Preparation and Characterization of Hydroxyapatite-Alumina-Zirconia Composite

Dissertation submitted in partial fulfillment

of the requirements for the degree of

Master of Technology

in

Industrial Ceramics

by

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Based on the research carried out
Under supervision of
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July, 2017

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Supervisors' Certificate

This is to certify that the work presented in this dissertation entitled *Preparation and Characterization of Hydroxyapatite-Alumina-Zirconia Composite* by *Navneet Tiwari*, Roll Number 215CR2062, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements for the degree of *Master of Technology* in *Industrial Ceramics*. Neither this dissertation nor any part of it has been submitted earlier for any degree or diploma to any institute or university in India or abroad.

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Declaration of Originality

I, *Navneet Tiwari*, Roll Number: *215CR2062* hereby declare that this dissertation entitled *Preparation and Characterization of Hydroxyapatite-Alumina-Zirconia Composite* presents my original work carried out as a doctoral student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "References" or "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in the case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

Navneet Tiwari

July, 2017
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Acknowledgement

This dissertation is a result of the research work that has been carried out at **National Institute of Technology, Rourkela**. During this period, the author came across with a great number of people whose contributions in various ways helped in the field of research and they deserve special thanks. It is a pleasure to convey the gratitude to all of them.

First of all the author expresses his heartiest gratitude to his supervisor and guide **Dr. Sudip Dasgupta,** for his valuable guidance, support and encouragement in the course of the present work. The successful and timely completion of the work is due to his constant inspiration and constructive criticisms.

The author takes this opportunity to express his deepest gratitude to **Prof. Bibhuti Bhusan Nayak,** Head of the Department of the Department of Ceramic Engineering, NIT Rourkela and all other **DSC Members** for their constant advice, useful discussions, encouragement and support in pursuing the research work.

The author is willing to extend his thanks to his **parents**, to his **friends** and all his **seniors** for their continuous support.

Last, but not the least, the author thanks the one above all, the omnipresent **Goddess**, for giving him the strength during the course of this research work.

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Abstract

In this present work, hydroxyapatite-alumina-zirconia composites were prepared and subsequent characterization was performed. This work makes zirconia as a central layer, alumina as an intermediate layer and then hydroxyapatite as an outer shell. The resultant composite was expected to have both improved mechanical properties and improved phase purity because of separation of two reactive phases, zirconia and hydroxyapatite by the alumina layer.

In the first step of work synthesis of hydrous zirconia was prepared by using zirconium oxychloride and ammonium hydroxide solution and from it stabilization of tetragonal zirconia was performed after doping 3mol% Y_2O_3 during synthesis of hydrous zirconia. Treating yttria stabilized zirconia (YSZ) as core and using urea as the precipitant, subsequent coating on particle surface was performed in two steps, first aluminum nitrate as the source of Al^{3+} to generate alumina coating on YSZ and secondly using calcium nitrate as a source of Ca^{2+} and diammonium hydrogen phosphate as the source of P(Ca/P ratio 1.67) to produce hydroxyapatite coating on top of alumina coating on YSZ. Layered coating was ensured by drop wise addition of aluminum nitrate solution on zirconia precipitate and the similar procedure was followed for coating of hydroxyapatite on ZrO_2-Al_2O_3 particles synthesized using urea decomposition method above 85^oC in aqueous media. The resultant precipitate was freeze dried and then calcined at 800^oC/4h followed by compaction of calcined powder into pellets and sintering at 1300^oC. Particle size distribution, phase composition and microstructural analysis of sintered compacts were performed using TEM, XRD and FESEM respectively.

Keywords: Hydroxyapatite, Zirconia, Decomposition, XRD, TEM analysis.

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Chapter 1

INTRODUCTION

1.1 Overview

With the advancement of human living standard, there is a strong development in research of areas related to biological sciences. Due to this, very fast development is taking place in the field of medicine also. One of the major examples of that is the replacement of the damaged organ by regenerating the damaged organ by complex and long processes after implanting a new artificial organ. The use of artificial organs was started after a long research on the growth of stem cells on bioactive scaffolds and these will be commonly available after biomedical research and progression. Hard tissue and bone replacements are mainly performed by bioactive and strong materials which are having the basic structure and chemical structure same as hard tissue. Now biomedical researchers are focusing on the present biomaterials and use them in new composite materials with enhanced properties, modified microstructure to generate novel biomaterials. Among different biomaterials, hydroxyapatite and calcium phosphate are the important biomaterials that have better biological properties than other ceramic biomaterials. In the current scenario, material scientists are focusing on the project of artificial biomaterials which mimic the natural bone.

The common property of all the biomaterials is biocompatibility or non-toxicity which is the definition of a material that is not recognized by the body as a potentially harmful foreign substance. The cells and the fluid inside the body can react instantly with foreign materials and starts an inflammation reaction followed by a wound healing process. When any implant is placed inside the body, the cells and tissue start the response towards the injury that results in inflammation as a reaction to local injury.

Biocompatible materials are categorized into bioinert, resorbable and bioactive materials according to tissue response. Bioinert materials form fibrous tissue of variable thickness, whereas bioactive materials form the interfacial bond and bioresorbable materials are replaced by surrounding tissue [1]. Materials capable of evading attack by the body's immune system, and of stimulating tissue growth, are potentially far more effective and less costly.

One of the important parameter is the similarity in the mechanical property between biomaterials and the host or replaced hard tissue. Especially in the case of hard tissue

replacement, the biomaterial has to support or share a major portion of the load. Even when different materials are combined at that time, many factors are kept in mind to ensure the integrity of the resultant structure. The physical and chemical property, the coefficient of thermal expansion, compressive strength, fracture toughness, hardness, and processing conditions (temperature, atmosphere etc.) of biomaterials are important in these cases.

1.2 Bioceramics

In last 30-40 years, there are major developments in ceramics materials has taken place especially in skeletal repair and reconstruction. The materials within this class of medical implant are often referred to as "Bioceramics". Bioceramics are an important subset of biomaterials. According to the type of bioceramics used and their interaction with the host tissue, they can be categorized as either "bioinert" or "bioactive" and the bioactive ceramics may be resorbable or non-resorbable. The materials used include polycrystalline materials; glasses, glass ceramics and ceramic-filled bioactive composites, and all these may be manufactured either in porous or in the dense form in bulk, as granules or in the form of coatings.

Bioceramics are manufactured in different forms and phases and used in many different functions in repair of the body, which are summarized in table 1. They can be single crystals (sapphire), polycrystalline (alumina or hydroxyapatite), glass (bioglass), glass-ceramics, and composites (polyethylene-hydroxyapatite). The use of phase depends on the function and characteristics required.

Table 1 Form Phase and Function of Bioceramics [2]

Forms	Phase	Function
Powder	Polycrystalline Glass	Space-filling, therapeutic treatment, regeneration of tissues
Coating	Polycrystalline Glass Glass-Ceramic	Tissue bonding, thromboresistance, corrosion protection
Bulk	Single Crystal Polycrystalline Glass Glass-Ceramic Composite (Multi-Phase)	Replacement and augmentation of tissue, replace functioning parts

1.3 Hydroxyapatite

Hydroxyapatite (HAp: Ca_{10} $(PO_4)_6(OH)_2$) has attracted much attention over the past several decades, because of its crystallographic and chemical similarity with human hard tissues. HAp is a class of apatite, that is found as the main component in bone and teeth. HAp is commonly used as coating on bone implants and scaffolds because of its excellent biocompatibility and osteoconduction, but cannot be used directly for bone replacement because of its lack of mechanical properties like low fracture toughness (< 1 MPa*$m^{1/2}$)and hardness as compared to human bones of 2~12MPa•$m^{1/2}$. Both mechanical strength and bioactivity of HAp depend upon its microstructure such as grain size and grain size distribution, porosity and its shape and distribution, and material crystallinity. This gives much freedom to the materials designers to modify and improve the properties of this material according to the application. Therefore, HAp powders have been synthesized by several methods including wet chemical method in aqueous solutions, sol–gel method, hydrothermal method, thermal deposition, conversion of coastal corals, and continuous precipitation. Besides HAp coating, efforts have also been made

to improve the mechanical properties of HAp based ceramics in order to utilize its bone-bonding ability of the material.

Hydroxyapatite is a thermally unstable compound, decomposing at temperatures from around 800-1200°C depending on its stoichiometry. Calcium phosphate phases of alpha and beta-tricalcium phosphate, tetracalcium phosphate occur by slight differences in the stoichiometric ratio of calcium and phosphorus than HAp from in the molar ratio of 1.67. It is also important to know that the stoichiometry, acidity and solubility are closely related to each other.

Applications of hydroxyapatite include surface coating of orthopedic and dental metal implants where HAp both promote osseointegration process and reduce metal ion release by acting as a physical barrier. Bioceramic preparation is aimed at replacements of bone fragments, repair of periodontal bony defects; and use as drug carrier for controlled drug release with promising potential to heal bone fractions and suppress inflammation process. Hydroxyapatite has been used clinically in different applications. It has been utilized as a dense, sintered ceramic for middle ear implants, alveolar ridge reconstruction, and augmentation, in porous form as granules for filling body defects in dental and orthopedic surgery and as a coating on metal implants [3]. Mechanical properties of dense hydroxyapatite are given in Table 2. [4]

Table 2 Mechanical properties of dense hydroxyapatite

Density	3157 kg/m^3
Tensile strength	0.04-0.1 GPa
Hardness	2000-3500 Knoop, 500-800 Vickers
Bend strength	0.02-0.08 GPa
Fracture toughness	approx. 1 MPa/m$^{1/2}$
Compressive strength	0.1-0.9 GPa
Young’s modulus	70-120 GPa

1.4 Alumina

Alumina is the most widely used biocompatible ceramic material with good mechanical properties (comparable to metals). Biocompatible ceramics with mechanical properties comparable to metals are preferred in parts of the body that have high wear risk. Because of its excellent high strength, corrosion resistance, and high wear resistance, alumina is used in load bearing hip prosthesis and dental implants in a pure and dense state. Alumina's long term use in orthopedic surgery has been motivated by its excellent biocompatibility and very thin capsule formation which permits cementless fixation of prostheses as well as its very low coefficients of friction and wear. Alumina has the exceptional tribologic properties due to narrow grain size distribution and small grain sizes less than 4 microns which leads to very low surface roughness. Rapid wear of bearing surfaces takes place in the case of large grain presence owing to grain pull out due to local dry friction. As a mechanically strong ceramic, alumina is also used as a reinforcing material in biocomposites. Strength, fatigue resistance and fracture toughness of polycrystalline alpha alumina are functions of grain size and purity. Good flexural strength, excellent resistance to dynamic and impact fatigue, resistance to subcritical crack growth and excellent compressive strength are obtained with average grain sizes <4 microns and purity >99.7% [5]. Mechanical properties of alumina used in implants are listed in Table 5. Clinical applications of alumina include knee prostheses, bone and dental screws, alveolar ridge and maxillofacial reconstruction, ossicular bone substitutes, corneal replacements and segmental bone replacements.

Table 3 Mechanical properties of biomedical grade alumina

Hardness	2200 Vickers
Density	3970kg/m^3
Bend Strength	0.5 GPa
Compressive Strength	4.1 GPa
Youngs modulus	380 GPa
Fracture Toughness	4 MPa/$m^{1/2}$
Thermal expansion coefficient	8 x 10^{-6} 1/K

1.5 Zirconia

Zirconia, an inert ceramic possesses extraordinary properties when being doped with some stabilizing oxides like magnesia, yttria and calcia. It is an established polymorph that is found to exist in three forms ie., tetragonal (T), monoclinic (M) and cubic (C). Pure zirconia at room temperature is monoclinic which is stable till 1170°C and going above this temperature, tetragonal phase is formed which again is finally converted into cubic phase at 2370°C. When temperature is lowered, a T→M transformation is observed at temperatures ranging from 100°C to 1070°C. Utilising the transformation toughening property of tetragonal zirconia, which imparts improved mechanical properties to it, we can use zirconia in certain applications due to its biocompatibility. Here, the properties of interest are toughness, hardness, strength, thermal properties and wear resistance. The most important variable in the composition of zirconia that affects its mechanical properties is the type and amount of additives used to stabilize zirconia existing in the tetragonal crystal structure. Besides this, yttria content is noteworthy for processing of yttria stabilized zirconia. To modify the mechanical assets it is vital to have a microstructure that is free of any monoclinic phase which if present will introduce flaws, and because of this, we confine the level of stabilizers added. The maximum value of fracture strength is obtained at the 3 mol % yttria composition (as established in research work done so far). Tetragonal zirconia also experiences a downgrade when it is brought in contact with water (at temperatures in the 200-300 °C) which is reasoned with the ageing of the metastable phase confining its use in long term applications [6]. Based on reports, it is seen that biomedical grade zirconia has the best mechanical properties among oxide ceramics, because of which today, above 600,000 zirconia femoral heads have been successfully implanted in joint replacement operations occurring worldwide. The mechanical properties of commercial yttria stabilized zirconia are given in Table 3 [7].

Table 4 Mechanical properties of 3mol% YTZ

Density	6050 kg/m^3
Hardness	1200 HV
Compressive strength	2 GPa
Bend strength	0.9-1.2 GPa
Fracture toughness	7-10 MPa/$m^{1/2}$
Thermal expansion coefficient	11x10^{-6} 1/K
Young's modulus	210 GPa

1.6 Hard Tissue Replacement

When any part of skeletal system bears high impact, the effect of impact is usually a crack/fracture in hard tissue that needs medical attention to cure or rapidly replace hard tissue injuries. Additionally, worsening chronic diseases can produce similar effects to hard tissues through local corrosion or excessive wear. The most common hard tissue lesions take place in the active parts of the body, for example, hip joints, trabecular bones, and dental parts. While some lesions do not require surgical actions, there is some hard tissue damage that requires direct and rapid substitution and medical treatment of the injured part. Regardless of the considerable efforts in the synthesis of bone replacement materials for use in medical applications including biocompatibility, long-term stability, and physiological resilience, there has been only limited success demonstrating the superiority and complexity of natural structures where they can withstand such loads up to 1650 kg [8].

It has been detected that among all various joints, joints of the knee and hip are the most important joints of our body. The hip joint has two separate articular cartilage and a synovial fluid having a pH within the range of 7.3 to 7.45 for joint surfaces. Excessive wear at the interfaces due to deterioration of diseases, for example, osteoarthritis, it is necessary to replace the entire hip joint. In a hip joint arrangement, the head of the femoral element is placed inside a cup to allow the articulation to take place. These two specified parts of the hip prosthesis are made with various materials, for example polymers, ceramics, composites metals etc. Certain polymeric materials themselves are too weak to be considered suitable for any substitution process. In the above materials, it has been discovered that metals have good mechanical properties but are poor in terms of biocompatibility due to its tendency to emphasize shielding

and release dangerous metal ions causing malfunctions in the implant. In addition, ceramics generally shows good biocompatibility but little resistance to the fracture because of its fragile nature. However, composites that have engineering interfaces that give them biocompatibility advantage combined with mechanical strength and toughness aroused interest in research and therefore is the focus of this present study.

One of the major problems that engineers who are currently engaged in researching improved materials in current implants have to face the fact that compound biomaterials are much stiffer than human cortical bone. As indicated by Wolff's law, the load sharing principle based on the theory of composite, If a ceramic or any rigid metal implant inside the bone is placed, the bone is subjected to lower mechanical stresses, and hence the bone resorb. Now, with the changing stress or strain conditions imposed on it, the bone is redesigned so that the stress/deformation level is constrained to specific levels. Another phenomenon called aseptic mobilization of the prosthesis that in the case of total hip substitution occurs because the bone resorption of the proximal femur should be produced by the stress state and the tension in the femoral cortex that occurs after the femoral metal hip prosthesis has been implemented. Here, the elastic properties of the prosthesis play an important role in allowing the femur to reach a satisfactory state of physiological stress. To address the issue of non-matching the modulus, the concept of analogue biomaterials was introduced in the early eighties prevalent between bone and implant materials to support the development of a secure connection between the host tissue and the implant. After that, a series of bioactive composites were synthesized and studied.

In the current era of growing science and technology, it is first necessary to study the structural properties of the tissue (which must be replaced), meanwhile if the properties of the newly synthesized material are found to be dissimilar to those of the host tissue, the growth of material will cause serious changes in the host tissue after implementing (as discussed in Wolff's law), and therefore not being able to accomplish the desired objectives as envisaged in the original theoretical design.

In a human body, the bone serves as a means of creating new materials for the substitution of hard tissues. Bone, being a composite natural material, has a complex structure in which there are many levels of organization, starting from the macroscale to microscale, as recognized. In the development of bone substitutes, two stages are considered for composite structures, the first is that it makes individual lamella scales of nano to micron "bone- apatite reinforced collagen" and, secondly, "the interstitial bone with osteon" again in the scale values of nano to micron. In this case, between the two types, it is actually composed of collagen-apatite

composite which provides the basis for the construction of "bio-ceramic-polymer composite" as analogue to be elaborated for subsequent biomaterials for bone replacement operations occurring at the microscopic position.

1.7 Bone

Current Bone is a composite of ceramic and organic elements with complex structure. The main elements of bone are calcium phosphate (69wt. %), collagen (20wt. %), and water. In addition to these, some minor elements are also present for example oligosaccharides, lipids, and proteins. Collagen which is considered like a matrix remains like small microfibers having the diameters of about 100 to 200 nm. Observation of distinct collagen fibers is very difficult due to its mass appearance like a net structure. Calcium phosphate is responsible for stiffness in the bone and is in the form of amorphous calcium phosphate and/or crystallized carbonated hydroxyapatite.

The main property of bone is its crystalline structure, particle size, composition, morphology, and orientation. Two main forms of mature bones are cancellous and compact. Compact bones contain mineralized fibers, which are arranged in millimeter thick in lamellar sheets. 4-20 lamellae in the form of osteon are arranged in the concentric rings around the Haversian canal. Inside the Haversian canals, blood vessels are located in the center of each osteon. Metabolic substances can be transported through the interconnected systems of Canaliculi, Lacunae, and Volkman canals, which are linked to the marrow cavity. Different interconnecting systems are filled with body fluids and their volume can be as high as 19%.

Bones can be considered as "living biominerals" because they have cells under permanent activity. The process of bone formation is started by the reaction of osteoblasts, special cells which synthesize collagen matrix in the form of a jelly substance and release it. It is later mineralized by the controlled decomposition of calcium phosphate. Osteoblasts are trapped inside the mineral phase, developing towards osteocytes, which keep the bone formation continuous. Meanwhile, another type of cells called the osteoclasts catabolise the bone and destroying it. This dynamic process of bone formation and destruction explains their growth during the phases of body development while maintaining their shape and consistency and allowing regeneration in case of fracture [8]. It contains a mechanism for storing and transporting two essential elements, phosphorus, and calcium, which are stored mainly in the bones. Bones may have different types of integration between organic and inorganic materials, causing significant variations in their mechanical properties. The relationship between the two

components reflects the compromise between toughness (high inorganic content) and resilience or fracture resistance (low inorganic). The mechanical properties of a compact bone are given in Table 4.

Table 5 Mechanical properties of a compact human bone

	Test direction related to bone axis	
	Parallel	Normal
Compressive Strength (GPa)	0.17-0.193	0.133
Tensile Strength (GPa)	0.124-0.174	0.049
Bending Strength (GPa)	0.16	
Shear Strength (GPa)	0.054	
Young's modulus (GPa)	17.0-18.95	11.5
K_{Ic} (MPa*$m^{1/2}$)	2-12	
Work of fracture (kJ/m^2)	6	
Ultimate compressive strain	0.0186-0.026	0.028
Ultimate tensile strain	0.014-0.030	0.007
Yield compressive strain	0.011	0.012
Yield tensile strain	0.008	0.005

1.8 Properties of Bone Implants

The bone substitute should be osteoinductive, osteoconductive, bio-resorbable, biocompatible, substantially as bone and experience redesigning. In an ideal world, a bone implant, for example, a hip implant should be a measure to demonstrate a charge indistinguishable from the reaction as a genuine bone and is also biocompatible with existing tissue. A ceramic with greater porosity and a structure of lower density gives a more important surface area for the vasculature and a hard ingrowth. Limited appropriations of interconnected pores with a size in the 150-300 micron range are the ideal conditions for osteoconductivity [9]. The mechanical properties and also the Osteoconductivity are influenced by the game plane of pores and size of interconnectivity. A suitable environment for bone proteins and bone cells is provided by the osteoconductive scaffold. The osteoconductive ceramic which is set recently will need

mechanical properties of bone; obtained slowly mechanical characteristics like cancellous bone due to bone development after adhesion. Designing of biochemical replacement bone implants has not yet been practically implemented since the breakage and its intrinsic rigidity is the main disadvantages in load bearing applications. The uses of bioceramics are now centered on creating non-load bearing for implants, such as parts for central ear surgery, filling of bone defects in orthopedic surgery and covering of dental implants and metal prosthesis. This deficiency is focused on bioceramics to overcome by synthesis of nanostructured ceramic as complex hierarchical structures of hard tissues having improved mechanical characteristics. A synthetic bone substitute should have a comparative quality of the cortical/cancellous bone to be replaced (> 200MPa). It should also have a bone elasticity comparison modulus (20GPa) trying to anticipate both fatigue failure and stress shielding under cyclic load maintaining a satisfactory toughness [10]

Chapter 2

Literature Review

Kong et al. 1999 [6], carried out an experiment on three components biocomposites to study the effect of the hydroxyapatite coating on ZrO_2 with Al_2O_3 and achieved better mechanical properties of the particles in the coated samples compared to the samples that are mechanically prepared by mixing of three elements. The preparation of the coated powder was carried out by TZP coating with boehmite. By hydrolyzing an aluminum isopropoxide solution preparation of the boehmite solution (AlOOH) was performed. So the prepared boehmite solution was dispersed in distilled water. The surface charges of the AlOOH and ZrO_2 were calculated as a function of the pH of the solution using a zeta meter. Various amounts of coated precipitate were mixed with HAp by ball milling with distilled water for 24 hours using Al_2O_3 balls as the source of the breakage of HAp agglomerates. The powder mixture was compressed in a graphite mould at 1200^oC in sliding atmosphere of Ar with an applied pressure of 20 MPa. The fracture strength and strength of hot-pressed HAp were significantly improved by the addition of Al_2O_3-coated tetragonal zirconia polycrystal. The coating was effective in reducing the deleterious reaction between HAp and ZrO_2. When the powder of 15vol% ZrO_2 and 30vol% Al_2O_3 were added to HAp by method of coating, the strength and fracture toughness of the samples were respectively 300MPa and 3MPa.$m^{1/2}$, which is approximately three times as high as added pure HAp. The conservation of particles of ZrO_2 in tetragonal phase in the matrix of HAp has been attributed to improved mechanical properties. Improving the homogeneity of the microstructure in the coated samples has an advantage of this method.

Juliano Pierri et al. [9] prepared alumina coated zirconia composite using the biomimetic method. A bioactive zirconia-toughened alumina (ZTA) composite is used for orthopedic applications. This composite was prepared by slip casting of suspension powder mixtures. Biomimetic processes were used to grow a bone-like apatite layer on composite substrates using sodium silicate solution as a nucleating agent and simulated body fluids. The composites, with or without coating, were characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS), and their apparent density was determined by the Archimedes

method. The composites obtained by this process possessed the expected stiffness and dimensions and their density values were similar to those of the composite's theoretical density (98.8%TD). The morphology of the hydroxyapatite formed on the composite surface was homogeneous and composed of small globules, characterizing a carbonated hydroxyapatite. The results of the tests indicated that the method employed to produce the composite and its coating was efficient under the conditions of this study.

Chin-Yi Chiu et al [10] observed the effect of zirconia addition on the microstructural evolution of porous HAp. They studied the mechanical properties of HAp-alumina coated zirconia ceramics. The expected increase in the strength and toughness of HAp-ZrO_2 will be significant, provided there will be no reaction between HAp and ZrO_2. The product of the reaction between HAp and ZrO_2 is calcium zirconate ($CaZrO_3$), which is bio-inert to human tissue. The penalty of such a reaction is the consumption of the Ca from HAp. As the amount of ZrO_2 is large, HAp would be consumed completely after sintering, and α- or β-tricalcium phosphate (Ca_3 $(PO_4)_2$) formed. Previous studies were mostly concentrating on the reaction between HAp and ZrO_2.

Se-Wonyook et.al. performed a freeze drying of the camphene/hydroxyapatite mixture to study the processing of the porous hydroxyapatite scaffold. At low solids loading, low compressive strength and porous scaffolding cracking were observed. To remedy this factor polystyrene polymer of 10 to 30% by volume was added to a mixture of HAp/camphene. The compressive strength was 2.5 times without polystyrene structure.

Many researchers have observed and reported that HAp stability is also related to the HAp powder synthesis method [11]. Mobasherpour et.al. 2006 suggested a common method for the precipitation synthesis of HAp by the precipitation process using ammonium phosphate and calcium nitrate in the presence of ammonium hydroxide and the heat treatment of the hydroxyapatite powders. When the temperature increased from 100 to 1200 ° C, the grain of the hydroxyapatite is gradually increased in size, and hydroxyapatite hexagonal- dipyramidal phase has not converted to other phases of calcium phosphate up to 1200°C [12].

It has been analyzed by many researchers [13] that the properties of bioactivity and phase stability of HAp depend largely on the stoichiometry of HAp. The HAp stoichiometry will change depending on one transformation route to another; also change the particle size and bioactivity. Although the solid state route is economical and easy to use, this compromises the

purity of phase and stoichiometry. The process also requires processing at high temperature and often requires re-calcination steps to complete the reaction. Many of these problems are treated in the solution synthetic routes of precipitation, sol-gel, spray pyrolysis, freeze-drying and hydrothermal synthesis [14].

However, these processes can require expensive chemicals and detailed infrastructures. In the current scenario, almost all HAp synthesis routes are based on the solution. Therefore, this section will focus on the routes based on the chemistry of the solution. The route to the solid state will retain its standard significance.

In the present study, YSZ-Alumina-HAp composite was prepared and subsequent characterization of the composite was performed. In this work alumina coated YSZ composite was prepared then HAp coating was performed on the YSZ-Alumina composite using wet chemical precipitation route. The final precipitate was freeze dried and then calcined at 600^{o}C. Then the calcined powders were pressed into pellets and sintered at 1300^{o}C for 4 hours. The characterization of pallets was performed by FESEM and XRD analysis.

Chapter 3

Experimental Procedure

3.1 Chemicals Used

Table 6 Chemicals used in this work

Powders/Chemicals	Chemical Formula	Molecular Weight (g/mol)	Purity/Source
Zirconium Oxychloride Octahydrate	$ZrOCl_2.8H_2O$	322.25	98% LOBACHEMIE
Yttrium Oxide	Y_2O_3	225.81	99.9% LOBACHEMIE
Aluminium Nitrate (Nonahydrete) L.R.	$Al(NO_3)_3.9H_2O$	375.13	98% OSTER
Calcium Nitrate Tetrahydrate	$Ca(NO_3)_2.4H_2O$	236.15	98% MERCK
Ammonium Dihydrogen Orthophosphate	$NH_4H_2PO_4$	115.03	98% QUALIGENS
Urea	$NH_2.CONH_2$	60.06	99% LOBACHEMIE

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3.2 Synthesis of yttria stabilized zirconia (YSZ)

Yttria is used as a stabilizing agent to keep the tetragonal form of zirconium at room temperature. 3mol% of Y_2O_3 is used in this process. NH_4OH is used as a precipitant agent. Initially, 3% moles of Y_2O_3 was taken and digested in conc. HNO_3 solution along with the addition of ethanol to increase the yttria solubility. The above solution was kept on a magnetic stirrer for 6 hours, so that a clear solution was formed, i.e. yttrium nitrate.

$Y_2O_3 + 6HNO_3 \rightarrow 2Y\ (NO_3)_3 + 3H_2O$

Then this clear solution was poured into pre-prepared $ZrOCl_2.8H_2O$ solution. Both of this solution was mixed by constant stirring on the magnetic stirrer.

Now the precipitating agent NH_4OH was added drop by drop into above solution, then after some time as the concentration of ammonium hydroxide increased, precipitate formation occurred. Ammonium hydroxide was added till the pH value reached around 9 so that $ZrOCl_2.8H_2O$ transformed into $Zr(OH)_4$.

$$ZrOCl_2.8H_2O + 2NH_4OH \rightarrow Zr(OH)_4 + 2NH_4Cl$$

The precipitates of the solution were allowed to settle down overnight followed by decantation. Then the obtained powder was washed by centrifuging 4 times (at 5000rpm for 5 minutes) with distilled water and dehydrated alcohol (2 times each).

3.3 Preparation of Alumina coated Zirconia composite

For synthesis of zirconia-alumina composite samples, prepared YSZ, aluminium nitrate (Nonahydrete) L.R. and urea were used. The molar ratio of alumina to zirconia and urea to alumina were calculated as 1.6 and 10 respectively. First YSZ was taken in the aqueous solution and required amount of urea was added to the solution, then the aqueous solution of aluminium nitrate was added dropwise in the previous solution. The solution was kept on the hot plate magnetic stirrer under constant stirring for 6 hours and the temperature was maintained above 85^oC during stirring for decomposition of urea.

After synthesis, the obtained powder was washed 4 times by centrifuging (5000rpm for 5 minutes) with distilled water and dehydrated alcohol (2 times each).

3.4 Preparation of HAp coated alumina-zirconia composite

For the coating of HAp on alumina-zirconia nanocomposites Calcium Nitrate Tetrahydrate and Ammonium Dihydrogen Orthophosphate, urea and alumina-zirconia nanocomposites core were used. The Ca/P precursor ratio was maintained at 1.67 for the formation of Hap. First, the calcium nitrate and ammonium phosphate were taken into the aqueous solution and stirred for two hours. During stirring a few drops of nitric acid was added to maintain the pH of the solution at 2. Then the pre-coated alumina-zirconia suspension was taken on the hot plate magnetic stirrer and heated above 85^oC and the precipitating agent urea was added calcium nitrate and phosphate solution was poured drop wise into solution. To maintain the pH of the solution almost equal to 10 few drops of NH_4OH was added during precipitation of HAp.

After synthesis, the obtained powder was washed 4 times by centrifuging (5000rpm for 5 minutes) with distilled water and dehydrated alcohol (2 times each). The prepared composite powder was characterized using zetasizer, TEM and SEM, EDX and XRD analysis for investigation on phase purity, composition and particle size.

3.5 Characterization of the composite

3.5.1 X-Ray Diffraction Method

X-ray diffraction is based on the dual wave/particle nature of X-rays to obtain information about the crystalline material structure. The main use of the technique is the identification and characterization of compounds according to their diffraction pattern. Bragg's Law describes the X-rays diffraction for crystal, [$n\lambda = 2d \sin\theta$, where λ = wavelength of x-ray, n = diffraction order.]. The directions of possible diffractions depend on the size and shape of the unit cell of material. Powder X-ray diffraction (XRD) patterns obtained with X'Pert High Score diffractometer (Rigaku, Japan) using CuKα (λ- 1.5418˚ A) radiation at 40 mA, 40 kV. A step size of 0.05˚ was used in the scan range of 10-80˚ (2θ). The instrument model used here is X-Pert, PANalytical, PW 3040/00, Netherlands.

3.5.2 Zetasizer –Particle Size Analysis

The particle size analyzer measures the particle size in a sample. It measures particle size in the size range of 1nm- 3µm. Dynamic light scattering at 90 degrees is used to measure the particle size of the sample. Therefore, it helps in determining the size of nanoparticle, surfactants, micelles, and colloids. The instrument model used is MicrotracZetatrac, PA (USA).

3.5.3 Transmission Electron Microscopy (TEM)

In this Transmission Electron microscope, an electron beam from an electron gun is transmitted through an ultra-thin section of the microscopic object and the image is magnified by the electromagnetic fields. It is used to observe finer details of internal structures of microscopic objects like bacteria and other cells. Particle size and morphology of samples were examined using a transmission electron microscope (TEM) (Tecnai G2 30ST FEI, Netherland) operated at an acceleration voltage of 120 KV.

3.5.4 Field Emission Scanning Electron Microscopy (FESEM)

FESEM means Field Emission Scanning Electron Microscope and facilitates ultra-high resolution microstructural characterization and analysis of ceramic and metallic samples. It combines advanced optics (including a two mode final lens), SE/BSE (Secondary Electrons /Back-scattered Electrons) in lens detection and beam declaration. Since being equipped with EDAX, it helps in composition mapping and elemental analysis. The instrument model used for the experiment is Nova Nano SEM/ FEI.

Chapter 4

Results and Discussion

4.1 Urea Precipitation Method

Heterogeneous precipitation method has been applied for the synthesis of alumina coated zirconia cores and HAp coated alumina-zirconia nanocomposites using urea as the precipitation agent. In this technique, the hydroxyl ions discharged by decomposed urea react with Al^{3+} ions to form boehmite on the surface of the 3mol% YSZ cores. For complete coating of the added alumina precursor, decomposition of urea must occur in a uniform manner for the amount of time required. Therefore urea concentration, duration and precipitation temperature are essential factors which determine the success of the coating process.

4.2 Composite Particle Model

Developing a theoretical particle model for core-shell structure composite synthesis using the above-mentioned precipitation routes aids in setting criteria for successful synthesis. In the case of a complete coating, homogeneous distribution of coated layers around the core in a perfectly spherical particle can be assumed as an ideal product as schematically given in Figure 1 with the corresponding radii calculated for the three phases forming the biocomposite according to the 10:20:70 volume ratio. Comparing this model with the characterized powder product of synthesis, it is possible to evaluate the syntheses as suitable or not. Based on this assumption the minimum particle size for alumina-zirconia composite particles is calculated as 260nm and for the HAp-alumina-zirconia composite particles as 400nm according to the desired 10:20:70 volume ratio. The average size of the core zirconia particles is assumed to be 180nm for this calculation. The molar ratio of alumina to zirconia and hydroxyapatite to zirconia in completely coated particles prepared according to the 10:20:70 volume ratio are calculated as 1.6 and 4.58 respectively. The theoretical density of the composite for this specific ratio is 3.6. Results from particle size characterization with TEM or Zetasizer were compared to these minimum values and the syntheses that produced particles with higher average sizes were considered to yield satisfactory coatings on the previous core phase.

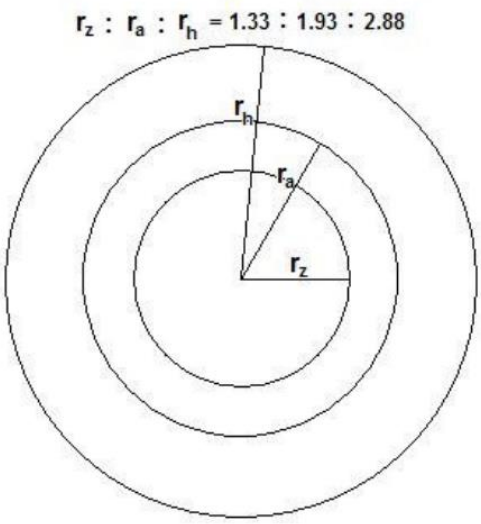


Figure 1: Spherical Particle Model

4.3 Alumina coating on Zirconia

XRD pattern of synthesized 3mol% YSZ-Alumina composite nanopowder is shown in Figures 2 below. After drying at 60^{o}C mostly amorphous phase were observed due to the presence of hydrous zirconia powder, however a moderate plateau of tetragonal ZrO2 was found at 2Θ-30˚, indicating that there is initial crystalline structure in the synthesized powder.

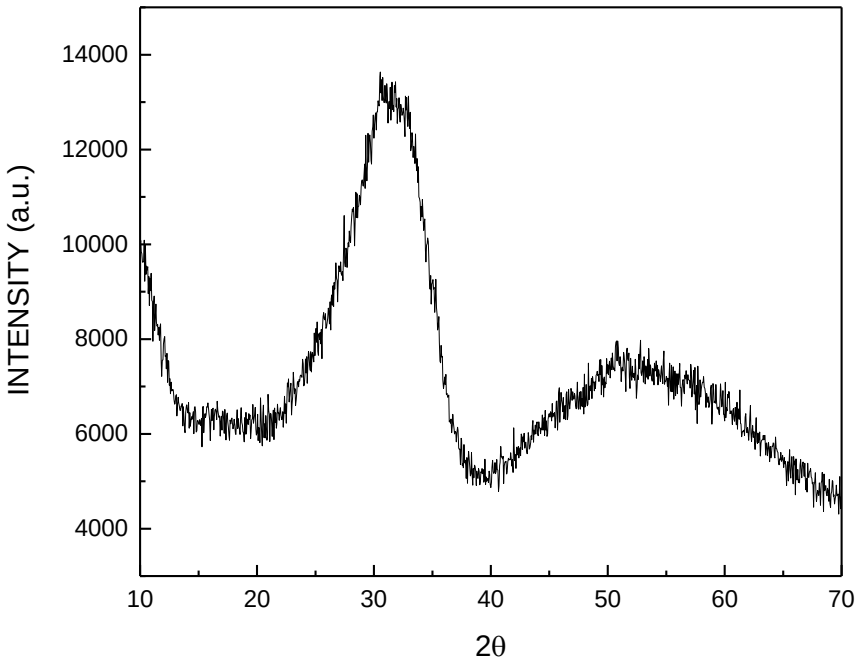


Figure 2: XRD pattern of synthesized 3mol% YSZ-Alumina composite nanopowder

Zetasizer analyses were performed on diluted sample suspensions ultrasonically treated to eliminate agglomerations through dynamic light scattering technique (Zetasizer nanoZS, Malvern). Zetasizer readings of the 3mol% YSZ sample is given in figure.3. The resultant particle size distribution came between 26-52nm with an average size of 34 nm. After the coating of alumina, there is an increase in the average particle size. The average particle size of the alumina coated 3mol% YSZ sample was 44nm as shown in figure 4.

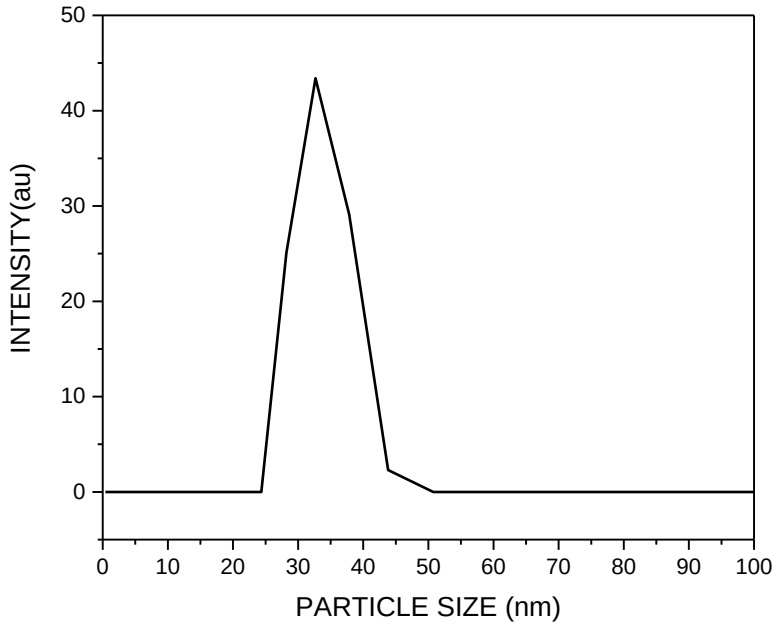


Figure 3: Particle size distribution of 3mol% YSZ

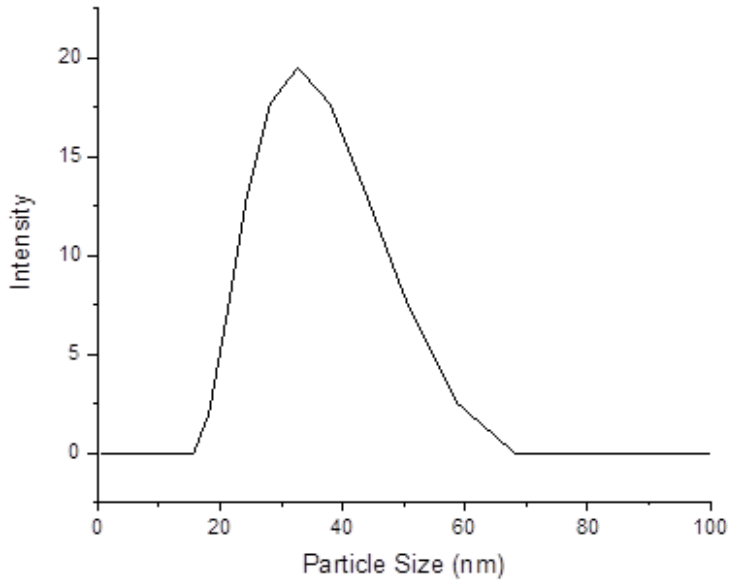


Figure 4: Particle size distribution of 3mol% YSZ-Alumina composite nanopowder

TEM analysis of alumina-YSZ composite nanopowder is shown in figure 5. Uniform coating under homogeneous stirring conditions was obtained around zirconia cores due to the use of high urea/Al $(NO_3)_3$ for the stoichiometric Al $(NO_3)_3$/zirconia. Figure 5 indicates the presence of equiaxed particles consisting of agglomerates of particles less than 250nm in diameter.

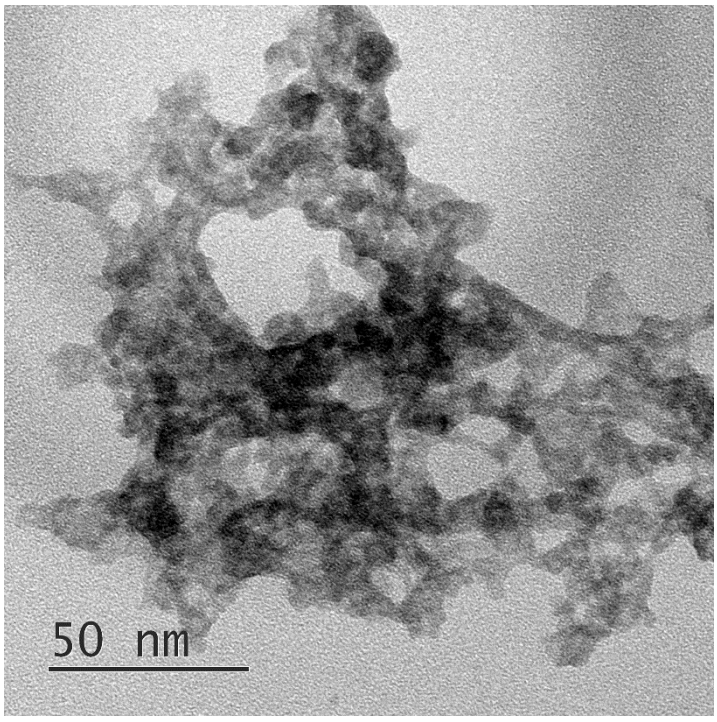


Figure 5: TEM Analysis of 3mol% YSZ-Alumina composite nanopowder

SAED Analysis of Alumina-YSZ composite nanopowder is shown in the figure 6. In this image diffuse rings appear which indicates the amorphous phase of the material.

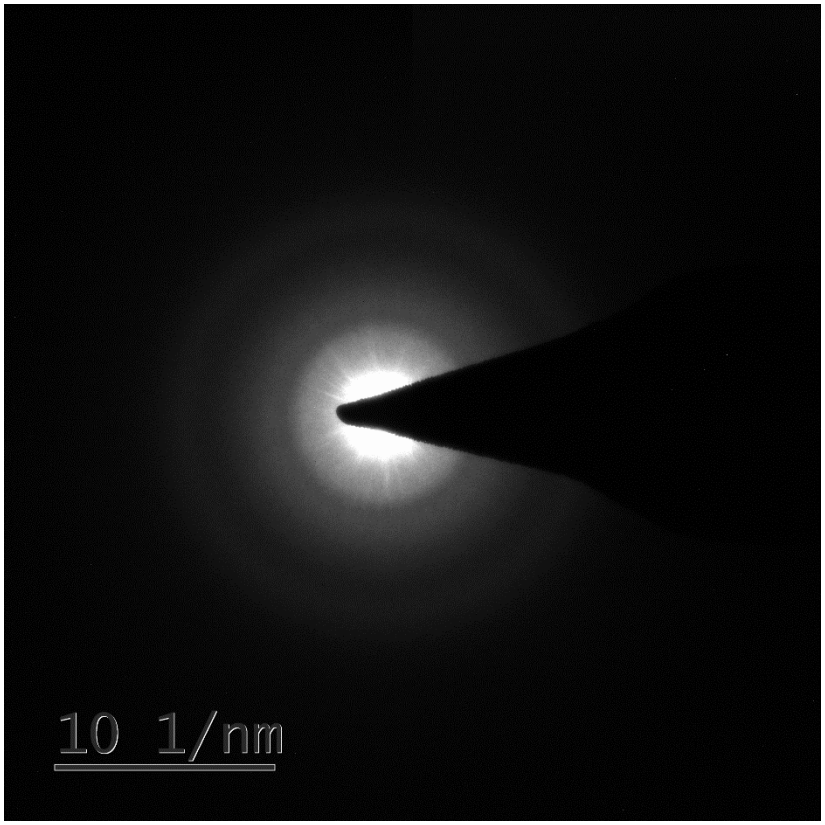


Figure 6: SAED Analysis of Alumina-YSZ composite nanopowders

The ratio of Al to Zr for completely coated theoretical Al_2O_3:ZrO_2 10:20 volume ratio spherical particles were calculated as 3.2 from EDS spectra. This ratio in the EDX analysis results indicates sufficient and successful coating. Comparison between the Al/Zr ratio of precursors for the sample and the corresponding EDX ratio provides efficiency of the coating process as shown in table 7.

Table 7 EDS Analysis of Alumina-YSZ composite nanopowders

Elements	**Atomic Percent (%)**
O	71.91
Al	21.34
Zr	6.27
Ca	0.48

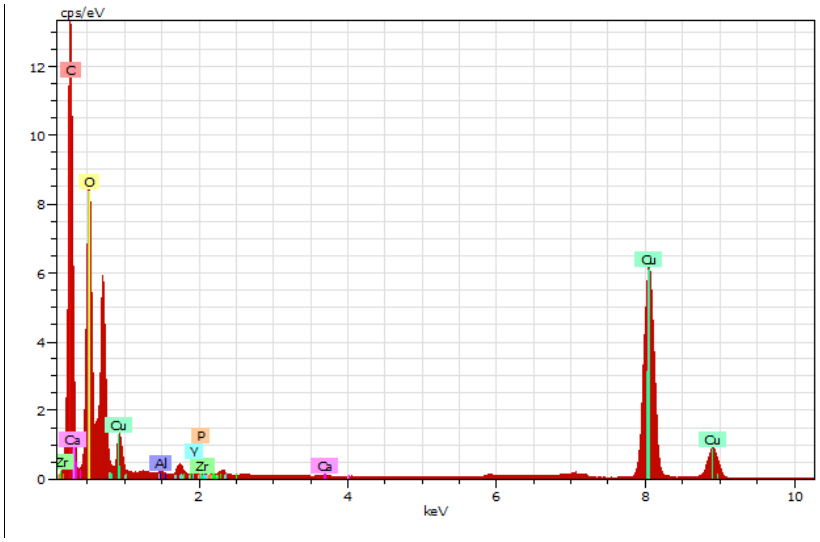


Figure 7: EDS Analysis of Alumina-YSZ composite nanopowders

4.4 Hydroxyapatite Coated Alumina-Zirconia Particles

XRD pattern of synthesized 3mol% YSZ-Alumina-HAp composite nanopowder shows intense hydroxyapatite peaks indicating that hydroxyapatite was precipitated uniformly as the major phase and the calcium and phosphate precursors were largely consumed.

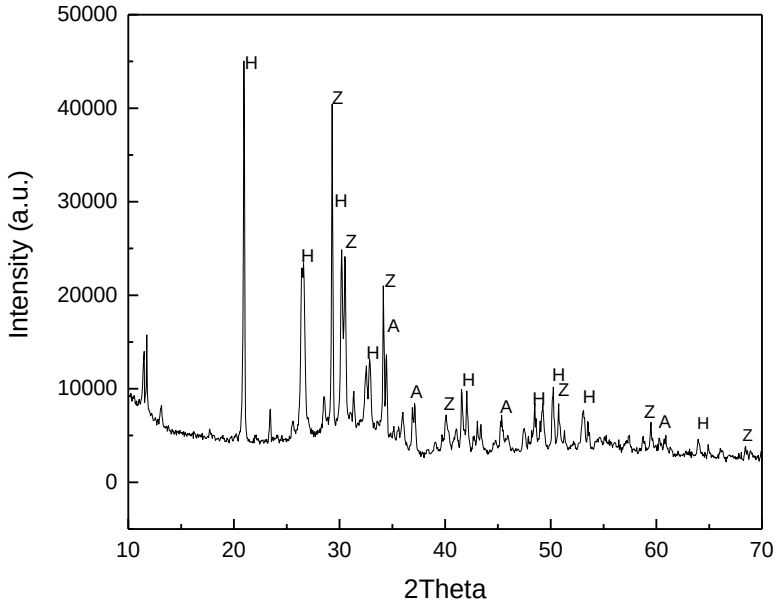


Figure 8: XRD pattern of synthesized 3mol% YSZ-Alumina-HAp composite nanopowder

The average particle size for sufficiently coated spherical three component composite particle is expected to be at least 65nm and the thickness of hydroxyapatite coating layer is expected to

be greater than 20nm. However, the resultant particle size distribution came in the range of 43-68nm with average particle size of 58nm as evident from figure 9.

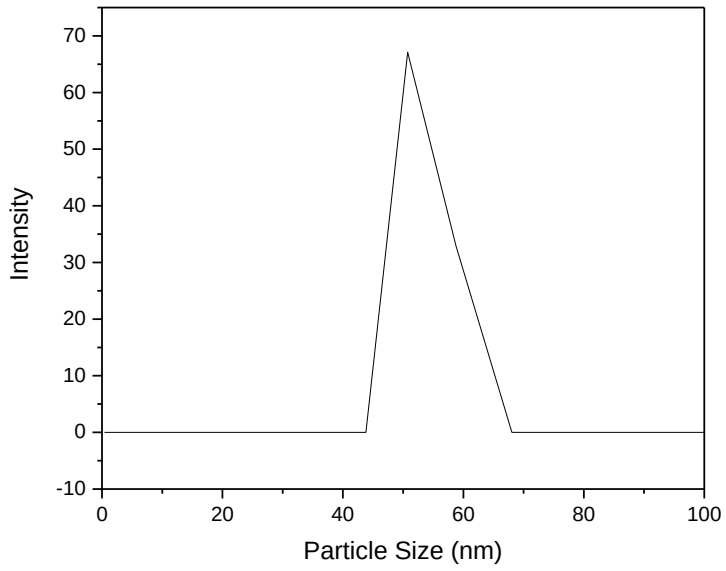


Figure 9: Particle size distributions of 3mol% YSZ-Alumina-HAp composite nanopowders

TEM analysis of HAp-Alumina-YSZ composite nanopowder is shown in the figure10. Hydroxyapatite-coated sample consists of spherical particles with rounded hydroxyapatite crystals on Alumina-YSZ cores. Homogeneously precipitated small round particles are seen in Figures 10.

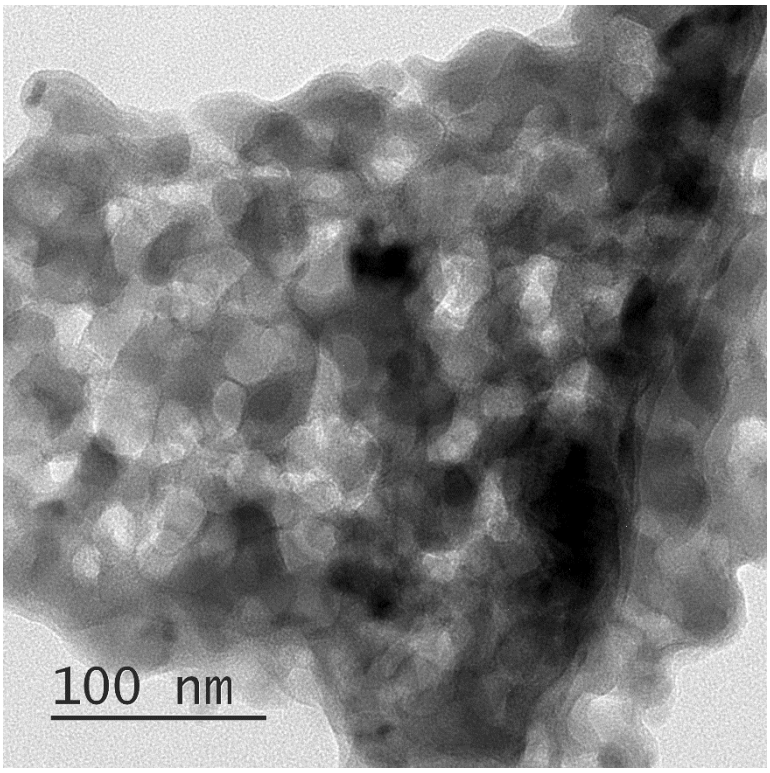


Figure 10: TEM Analysis of HAp-Alumina-YSZ composite nanopowders

SAED Analysis of HAp-Alumina-YSZ composite nanopowder is shown in figure 11. In this image bright spots appear which indicate the crystalline phase of the material.

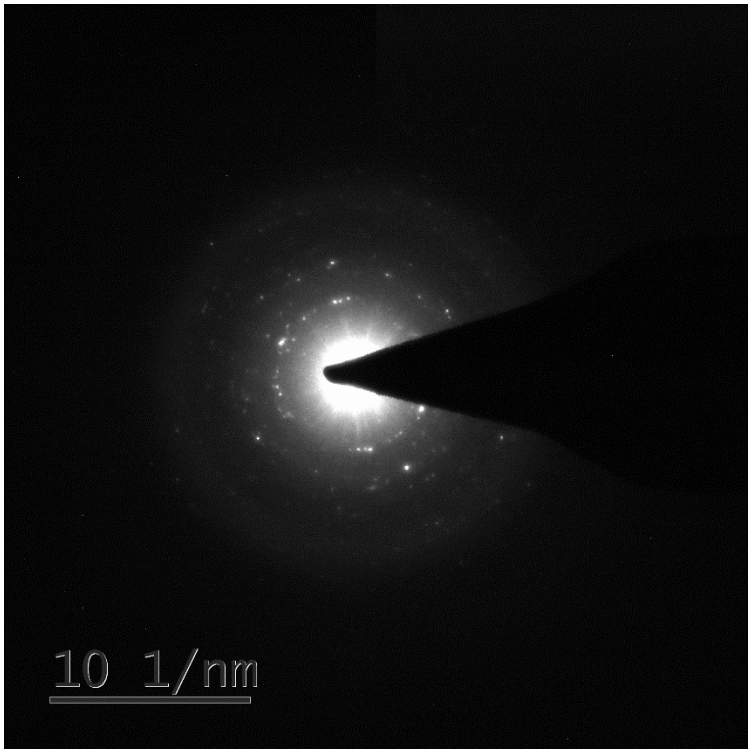


Figure 11: SAED Analysis of HAp-Alumina-YSZ composite nanopowders

From the EDS analysis of HAp-Alumina-YSZ composite nanopowders, it is clear that Ca:P ratio (1.691) in the synthesized powder closely resembled with the theoretical composition (Ca: P= 1.67) (table 8).

Table 8 EDS Analysis of HAp-Alumina-YSZ composite nanopowders

Elements	**Atomic Percent (%)**
O	78.85
Ca	10.84
P	6.41
Al	2.08
Zr	1.82

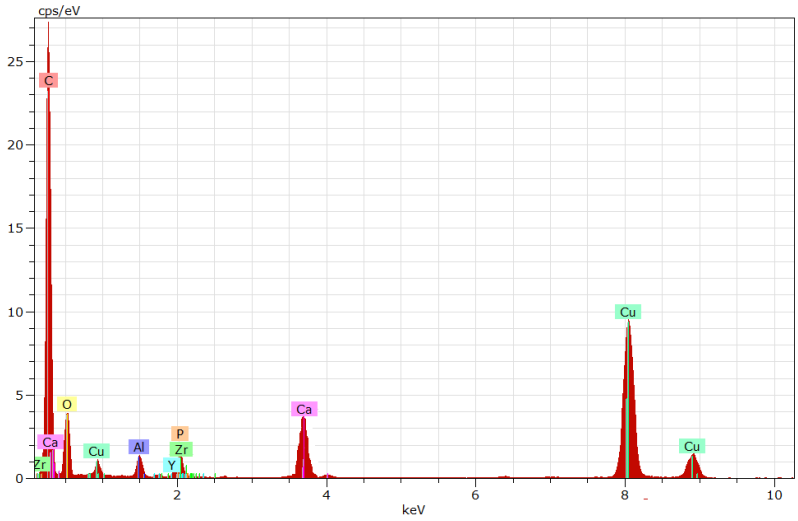


Figure 12: EDS Analysis of HAp-Alumina-YSZ composite nanopowders

4.5 Phase Purity of the Composite

The presence of three ceramic materials with many possible phases formed by the decomposition or transformation makes the investigation of the phase structure of the composite material an important research topic. The reactivity of all the three components is considerable under normal conditions and requires thorough examination in order to optimize the temperature of the heat treatment at temperatures above 1300°C. The phases which ideally should be present in the material are tetragonal yttria-stabilized zirconia, alumina, and hydroxyapatite. The possible phases commonly found in the literature that can be formed due to the reaction between the phases under extreme conditions are calcium oxide, alpha and

beta-tricalcium phosphate, calcium aluminate, tetracalcium phosphate, calcium zirconate and monoclinic zirconia. [15]

Hydroxyapatite decomposes into beta-tricalcium phosphate, alpha-tricalcium phosphate and tetracalcium phosphate at high sintering conditions. These phases are resorbable and tolerated in the HAp matrix to some magnitude. However, the presence of high quantities of these phases results in a lower HAp resistance and sinterability.

Hydroxyapatite presence in XRD graphs of composite that was sintered at 1300°C indicates that decomposition dis not take place at this temperature.

Zirconia phase in all composites sintered up to 1300°C remained as tetragonal zirconia as seen in the XRD graph figure 13.

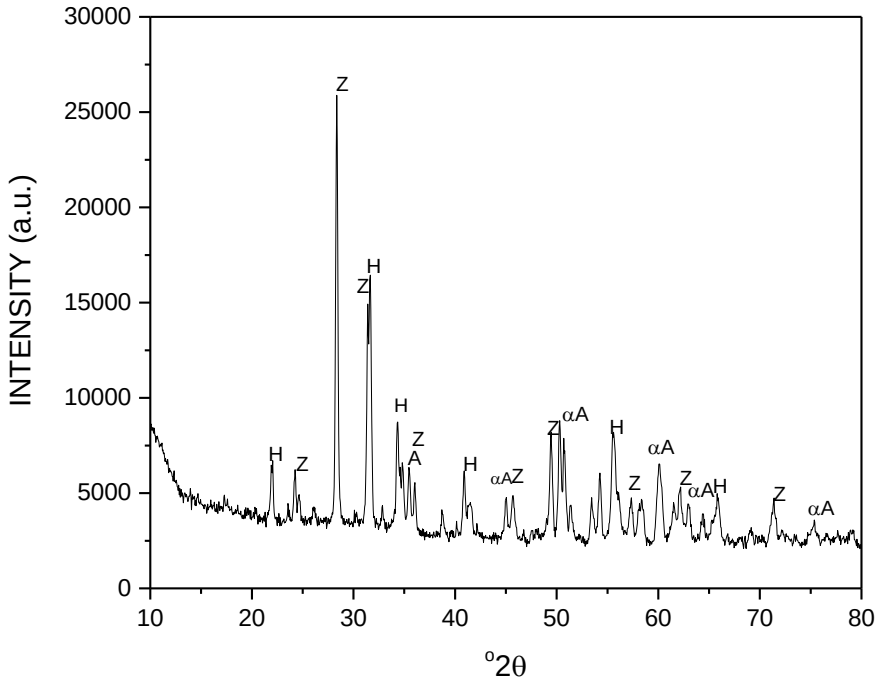
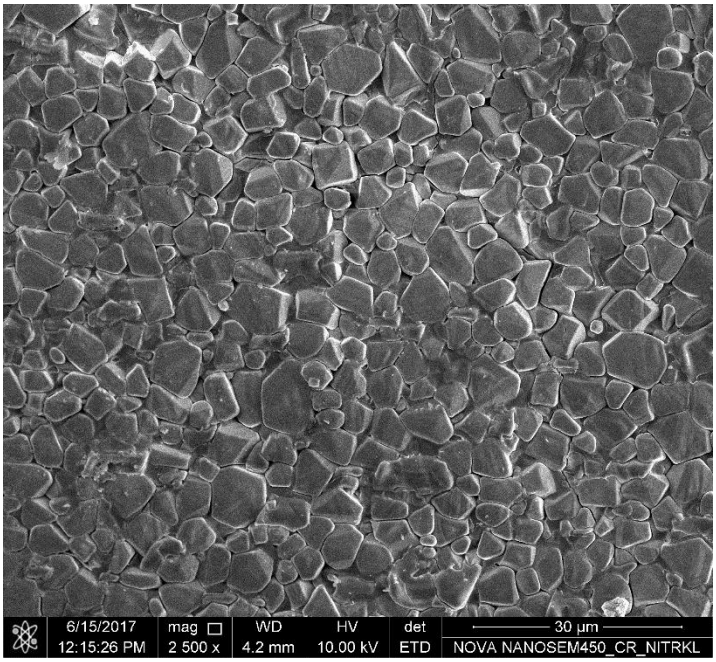


Figure 13: XRD pattern of 3mol% YSZ-Alumina-HAp composite sintered at 1300^{o}C

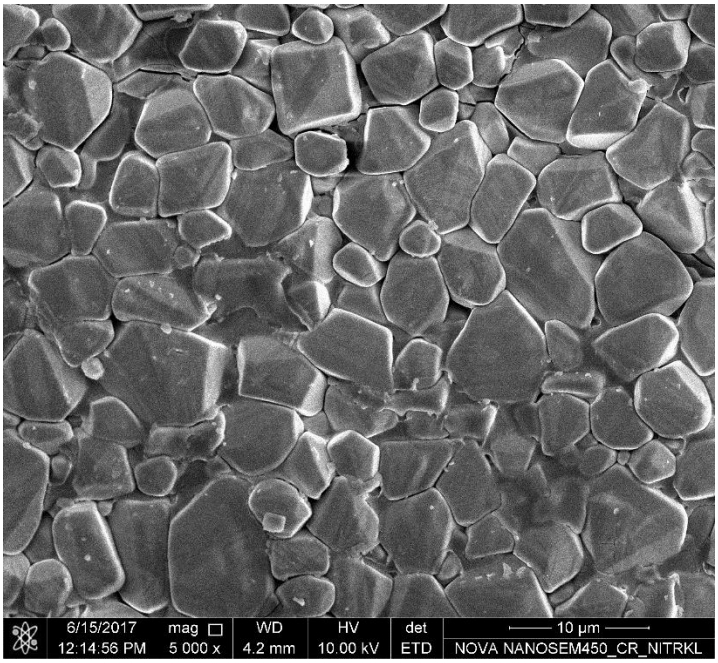
4.6 Microstructure of the Sintered Composite

The 3mol% YSZ-Alumina-HAp composite sample was pressed into pellets and sintered at 1200^{o}C and 1300 °C for 3 hours. No phase segregation has observed at the edge and corners of the grain boundaries. The matrix consisted of continuous hydroxyapatite crystals with alumina and zirconia embedded in the grains. Average grain size is between 1 to 3 microns and a

uniform size distribution of grains could be observed. Fracture in the composite was occurred inter granularly leaving grains with sharp boundaries.

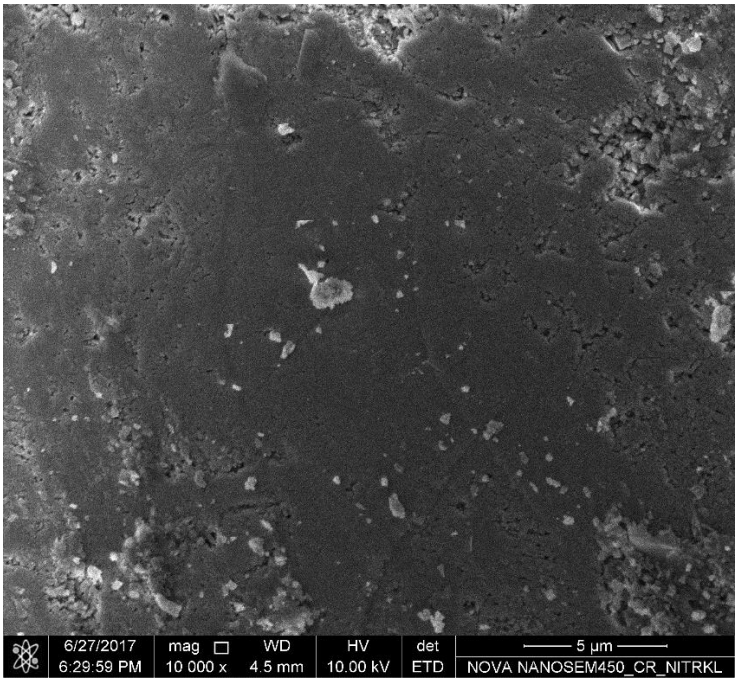


(a)

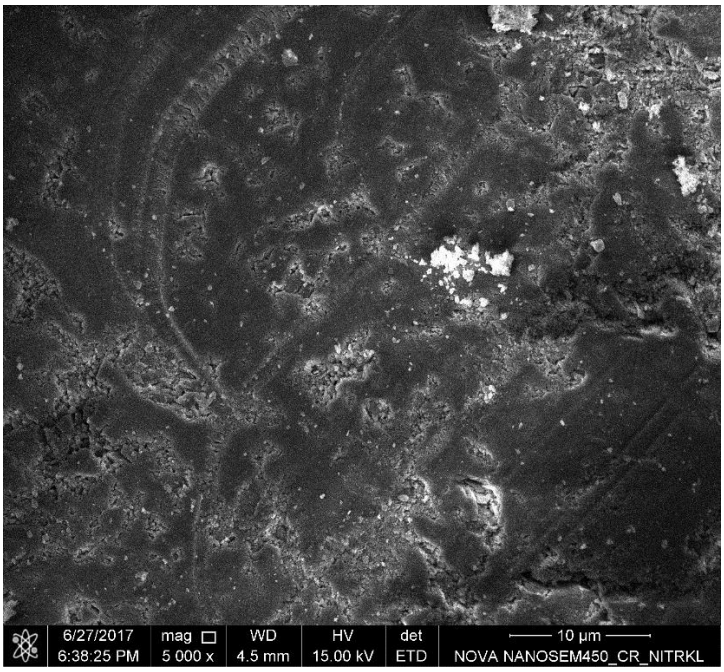


(b)

Figure 14: FESEM analysis of YSZ-Alumina-HAp composite sintered at 1300^{o}C (Calcined at 600^{o}C), (a) for magnification 2500x, (b) for magnification 5000x



(a)



(b)

Figure 15: FESEM analysis of YSZ-Alumina-HAp composite sintered at 1300^{o}C (Calcined at 800^{o}C), (a) for magnification 10000x, (b) for magnification 5000x

Chapter 5

Conclusion

Synthesis of hydroxyapatite-alumina-zirconia composite was achieved after a heterogeneous route of precipitation with urea. The heterogeneous precipitation synthesis process was carried out in two phases; Synthesis of alumina coated yttria stabilized zirconia cores and hydroxyapatite coating the cores. The two processes for the synthesis of 20/10/70 vol% zirconium-alumina-hydroxyapatite composite powders were examined to optimize particle size, phase purity and particle morphology. The stoichiometry of the precursor, the urea/precipitant ratio of 10, homogeneous heating of the precipitation medium above 85 ° C, mild stirring of at least 6 hours, calcination above 600 ° C before sintering, sintering at 1300 ° C should encourage the formation of nanoscale composite particles with satisfactory microstructural characteristics. It was found that alumina effectively eliminated the decomposition reaction between the hydroxyapatite and zirconium as the intermediate layer in the particles. X-ray diffraction graphs show no trace of CaZrO3 and alpha tricalcium phosphate as the decomposition product. Further mechanical tests are required for the consolidated composite in the highly dense form, that includes fracture strength, flexural strength etc. Consequently, the present work opens up possibilities for the production of ceramic matrix composites containing bioactive hydroxyapatite with a variety of mechanical properties that may satisfy the needs of the various load-bearing orthopedic applications.

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