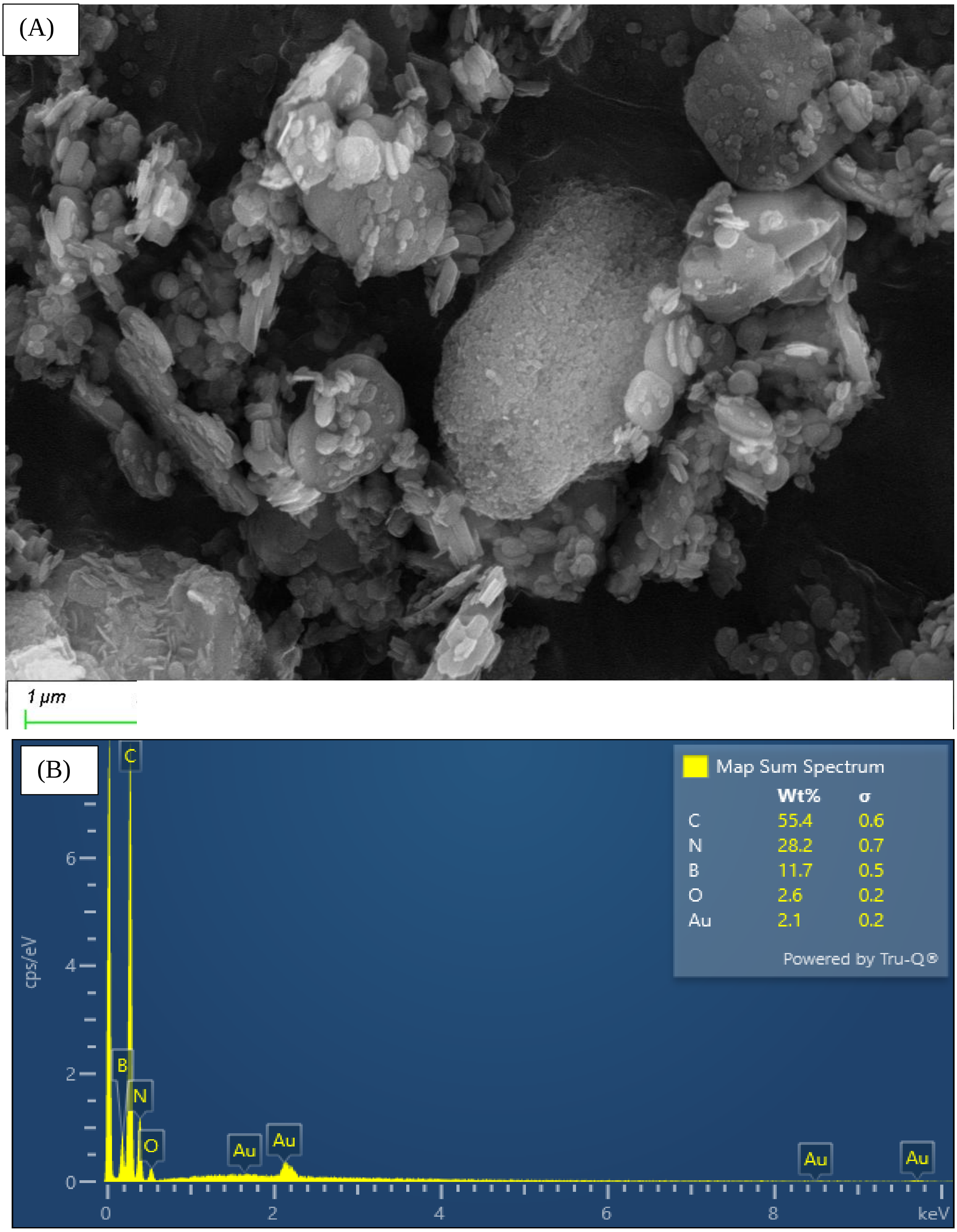
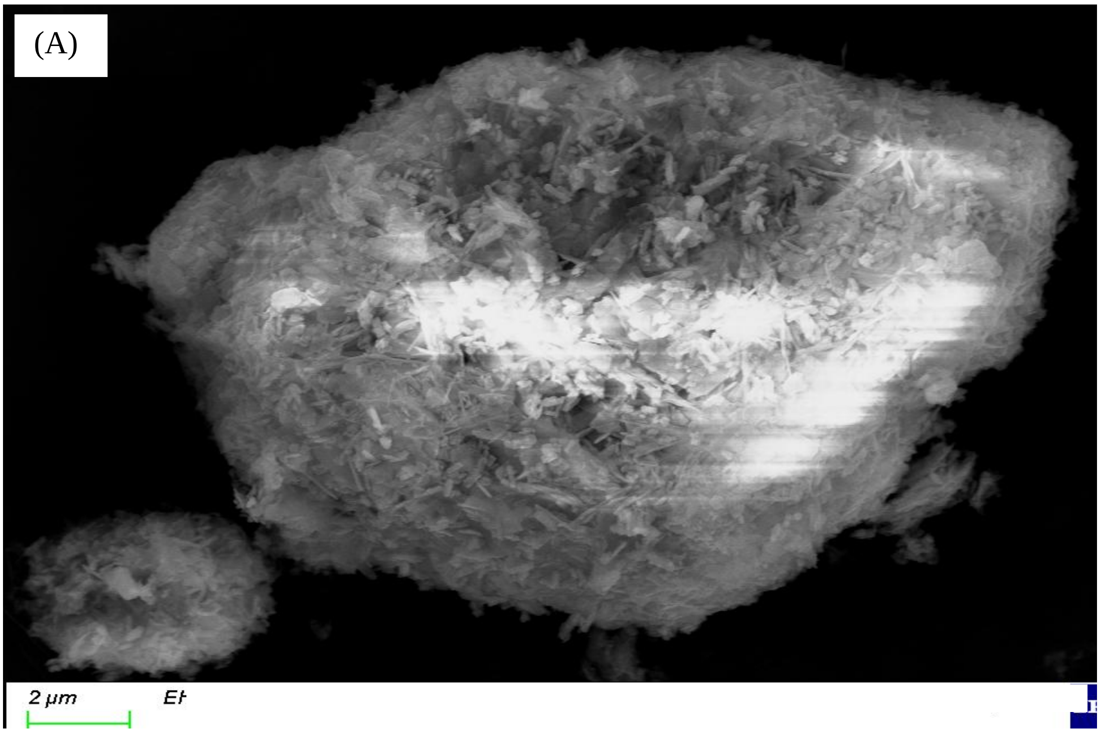


Figure 11. EDX of BN

Fig 6 represents the energy dispersive x-ray spectroscopy of boron nitride with peak of the each element present in the material under observation in SEM. The peak of C is higher as compared to Boron and nitrogen due to gold spurting and contamination. The peak of carbon is due technique used for clear morphological and structural study of material. A gold Au present in the peak is spattered to reduce the conductivity of a material. Where the average particle size is less than 200nm.

Hydroxyapatite



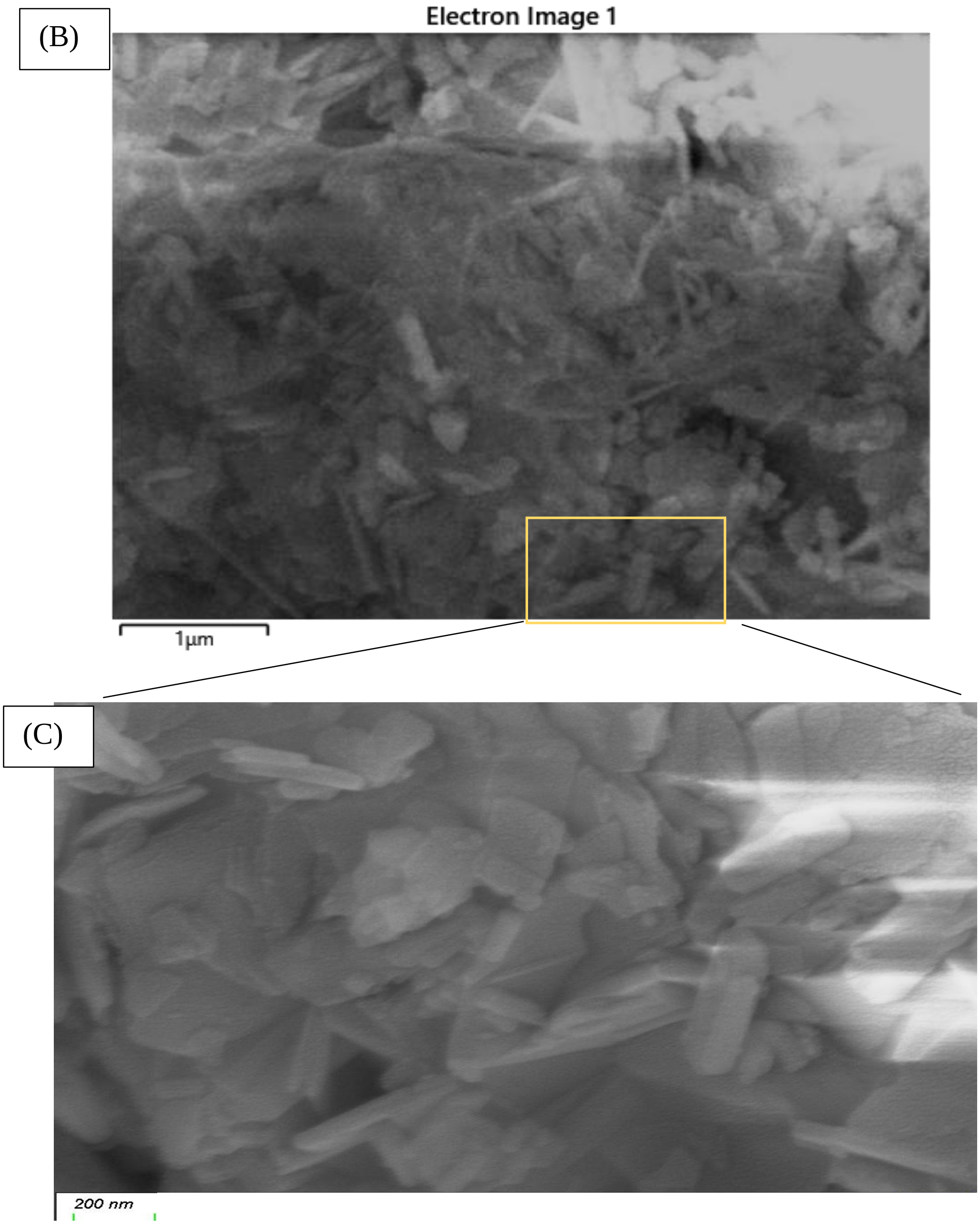
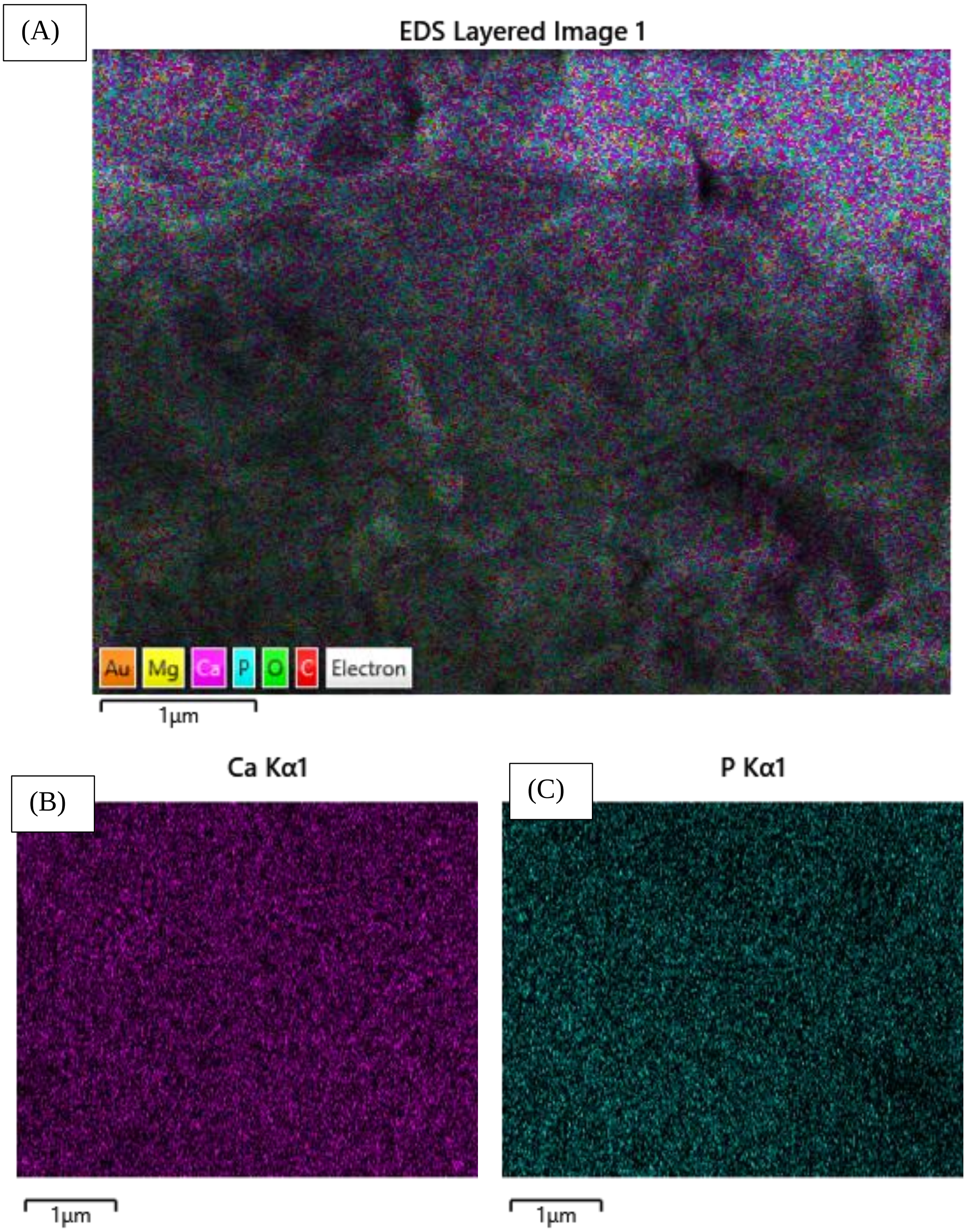


Figure 12. SEM OF HA

Fig 12 represents SEM images of hydroxyapatite with an average size of 200nm. From the figure, the morphology of hydroxyapatite be determined. From the figure 8 label C, the morphology of hydroxyapatite is shown which is cubical in structure.


(A)
EDS Layered Image 1
Au
Mg
Ca
P
O
C
Electron
1µm
(B)
Ca Kα1
1µm
(C)
P Kα1
1µm

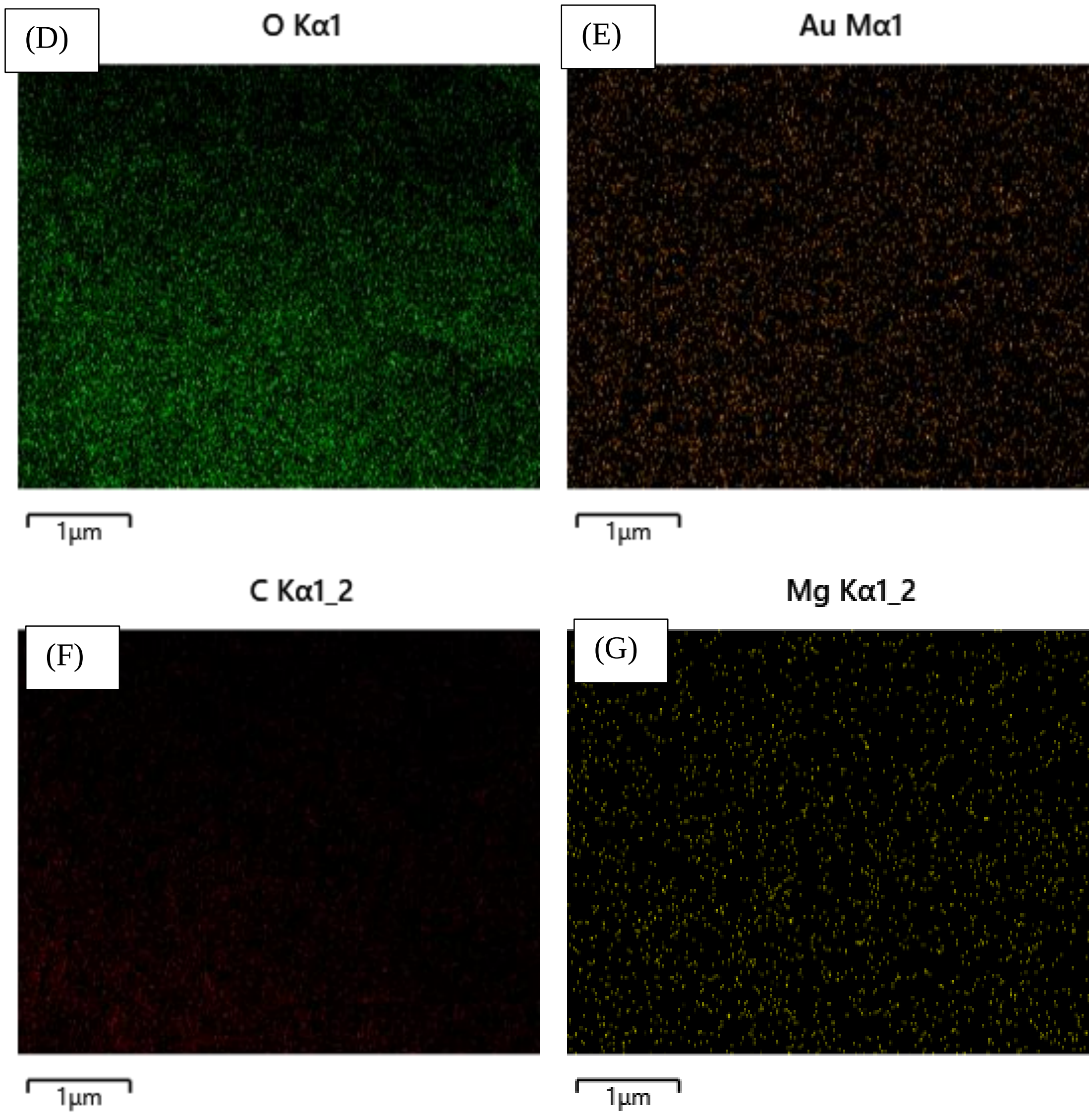


Figure 13. Elemental Mapping of HA

Figure 13 represents the elemental mapping of hydroxyapatite from the figure concentration distribution of each element can be determined. Where calcium and palpate are the main constituents of hydroxyapatite while the other element is due to the gold sputtering for lowering conductive on charges of element for better SEM images. The atomic distribution can be demonstrated with a high intensity of calcium and phosphate represented by label C and D.

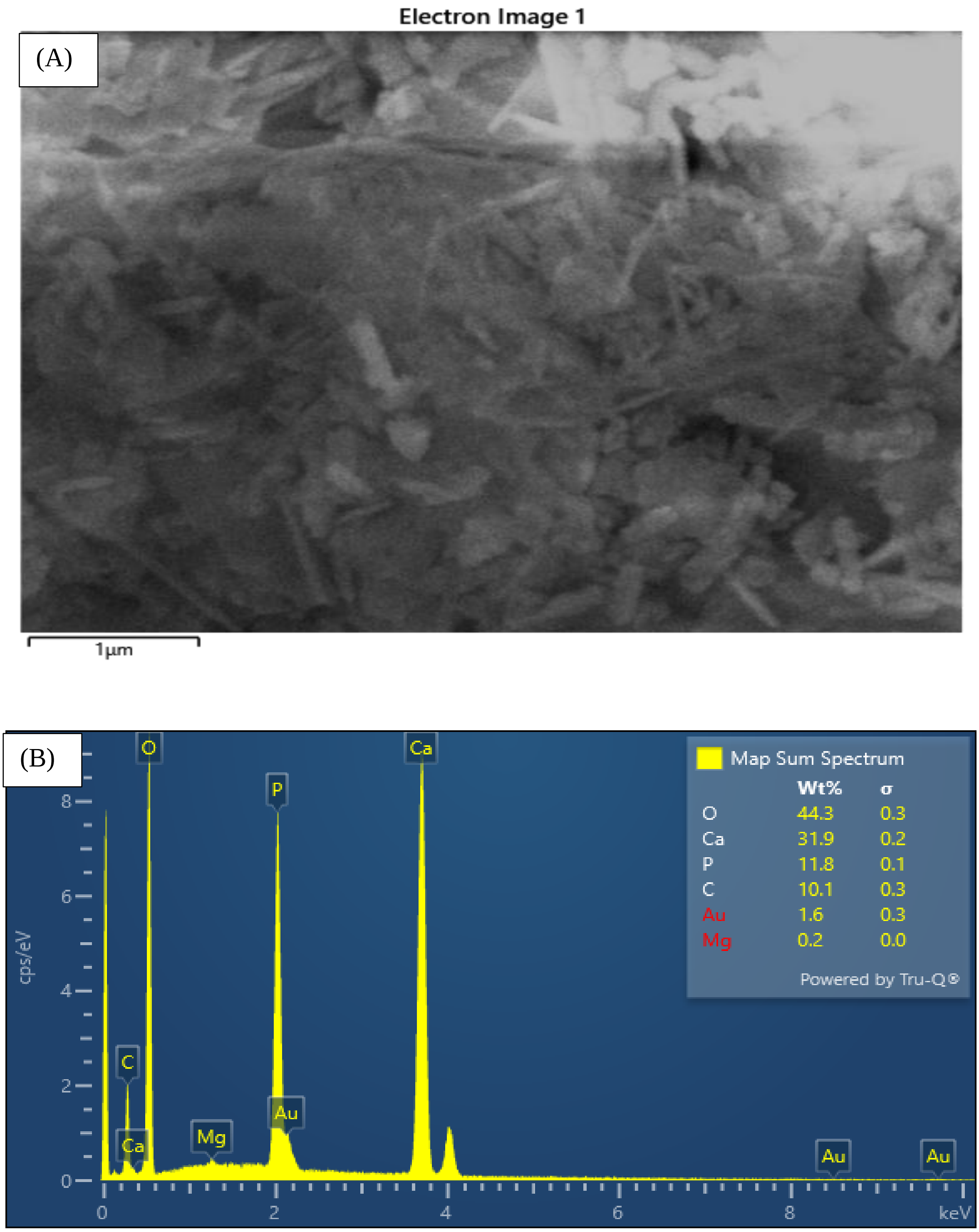


Figure 14. EDX pattern of HA

Figure 14 represent energy dispersive X-ray spectroscopy of hydroxyapatite demonstrated the peak of calcium and phosphate which is the main constituent used as raw material for coating

EPD coating of HA and BN on Pure Mg

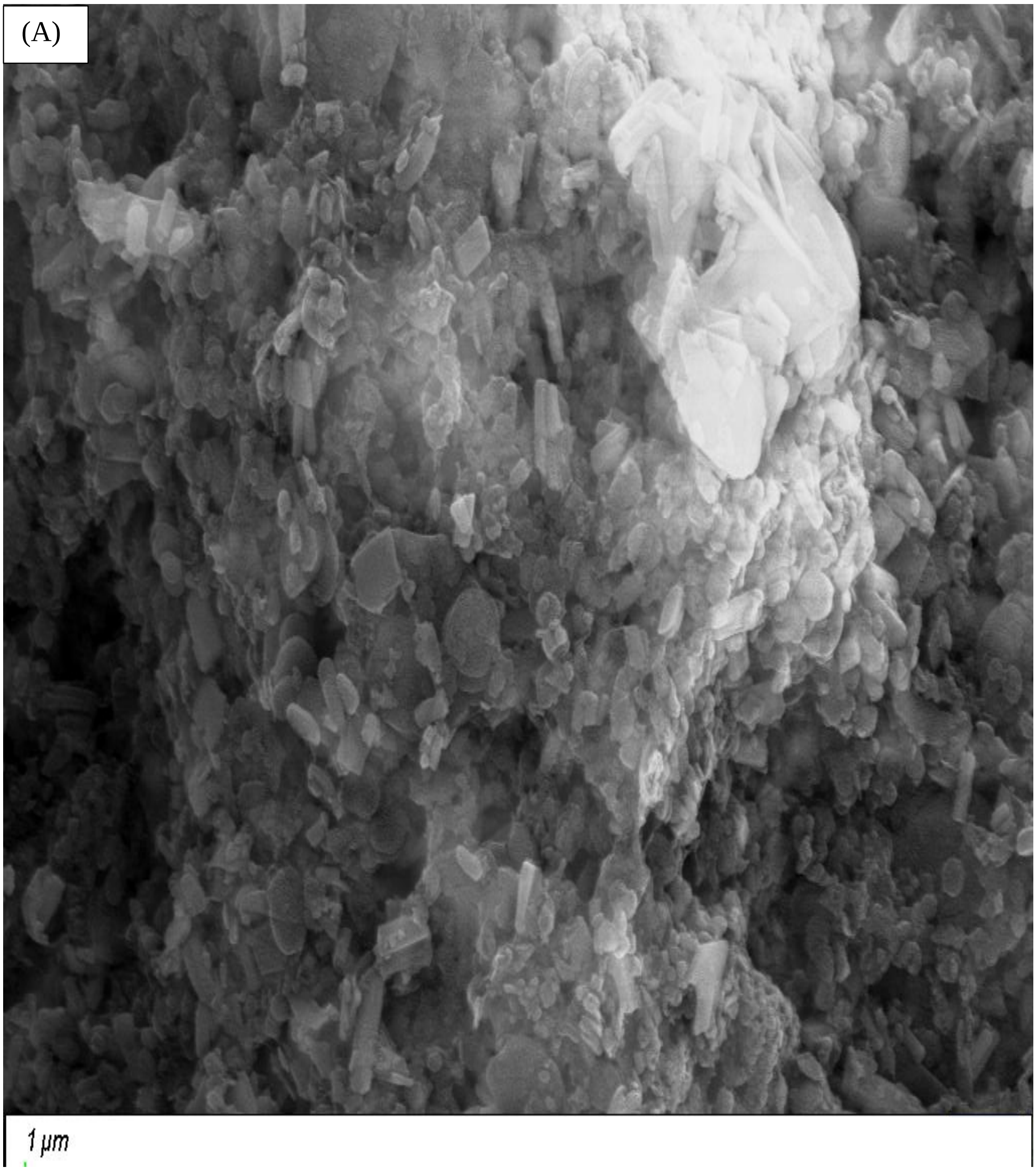
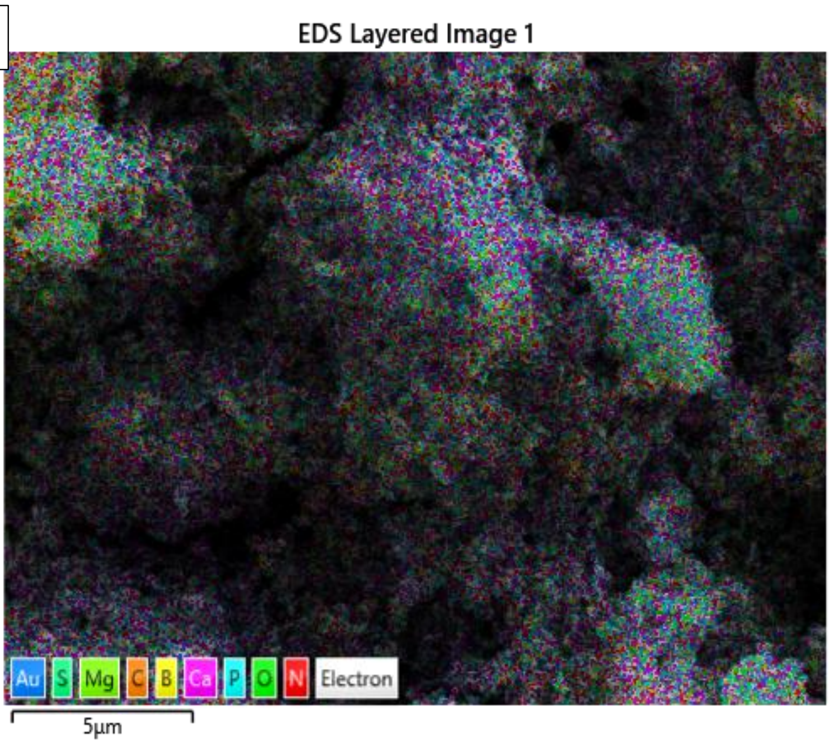


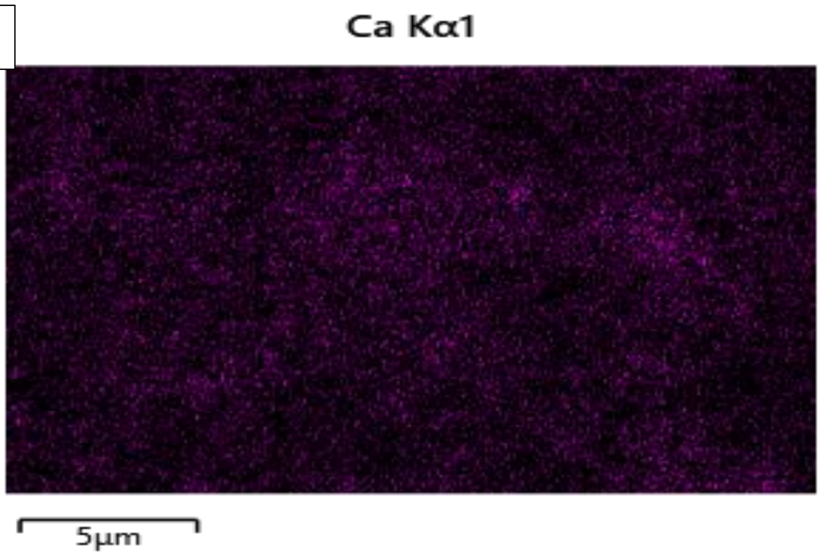
Figure 15. SEM of Composite coating of HA and BN on Pure Mg

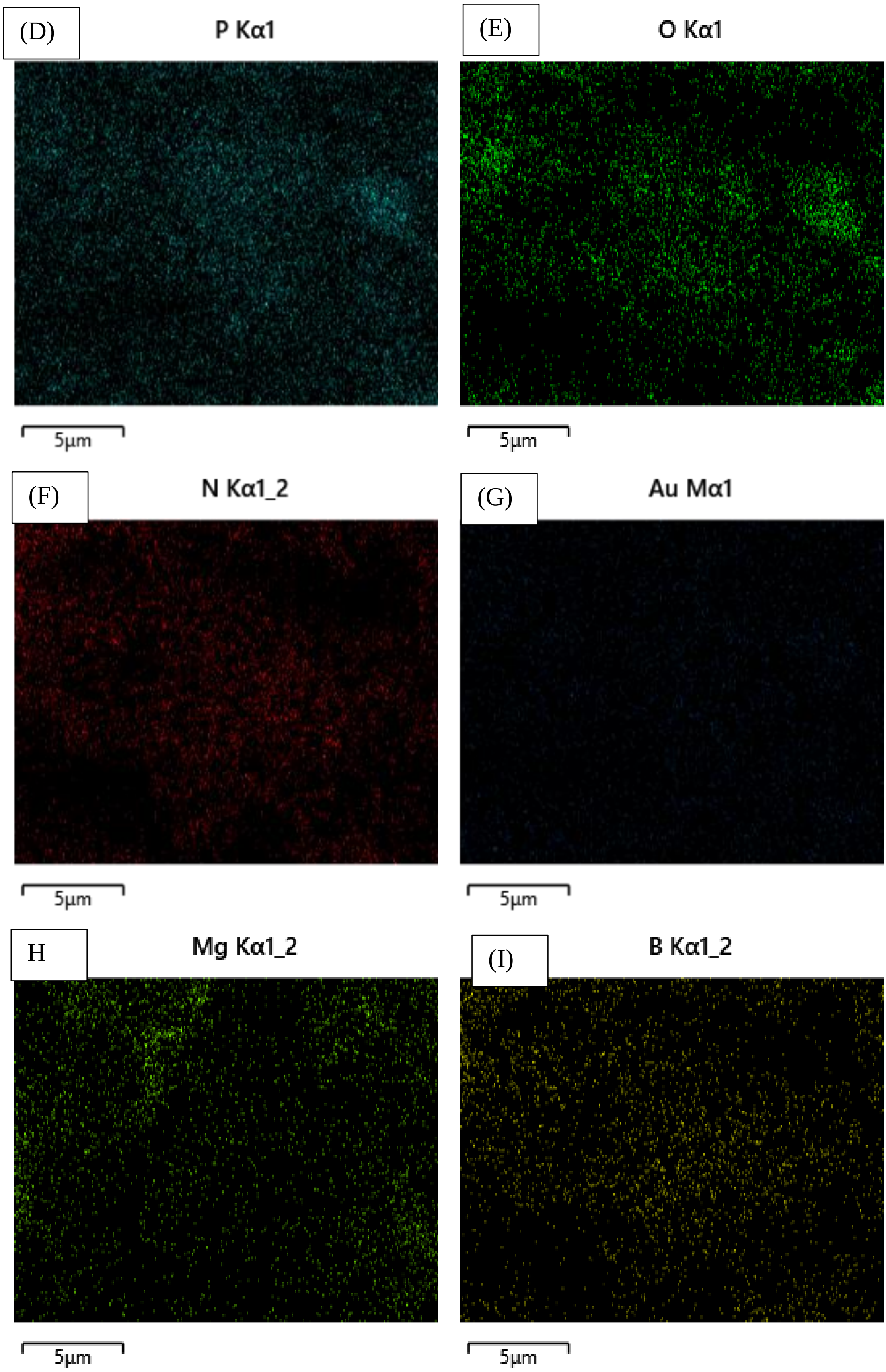
Figure 15 represent SEM of coating on pure Mg substrate from figure 8 homogeneity and particle dispersion can be observe.

(B)



(C)




(D)
P Kα1
5µm
(E)
O Kα1
5µm
(F)
N Kα1_2
5µm
(G)
Au Mα1
5µm
H
Mg Kα1_2
5µm
(I)
B Kα1_2
5µm

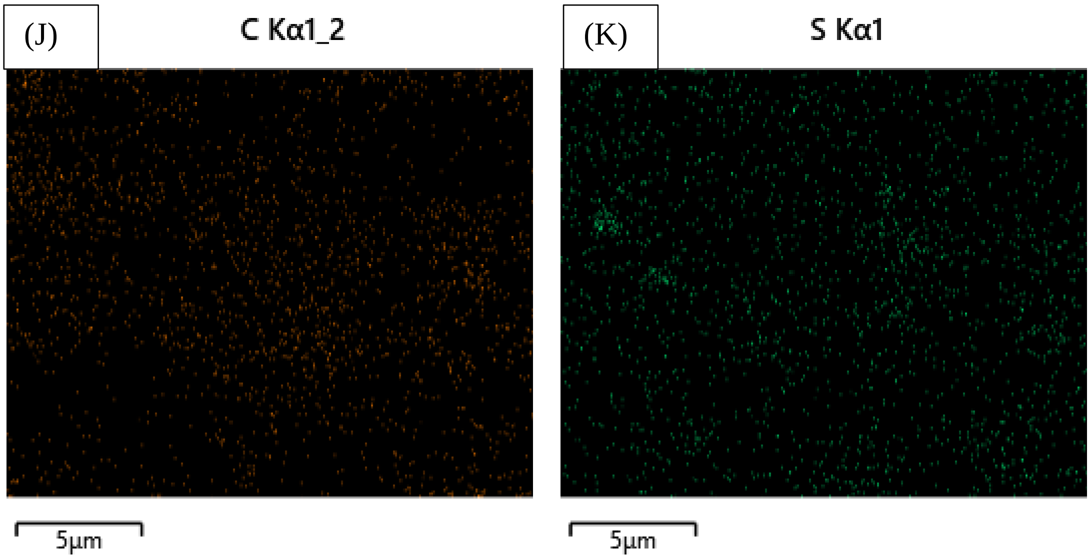


Figure 16. SEM of coating

Figure 16 represents an elemental mapping of the coating, where the particle dispersion is studied. This figure demonstrates the concentration of each element present in the coating.

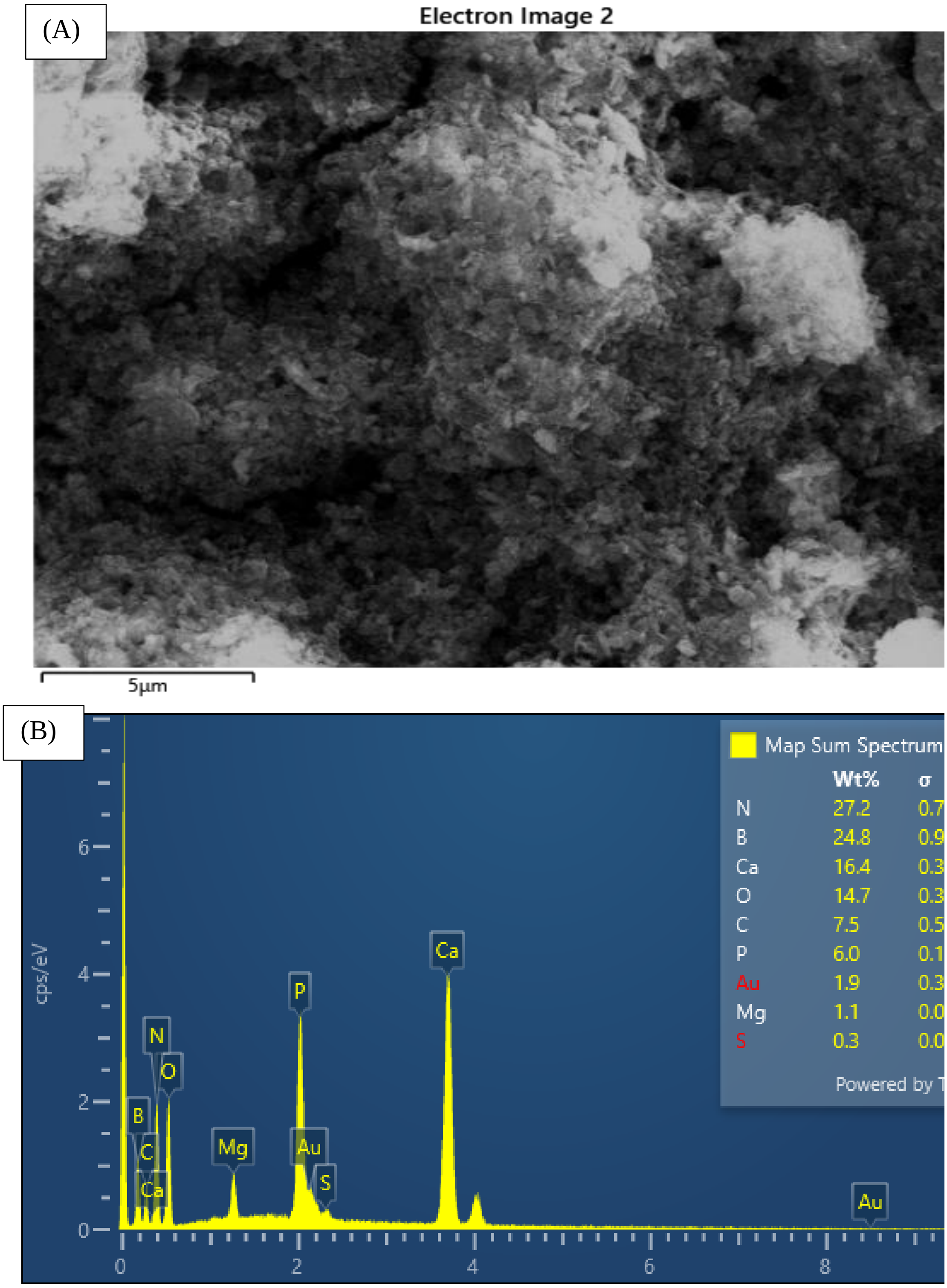


Figure 17. EDX of Composite coating of HA with BN on Pure Mg

Figure 17 represent the EDX spectrum of the coated substrate where the peaks of our raw materials can be verified and index of each peak represent higher concentration of our biomaterials

Coating Thickness

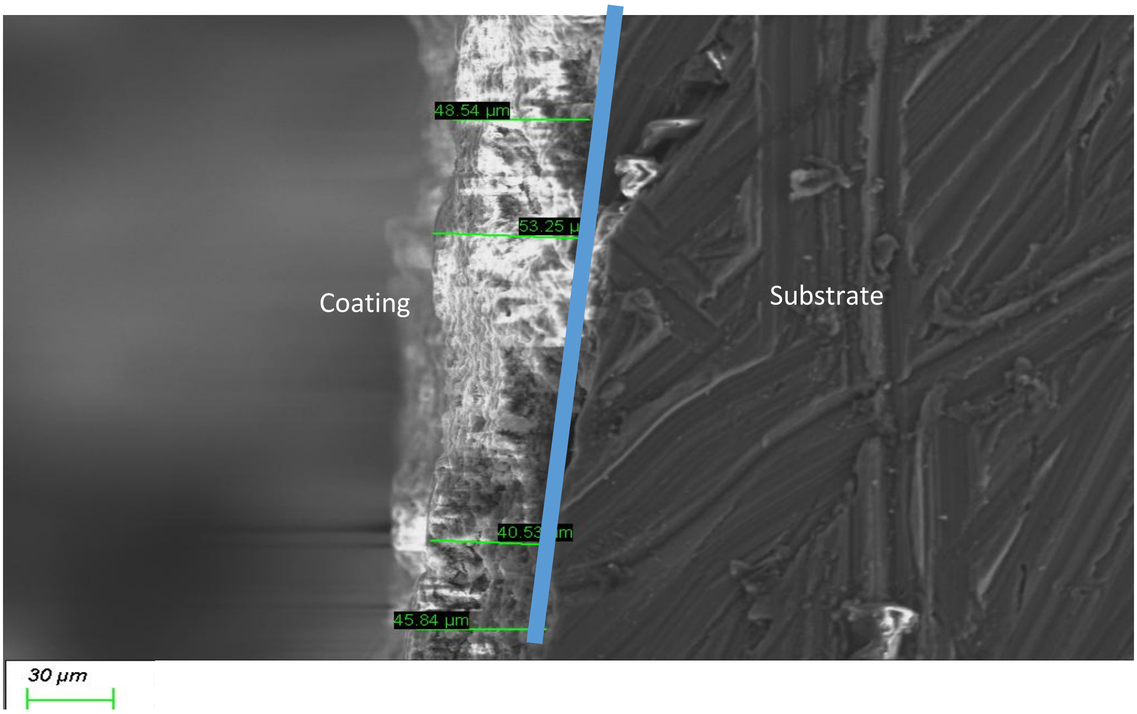


Figure 18. Coating Thickness

The above figure 18 represents the coating thickness. The SEM cross-sectional image indicates the coating thickness measurements at different points, which range between 40.53 µm to 53.25 µm. The interface between the coated layer on the left side and the substrate on the right side is shown in the image with clear structural features.

Contact Angle

Surface wettability is one of the most prominent factors that explain whether a compound is hydrophobic or hydrophilic, and the measure of the contact angle of an applied water droplet is necessary to determine its value. Therefore, hydrophobicity of a substance takes place if a contact angle appears to be larger than 90°, whereas hydrophilicity is seen as the contact angle less than 90°. In comparison, different Mg surfaces covered as well as non-covered wettability according to their differing contact angles will be presented here.

Figure 19: Contact Angle of Pure Mg

Figure 19 represents the contact angle of the bear Mg obtained using ImageJ software which is 42.562 degrees.

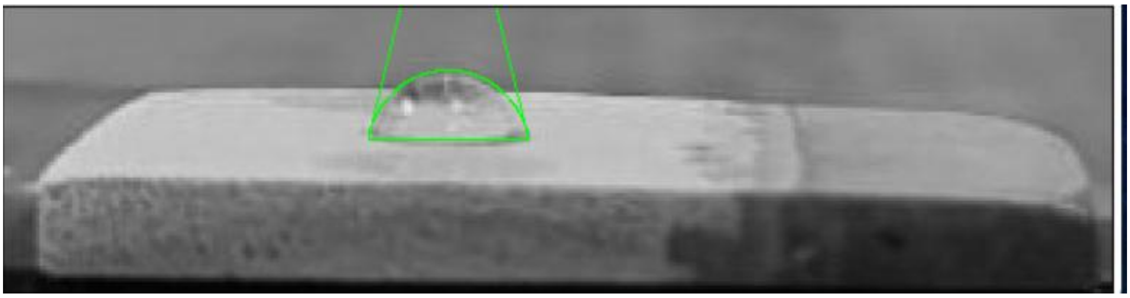


Figure 20. Contact Angle of Coating

Figure 20 represents the contact angle of coated Mg with Boon nitride with hydroxyapatites.

The bare Mg Surface contact angle is 42.562°, which is hydrophilic. The droplet spreads more on the surface, indicating higher surface energy and better interaction with water. This hydrophilic nature can accelerate degradation in aqueous environments, making the material more susceptible to corrosion.

The coated Mg surface with boron nitride and HA contact angle is 76.931°, which exhibits a considerable increase in hydrophobicity compared to the bare surface. The droplet remains more spherical, reducing its interaction with the surface. This coating enhances water resistance, which reduces the degradation rate of the material and improves its corrosion protection.

Surface Roughness

Surface Roughness Tester measuring the roughness of a sample, displaying in figure 21 that is Ra (Roughness Average) value of 3.812 µm, Ra (Arithmetic Mean Roughness) is the most common parameter used to quantify surface roughness. It represents the average deviation of the surface profile from the mean line.

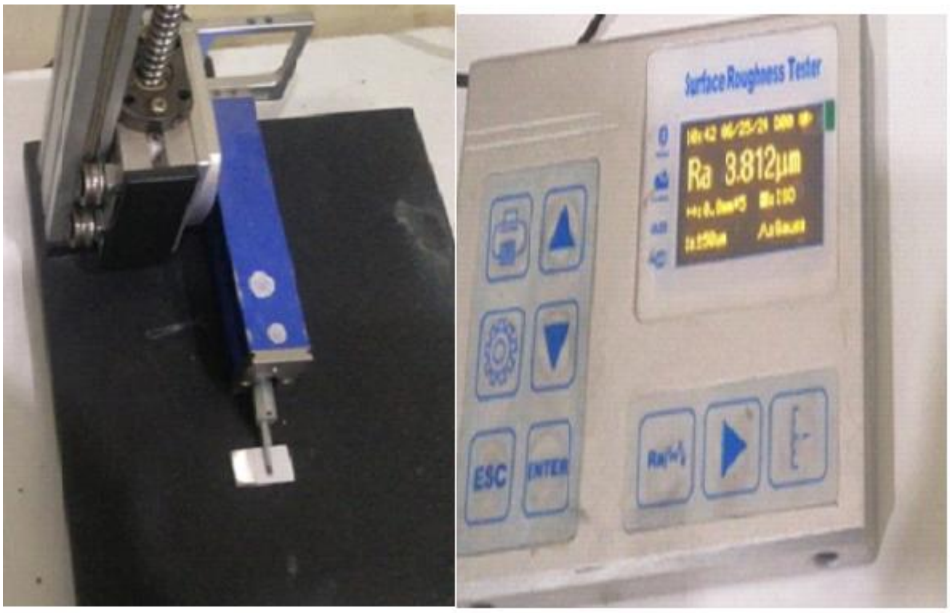


Figure 21. Roughness of coating

A higher Ra value indicates a rougher surface, while a lower Ra value suggests a smoother surface. Analysis of the Obtained Value (3.812 µm). A Ra value of 3.812 µm suggests a moderately rough surface. For biomedical applications (such as coatings on Mg implants), roughness affects cell adhesion, wettability, and corrosion resistance. Smooth surfaces (Ra < 0.5 µm) Used in high-precision engineering and medical implants where minimal roughness is needed. Moderate roughness (Ra 1-4 µm) are commonly in coatings, biomedical materials, and machined surfaces where adhesion properties are important. High roughness (Ra > 4 µm) are often used in surfaces requiring strong mechanical bonding or friction. Higher roughness can enhance mechanical interlocking of coatings, improving adhesion. Excessive roughness may lead to increased corrosion susceptibility in certain applications. it suggests that the surface preparation has introduced significant roughness, which may aid in coating adhesion but requires further analysis for corrosion resistance. The measured Ra =

3.812 µm indicates a moderately rough surface, suitable for applications where a balance between adhesion and performance is needed.

X-Ray Diffraction Spectroscopy

X-ray diffraction (XRD) pattern, showing the phase identification of different samples Mg (Magnesium), Black line, BN (Boron Nitride) , Red line, HA (Hydroxyapatite) , Green line, Coated Sample (Mg+HA+BN) – Blue line. XRD in the below figure 22. which is a powerful technique used to determine the crystalline structure of materials. The peaks in the graph represent different phases present in the sample, with their position (2θ angle) and intensity indicating the structure and relative abundance of the phases.

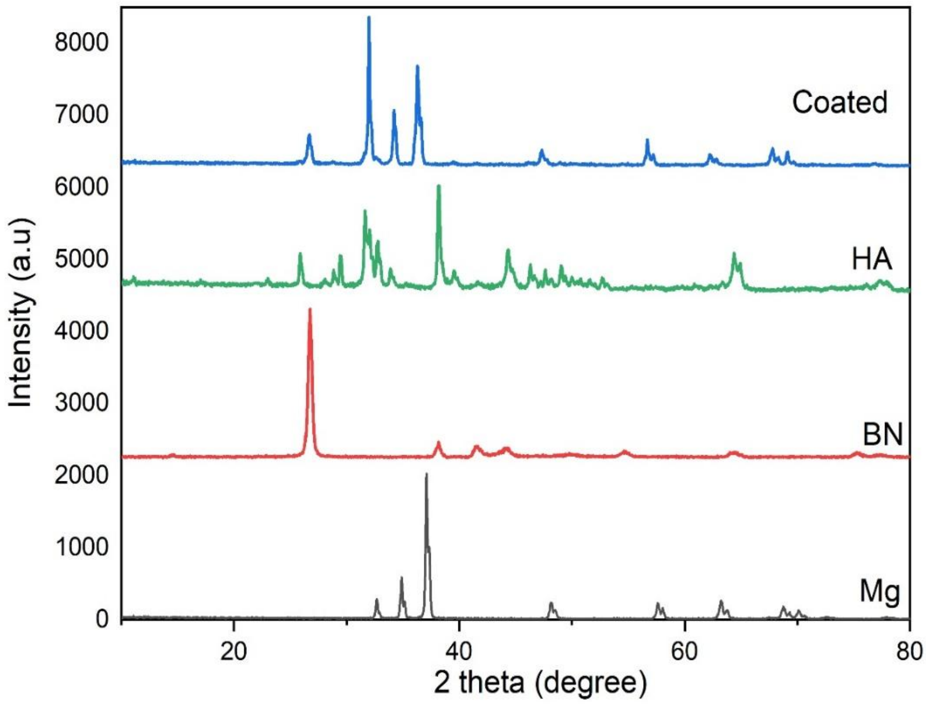


Figure 22. XRD

Bare Magnesium (Mg) Black Line, The lowest intensity spectrum. Peaks around 2θ = 30–40° correspond to magnesium (Mg). Weak peaks indicate a low level of crystallinity, as pure Mg degrades over time and may form oxide layers.

Boron Nitride (BN) Red Line, the BN sample shows strong peaks, particularly around 27° and 42°, characteristic of hexagonal boron nitride (h-BN).

Hydroxyapatite (HA) Green Line Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) exhibits multiple peaks, especially in the range 25–35°, which correspond to calcium phosphate phases.

The presence of HA is significant for biocompatibility, as it enhances cell adhesion and bone integration. Higher intensity suggests good crystallinity, which is essential for biomedical applications.

Coated Sample (Mg + HA + BN) Blue Line The coated sample integrates peaks from both HA and BN, forming a composite coating. High-intensity peaks (30–50°) indicate a well-structured composite layer. The shift or broadening of peaks suggests some degree of interaction between Mg, HA, and BN. The presence of multiple peaks from HA and BN implies successful coating deposition with good phase stability. Mg alone has weak diffraction peaks, indicating a lower crystalline structure and susceptibility to degradation. BN exhibits sharp peaks, confirming its stable crystalline phase. HA shows multiple high-intensity peaks, confirming its presence in the sample. The coated sample (Mg + HA + BN) retains the structural properties of both HA and BN, ensuring improved biocompatibility, corrosion resistance, and mechanical stability. The XRD results confirm successful coating of magnesium with HA and BN. The coated surface exhibits higher crystallinity and stability, which is beneficial for biomedical applications, such as implants. The presence of BN improves mechanical strength, while HA enhances biocompatibility.

X-ray diffractive spectroscopy of pure magnesium compared to reference data 9008506.cif data from the COD website illustrating in figure 23 which is an open database for crystallography of diffraction. From the graph, each peak of our used material consisted of reference data.

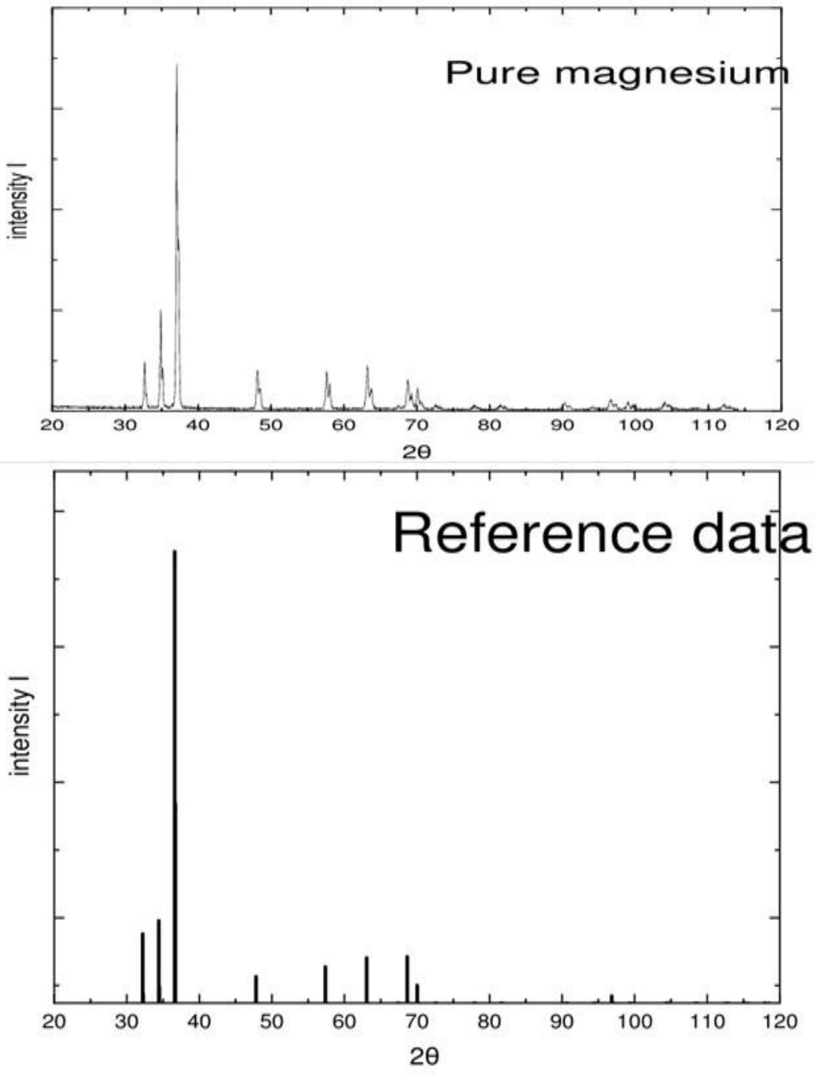


Figure 23. XRD of pure Mg with Reference data

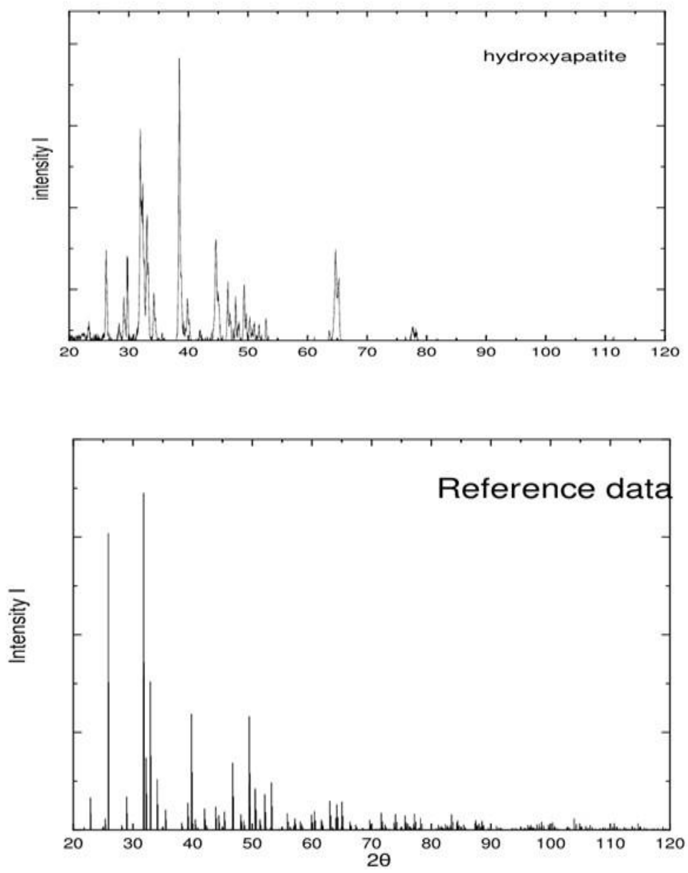


Figure 24. XRD of HA with Reference data

Figure 24 represents X-ray diffractive spectroscopy of Hydroxyapatite compared to reference data 2300273.cif data from the COD website which is an open database for crystallography of diffraction of material. From the graph, each peak of our used material aligned with reference data. The date for reference is interpreted in VESTA software. Meanwhile, ORIGEN software is used to plot each graph.

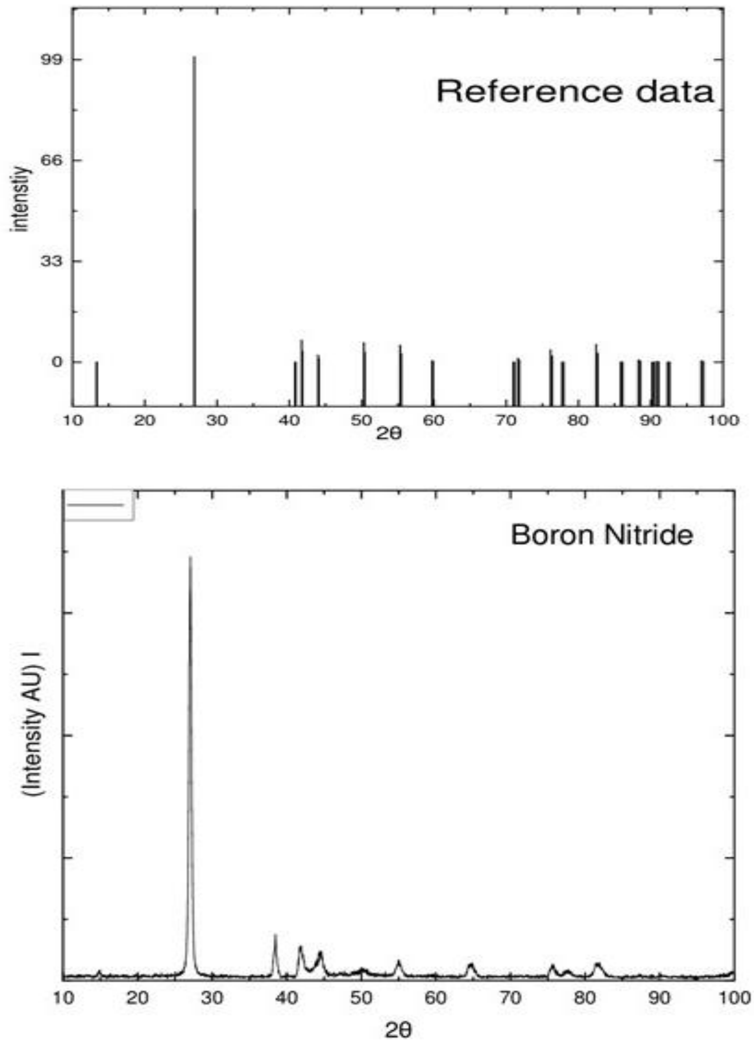


Figure 25. XRD of BN with reference data

Figure 25 represents X-ray diffractive spectroscopy of Boron nitride compared to reference data 2016170. CIF data from the COD website, which is an open database for crystallography of diffraction of material. From the graph, each peak of our used material aligned with the reference data. The date for reference is interpreted in VESTA software. Meanwhile, ORIGEN software is used to plot each graph.

Electrochemical Test

The compared graph of potentiodynamic data represented at tafel plot where the red cure represents bare pure Mg and the black cure represents a coated sample of pure Mg. Illustrating in Figure 26.

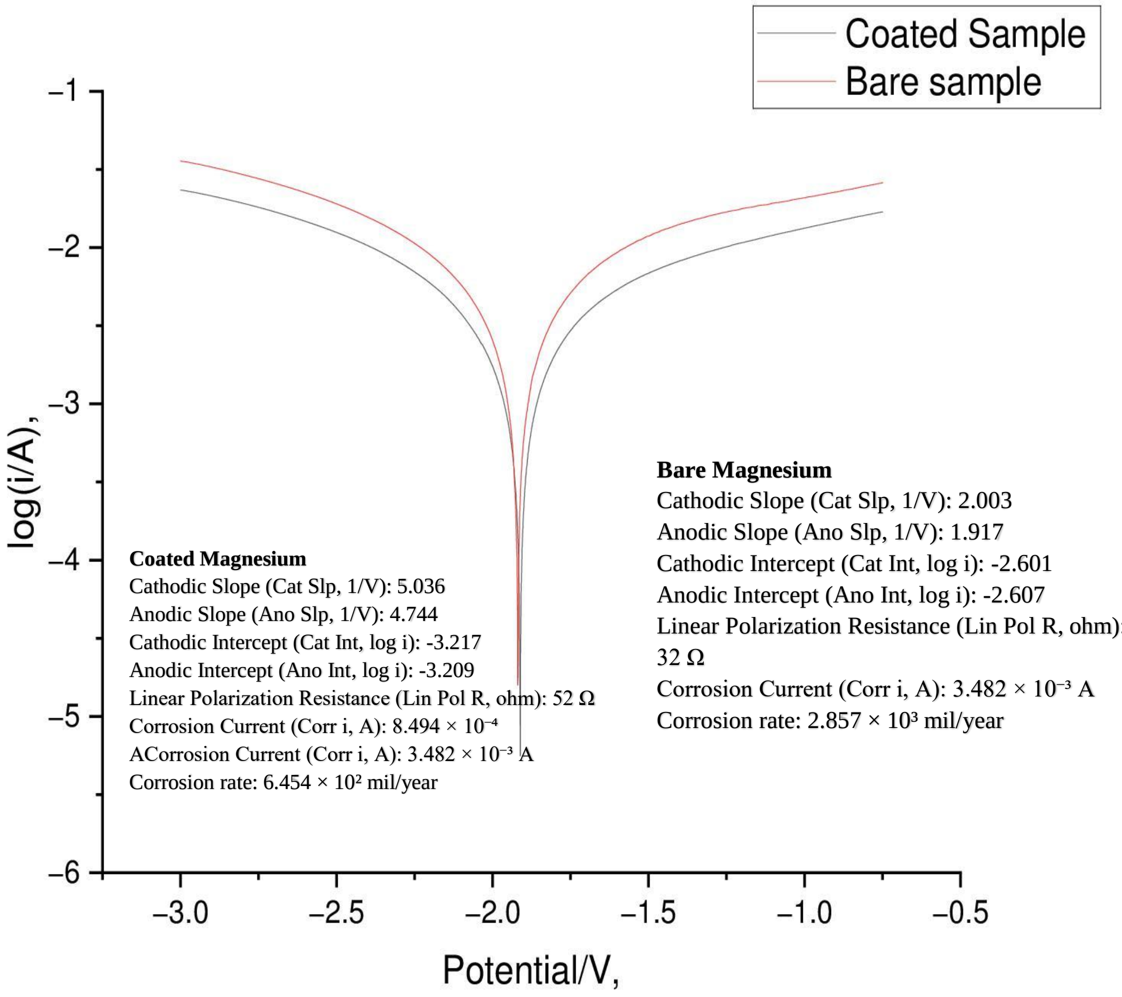


Figure 26. Tafel Plot of coated and bare materials

Table 4. Comparative details of Bear and coated Mg

Parameter	Bare Mg	Coated Mg	Improvement
Cathodic Slope (βc, 1/V)	2.003	5.036	Increased slope suggests better protection
Anodic Slope (βa, 1/V)	1.917	4.744	Higher anodic slope indicates slower oxidation
Cathodic Intercept (log i)	-2.601	-3.217	Lower log i means reduced cathodic reaction
Anodic Intercept (log i)	-2.607	-3.209	Reduced anodic reaction
Polarization Resistance (Ω)	32	52	Higher resistance suggests better corrosion resistance
Corrosion Current (i_corr, A)	3.482×10^{-3}	8.494×10^{-4}	Significant reduction
Corrosion Rate (mil/year)	2.857×10^{3}	6.454×10^{2}	4.4 times lower corrosion rate
Corrosion Rate (Å/min)	1.381×10^{3}	3.119×10^{2}	Slower material degradation
Corrosion Rate (g/hr)	1.624×10^{-3}	3.930×10^{-4}	Mass loss was reduced significantly

The coated magnesium shows a significant reduction in corrosion current (i_corr) and corrosion rate. The corrosion current decreased by almost 4 times, indicating much lower electrochemical activity. The corrosion rate dropped from 2.857×10^{3} mil/year to 6.454×10^{2} mil/year, confirming improved protection. Increase in polarization resistance (R_p) from 32 Ω to 52 Ω. This suggests the coated surface offers better resistance against electrochemical reactions. Higher cathodic and anodic slopes indicate a more stable and protective surface. This suggests that the coating alters the electrochemical kinetics, slowing down corrosion.

The Hydroxyapatite (HA) and Boron Nitride (BN) coating on magnesium significantly improves its corrosion resistance by reducing electrochemical activity and slowing down material degradation. These results strongly support the effectiveness of the coating for biomedical applications, where controlled degradation is crucial.

CHAPTER 5

CONCLUSION

The main objective of this research work is to address the rapid biodegradation of pure Mg through the application of coatings of HA and the addition of BN to increase its performance for biomedical applications. Mg has excellent biocompatibility and mechanical properties, thus making it an excellent material for biodegradable implants; however, it degrades too rapidly in physiological environments. Through a comprehensive experimental approach, the coatings of HA significantly improved the surface properties of pure magnesium, which allowed for a moderate decrement in the degradation rate.

Moreover, as BN was loaded into the matrix of HA, it showed a good cooperative ability to enhance anti-corrosive resistance and improve the stability of the degradation pattern. The results show that BN, with its superior chemical stability and mechanical reinforcement ability, is compatible with HA's biocompatibility, which makes the composite coating resist the fast degradation of Mg while retaining its bio-functional properties. From the electrochemical study 4.4 percent lower degradation rate of pure Mg. The results of the present study further highlight the capability of HA-BN coatings to be a highly effective strategy in enhancing the performance and durability of magnesium-based implants.

In conclusion, the incorporation of HA and BN addressed the critical issues of pure Mg and formed a promising foundation for advancing Mg-based biomaterials for clinical applications.

CHAPTER 6

FUTURE PERSPECTIVE

Some critical areas of further investigation of HA-BN coated magnesium to increase its potential for biomedical applications are:

To investigate further and enhance the roughness of the composite coating.

Optimizing the coating parameter for optimum coating thickness with ISO-recommended roughness.

To perform cellular studies to determine the future aspects of coating with in physiological condition.

Investigate the cytocompatibility of hBN in rats for cell interaction and reaction in the body.

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