USING HYDROXYAPATITE POWDER (HAP) IN COATING OF STAINLESS-STEEL SUBSTRATE FOR BIO-APPLIATION (A REVIEW)

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ABSTRACT

Around the world about millions of people using the medical devices or biomaterials that implanted in side human body in order to replace the function of unwell tissues or damaged parts. In spite of the importance roles of these implants in saving or improving human life, many of them are failed during short period or having complications. The main failure of the biomaterials caused by unqualified biocompatibility. Thus there are two materials types used for this field investment such as thin film nitinol and stainless steel. Stainless-Steel type 316L are widely used in biomaterial bone applications specially fixing devices such as plates, screws, pins and artificial joints. On the other hands, thin film nitinol indicates a high possibility for applying in a small new vascular devices like heart valves and covering stent grafts because of the singular beneficial properties of this material like super-elasticity and low-profile feature.

KEYWORDS: medial devise, biomaterials, implants, biocompatibility, 316L stainless steel and nitinol.

أستخدام مسحوق الهيدروكسي ابتايت في تغطية الفولاذ المقاوم للصدأ للاستخدامات الطبية (مراجعة)

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الخلاصة

حول العالم ملايين الاشخاص يستخدمون الاجزاء الطبية او المواد الحياتية كمزروعات داخل جسم الانسان او استبدال الاجزاء للقيام بوظيفتها بدل الجزء المتضرر. الهدف الاساسي لهذه المزروعات هو الحفاظ على حياة الاشخاص او تحسين حياتهم معظم هذه الاجزاء تتلف بعد وقت قصير. السبب الاساسي لفشل المواد الطبية هو عدم التوافق الحياتي بين المزروعة والنسيج الحي. لهذا فان الفولاذ المقاوم للصدأ والسبائك الذكية (نيكل-تيتانيوم) المطليان بطبقة رقيقة هما الاكثر استخداما من بين المواد الحياتية. يستخدم الفولاذ المقاوم للصدأ نوع 316L بشكل واسع في تطبيقات العظام كأجزاء التثبيت على سبيل المثال البراغي والصفائح والاطراف الصناعية . من جانب اخر ان الطلاء على السبائك الذكية يعطي حرية في تطبقات القلب مثل الصمامات بسبب خواص هذه المواد المميزة مثل المرونة الفائقة.

الكلمات الأساسية: المواد الحياتية، الاجزاء الطبية، المزروعات، التوافقية الحياتية، الفولاذ المقاوم للصدأ316L، السبائك الذكية (نيكل-تيتانيوم).

INTRODUCTION

The skeletal system, which is composed of bones, joints and teeth, have the ability to recover from a wide variety of injuries with minimal medical intervention. However, due to industrial environments, accidents of orthopedic produced much more complex types of injuries. In certain cases, orthopedic surgery is required to rebuild or to replace the damaged bone. Specifically, in the United States, more than 500000 joints are replaced yearly, with more than hundreds of thousands of people are being performed these operation worldwide **(Langer and Vacanti, 1993)** and total implants demand will be increased about thirty percentage during the next twenty years **(Overgaard, et.al., 1992**). In order to realize characteristics similar to the natural bone characteristics, it is important to imitative the natural bone composition and structure. Thus, having a look on the structure of the natural bone becomes important for achieving this purpose **(Neville-Smith, et.al., 2000).**

Moreover, according to **(NOF, 2003)** the osteoporosis patients numbers will be increased from (10.1 to 13.9) million between 2002 and 2020. In most cases, the use of these materials incorporates use of bone cements which are employed for fixing joints prosthesis. Bone cements work as a distributor for load on both the implants and the bone, also its filling bone and dental cavities by self-curing materials.

As well-known Steel suffering from corrosion in any severe environments and specially inside human body. So, **Babu et. al (2004)** try to make an improvement on bio-active coating of implants by using dip-coating method. The study was carried out by using Stainless-Steel type 316L as a substrate which coated by hydroxyapatite with biphasic calcium phosphate. At first, the substrate specimens were putting in a solution contains 20% of (HNO_3) for fifteen minutes at (600℃) in order to produce unreactive substrate surfaces. After that substrate specimens immerged in the solution to stat coating process. They have been found that, the using of this method with appropriate temperatures improves the bonding between the coating layer and the substrate. A little work has been found dealing the treating of metals thermally to reduce the corrosion. Many researchers try to using ceramics powder as an additive with coating solutions to produce ceramic layer on the metals.

According to **(Eliaz, et.al., 2005)** the applying of HAP layer electrochemically increase the corrosion resistance of 316L Stainless-Steel comparison with uncoated 316L Stainless-Steel. While **Rakngarm, et.al., (2008)** produce bio-active coating by using hydroxyapatite layer on metals that used as implants inside human body in order to collect both the mechanical properties of metallic implants materials and biological affinity of natural tissue for hydroxyapatite surface.

On the other hand, **Sami, et.al., (2008)** coated synthetic HA on 316 l st.st. by using electrophoretic deposition method coating was carried out in various time intervals (from 1 to 5 minutes) at constant potential of 60 V. The electrochemical behavior of 316L stainless steel (uncoated and HAP coated specimens) was studied in simulated human body environment. The corrosion parameters obtained from open circuit potential and potential dynamic polarization for the specimens indicate nobler shift in the polarization parameters, OCP time, corrosion potential (Err) and corrosion current density (I_{corr}), for all coated specimens in comparison with the uncoated specimen.

Since 1960 poly Methyl Methacrylate (PMMA) is applied in which field because of the bio-stability and good mechanical properties for this material **(López, et.al., 2008).**

Choudhuri, et.al., (2009) present of an approach by depositing the bio-ceramic coatings using cold spray on the metals at low temperatures which is below metal melting point. These composite powders consist of titanium and HAP and the ratio of HAP was up to thirty percentage. The results have been used in this work indicate an decreasing of HAP ratio between the actual ratio in the coating solution and the deposition ratio. Moreover, the strength of the deposited bond was comparable to that of the plasma sprayed HAP.

One of the scientific methods that used to enhance the surface mechanical characteristics is coating. Also this technique is used in biomedical applications where most of the implants are mainly made from metals. In spite of the metallic devices have a very good properties such as high strength, corrosion resistance and biocompatibility for environment inside human body. However; these devices still metal and corroded in the inconsistent environments. Thus, implants are usually coated by metals with an inert material that has a high stability and biocompatibility called Hydroxy Apatite, **(Behera, et.al., 2010).**

Thus, the biomaterials used in these implants have been limited to bioinert titanium based alloys, stainless steel as well as to alumina and zirconia ceramics **(Park, 2012)**.

In (2016) **Mahdis Shayan**, two types of materials that are used for presenting these strategies include 316L stainless steel and thin film nitinol. After indicating the challenging issues of current treatments in each disease and presenting the techniques to obviate these obstacles, in the next step, appropriate *in vitro* tests have been used to examine the effectiveness of the new techniques in resolving the implied challenges. In the first part, four groups of 316L stainless steel surfaces with average grain sizes in the range of 42nm (*i.e.*, corresponding to 0°-tool-rake-angle-obtained chip) up to 22μm (*i.e.*, corresponding to bulk sample) have been used. The first generation of bone implants was filling the empty space of the lost tissue in the bone showing inert biological response.

Rasheed, (2018) coated 316L stainless-Steel substrates by HA coating using Pulsed laser deposition (PLD), which usually applied in thin films production with qualities comparable to the other techniques . The effects of pulses numbers (3000,4500 and 6000) on the coating layer properties were studied. As well as the effects of the annealing temperature (450 °C) for one hour and Under an empty atmosphere on the coating layer properties were studied along with studying of surface characterization for the coatings by using XRD,SEM,AFM and EDX to detect the amount of (Ca) and (P) in coating layer. Corrosion behavior and Ni ions release for uncoated and coated samples with different number of pulses in synthetic saliva and hanks solution by using OCP and potential static polarization test were achieved also. And the results of this study show that, the mechanical feature of the coating was evaluated by Vickers micro hardness and wear test. XRD analysis of coated sample indicate the formation of the HA layer. SEM results show evident improvement in microstructure and grow HA film with increasing in pulses number.

MATERIALS USED IN MEDICAL APPLICATION

Stainless Steel (316L)

In medical field there are numerous materials and stainless steels (SS) type (316L) is one of the widely applicable material that used as implantation for orthopaedic surgery purposes due to its favorite properties such as corrosion resistance, mechanical characteristics and cheaply. Stainless-Steel are usually used in implantation specially in pins and screws as well as using in orthopedic implants such as knee replacements and total hip. In spite of that, the clinical experiments show that Stainless-steel suffering from corrosion inside human body and then caused metal irons released into the implants surrounding tissues. And due to corrosion failure that happened in conditions of applying the device produced from this type of materials inside human body, open the way for many research in order to improve biocompatible and corrosion resistant and Table 1. demonstrate mechanical characteristics of 316L stainless steels comparison with natural bone properties, while the second table the chemical composition range for stainless-steel type (316L), **[(Höland, 1997) and (Long, et.al., 1998)].**

Hydroxyapatite: structure and properties

Hydroxyapatite is one of the ceramic materials that well-known in medical field as a bio-active materials, (Narayan, et.al., 2004). The inert biological component of bone made up apatites that work as storage for calcium and magnesium, phosphorus as well as sodium in order to give the skeleton its strength. The structure of the biological apatites are similar for mineral hydroxyapatite apatites and brushite ($Ca_{10}(PO_4)6(OH)_2$) & (B, $CaHPO_4.2H_2O$) respectively. At body fluid and temperature, there are two stable forms of calcium phosphates, the first one at (pH<4.2) is brushite phase, while the second forms at (pH>4.2) is hydroxyapatite phase.

Hydroxyapatite crystals are a forms of hexagonal rhombic prisms. The lattice variables for hydroxyapatite are (a=9.432 Ǻ)&(c=6.881 Ǻ) as shown in **(Figure 1)**. Hydroxyl ions (OH-) happen at the corners of the basal plane. Ions of are located at every 3.44 Ǻ (half of unit cell), which is parallel to (c-axis) and perpendicular to basal plane of the crystals. Therefore, in the unit cell about sixty percentage of calcium ions are related with the hydroxyl ions. And the density is 3.219 g/cm3 for this material **(Park and Lakes, 1992).** Around the world the annual turnover of the hard tissue (prosthetic implants) and replace amputated bones as well as hip replacement and dental implants as a coating about $2.3 billion and this number tend to increase. The successful of implants are depending on good biocompatibility and mechanical characteristics factors. On the other hand, applying metals inside human body were narrowed to minimum because of corrosion issues.

COATING TECHNIQUES

Many coating methods are used for improving the materials surface. And the following techniques are used for applying coatings on metals such as:

a. Electroplating :Electroplating is a process of coating a deposition on a cathode part immersed into an electrolyte solution, where the anode is made of the depositing material, which is dissolved into the solution in the form of the metal ions, that travel through the solution and deposit on the cathode surface.

b. Electroless plating :The process of deposition of metal ions from electrolyte solution onto the substrate when no electric current is involved and the plating is a result of chemical reactions occurring on the surface of the substrate.

c. Hot dipping :Immersing the part into a molten metal followed by removal of the substrate from the metal bath, which results in formation of the metal coating on the substrate surface.

d. Physical Vapour Deposition (PVD) :the process involving vaporization of the coating material in vacuum, transportation of the vapour to the substrate and condensation of the vapour on the substrate surface.

e. Chemical Vapour Deposition (CVD) :The process, in which the coating is formed on the hot substrate surface placed in an atmosphere of a mixture of gases, as a result of chemical reaction or decomposition of the gases on the substrate material.

f. Thermal spraying :Deposition of the atomized at high temperature metal, delivered to the substrate surface in a high velocity gas stream

On the other hand, the thickness of the coating layers are vary depending on the coating techniques as demonstrated in figure 2.

NATURAL BONE: STRUCTURE AND PROPERTIES

Mature bone is basically a two-phase composite. Its main constituents are a protein known as collagen and an inert mineral phase named hydroxyapatite (HA or HAP). It is not easy to say which phase is the main load-bearer; it could be that crystal acts as filler stiffening the collagen by restricting its movement under stress. It should be noted that collagen is only 1% as stiff as the mineral and, therefore, it is unsuitable to carry compressive or bending loads. Collagen is the only component that gives a fibrous texture to the bone. HA is much stiffer and twice as strong **(Table3)**.

Bone has a complex hierarchical structure **(Figure 3)** that affects its mechanical performance. The density and arrangement of mineralized platelets will regulate the trend and value of the stress which could sustain and the method of transferring via the bone. Collagen fibrils are arranged in two major methods: (i) inlayers with preferred orientation laid up to each other with the favored instructions (lamellar bone) and (ii) random (woven bone). Lamellar bone built into sheets in one plane (primary lamellar bone) or into cylinders (Haversian bone) or mixing with woven bone (laminar bone). All kinds are available in compact bone **(Elices, 2000).**

The structural unit of a bone is the osteon. That is basically a hollow tube, typically 200 μm diameter and about 1-2 cm long, which helps not only as a load bearing component but also as a blood vessel. The walls of the osteon are built with a helical arrangement of thin fibers of collagen broken with parallel platelets of HA. The result is a short column ability to carry the compressive loads effectively to avoid buckling. However, it is not designed mainly for toughness **(Elices, 2000).**

CONVENTIONAL ORTHOPEDIC: BIOMATERIALS AND BONE RESPONSE BY METAL BASE IMPLANTS

The current implant design is depending on the pioneering work carried out by Sir John Charnley **(Todd, et.al., 1972)**. The implant consist of two parts: (i) the metallic part (called femoral) made from stainless steel 316L, Co-Cr-Mo alloy, Co-Ni-Cr-Mo alloy, or a Ti-Al-V alloy, and (ii) the polymeric part which coats the head of the femoral and made from ultrahigh molecular weight polyethylene (**Figure 4**). The apparatuses are fixed in place using PMMA bone cement.

Current strategies have short lifespans. Thus, about (10 to 20)% of implants must be replaced after 10 years, and some of them could need replacing in a shorter period about 5 years **(Birtwistle, et.al., 1996)**. Loosening, wear, corrosion, uneven stress distributions, and tissue irritation contribute to these short lifetimes. The comparatively little lifespan for these devices or implants due to insufficient cement technology prompted Charnley himself to recommended that this implant be used only in elder patients with a limited life expectation **(Emery, et.al., 1997).**

Stress shielding is another phenomenon that affects the use of implants. This term refers to an uneven load distribution at the bone-implant interface that can lead to implant loosening **(Karachalios, et.al., 2004)**. This problematic affects every current metal implant component.

CONCLUSION

From the above presentation of the related works the main conclusion that can be drawn is the metals have wide applications in many different fields. The medical field is one of these fields due to the wide various properties such as high strength. While metals have another sides because they usually suffering from corrosion when applied in sever environment such as the environment inside human body. So these metals should be treated in many different way to prevent corrosion or minimized it to its lower ratio and coating one of these techniques. And the coating method was developing day after day and the coating materials were changed to investigate best and most suitable materials for human body. Many researchers found that using of (HAP) with any different metals improve the corrosion resistance inside human body.

Table1. Mechanical characteristics of bone and (SS 316L) in orthopedic implants (Long,et.al.,1998).

Materials	Elastic Modulus (GPa)	Tensile Stress (MPa)	Tensile yield Stress MPa
316L	210	485	170
BONE	10-30	70-15	120

Table 2. Chemical Composition for Stainless-Steel type 316L (Long, et.al., 1998).

Grade		C	Mn	Si	Pb	S	Cr	Mo	Ni	N
316L	Min	-	-	-	-	-	16.0	2.00	10.0	-
	Max	0.03	2.0	0.75	0.045	0.03	18.0	3.00	14.0	0.10

Table 3. Material characteristics of the main components of bone (Vincent, 1991).

Feature	Value
hydroxyapatite Strength	0.1 GPa
hydroxyapatite Stiffness	130 GPa
hydroxyapatite Ultimate strain	0.001
Stress in collagen at strain= 0.001	1 MPa
Strength of collagen	50 MPa

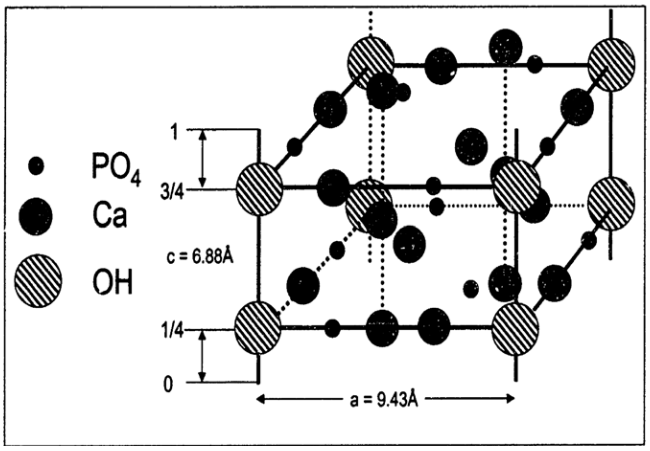


Figure 1. Simplified crystal structure of hydroxyapatite.

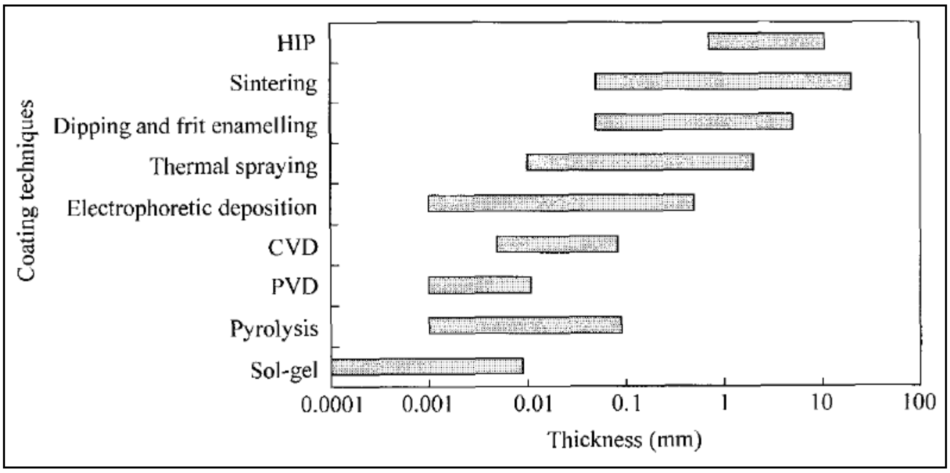


Figure 2. Thickness of coatings that applied by different processes.

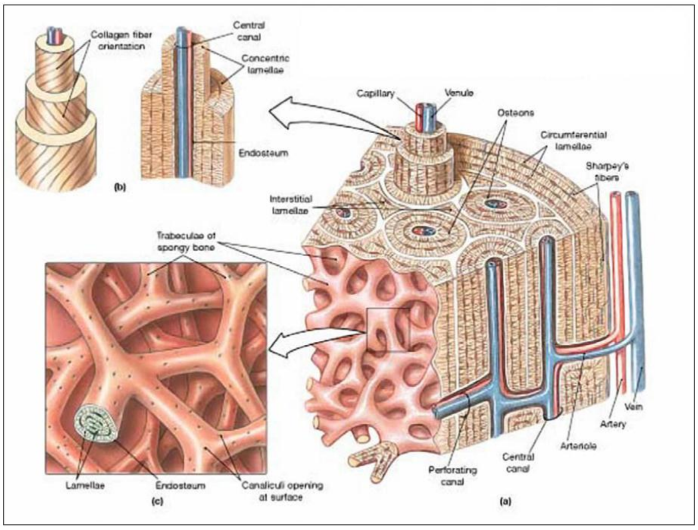
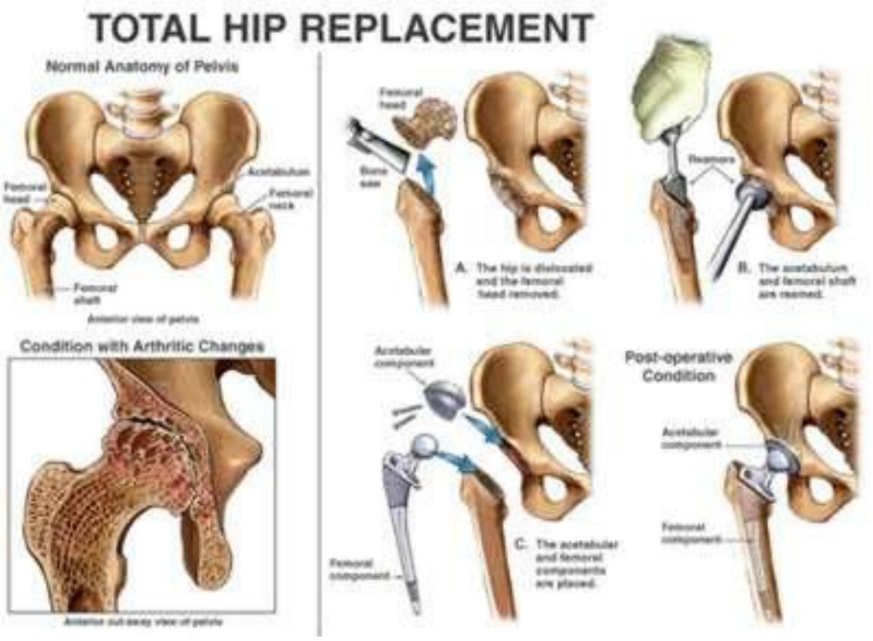
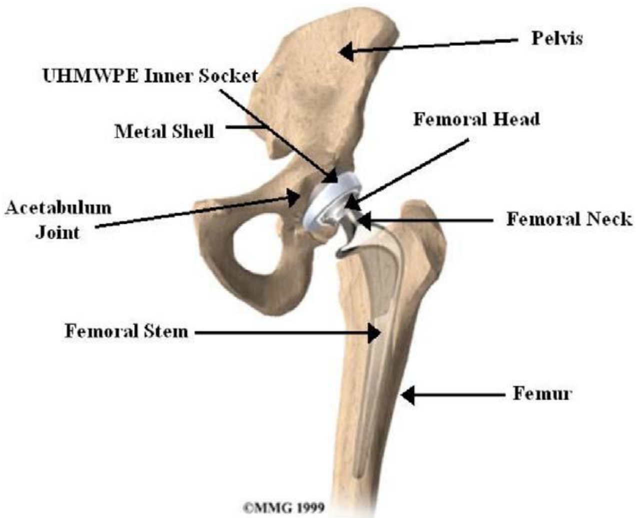


Figure 3. Structure of Osseous Tissue. (a) The relationships among spongy bone, compact bone, and the marrow cavity. The insets show (b) the orientation of cooagen fibers in adjacent lamellae and (c) s organization of spongy bone.



(A)



(B)

Figure 4. Model of an implanted total hip prosthesis ((MMG), 2002).

REFERENCES

Ajay, S. and Abhinandan, R., 2010. Study of hydroxyapatite and hydroxyapatite-chitosan composite coatings on stainless steel by electrophoretic deposition method. National Institute of Technology.

Babu, N.R., Manwatkar, S., Rao, K.P. and Kumar, T.S., 2004. Bioactive coatings on 316L stainless steel implants. Trends in Biomaterials & Artificial Organs, 17(2), pp.43-47.

Behera, P. and Bhaisare, D.K., 2010. Synthesis and characterization of ultrafine hydroxyapatite (HAp) powder coating on stainless steel substrate by electrophoretic deposition (Doctoral dissertation).

Birtwistle, S.J., Wilson, K. and Porter, M.L., 1996. Long-term survival analysis of total hip replacement. Annals of the Royal College of Surgeons of England, 78(3 Pt 1), p.180.

Choudhuri, A., Mohanty, P.S. and Karthikeyan, J., 2009, May. Bio-ceramic composite coatings by cold spray technology. In Thermal Spray 2009. Proc. Int. Thermal Spray Conf. Japan Association for Earthquake Engineering.

Eliaz, N.S.T.M., Sridhar, T.M., Kamachi Mudali, U. and Raj, B., 2005. Electrochemical and electrophoretic deposition of hydroxyapatite for orthopaedic applications. Surface Engineering, 21(3), pp.238-242.

Elices, M. ed., 2000. Structural biological materials: design and structure-property relationships (Vol. 4). Elsevier.

Emery, D.F.G., Clarke, H.J. and Grover, M.L., 1997. Stanmore total hip replacement in younger patients: review of a group of patients under 50 years of age at operation. The Journal of bone and joint surgery. British volume, 79(2), pp.240-246.

Farah Sami Rasheed, " Surface Modification by HA of 316 L S.S for Biomedical Applications", MSC thesis University of Babylon/ Collage of Materials Engineering/ Metallurgical Engineering Department, MSC thesis, 2018.

Höland, W., 1997. Biocompatible and bioactive glass-ceramics—state of the art and new directions. Journal of Non-Crystalline Solids, 219, pp.192-197.

Karachalios, T., Tsatsaronis, C., Efraimis, G., Papadelis, P., Lyritis, G. and Diakoumopoulos, G., 2004. The long-term clinical relevance of calcar atrophy caused by stress shielding in total hip arthroplasty: A 10-year, prospective, randomized study1. The Journal of arthroplasty, 19(4), pp.469-475.

Langer, R. and Vacanti, J. P., 1993. Tissue Engineering. Science, 260(5110): p920-926.

Long, M. and Rack, H.J., 1998. Titanium alloys in total joint replacement—a materials science perspective. Biomaterials, 19(18), pp.1621-1639.

López, M., Fuentes, G., González, R., González, J., Peón, E. and Toledo, C., 2008. PMMA/Ca2+ Bone cements: Part I. Physico chemical and thermoanalytical characterization. Latin American applied research, 38(3), pp.227-234.

Mahdis Shayan, "NOVEL SURFACE MODIFICATION TECHNIQUES TO ENHANCE BIOCOMPATIBILITY OF METSALLIC MATERIALS FOR MEDICAL IMPLANTS" PhD thesis University of Pittsburgh, 2016

Medical Multimedia Group (MMG), M., A Patient's Guide to Artificial Joint Replacement of the Hip. 2002, Montana Spine Center (Appalachian State University): Missoula, Montana.

National Osteoporosis Foundation (NOF) 2003.(www.nof.org) Siegel R W 1996 Sci. Am. 27542.

Narayan, R.J., Kumta, P.N., Sfeir, C., Lee, D.H., Choi, D. and Olton, D., 2004.

Nanostructured ceramics in medical devices: applications and prospects. Jom, 56(10), p.38.

Neville-Smith, M., Trujillo, L. and Ammundson, R., 2000. Special feature: Consistency in postoperative education programs following total hip replacement. Topics in Geriatric Rehabilitation, 15(4), pp.68-76.

Overgaard, S., Knudsen, H.M., Hansen, L.N. and Mossing, N., 1992. Hip arthroplasty in Jutland, Denmark: Age and sex–specific incidences of primary operations. Acta orthopaedica Scandinavica, 63(5), pp.536-538.

Park, J.B., 2012. Biomaterials science and engineering. Springer Science & Business Media.

Park, J.B. and Lakes, R.S., 1992. Biomaterials: an introduction. Plenum Press, New York, 4, pp.71-3.

Rakngarm, A., Miyashita, Y. and Mutoh, Y., 2008. Formation of hydroxyapatite layer on bioactive Ti and Ti–6Al–4V by simple chemical technique. Journal of Materials Science: Materials in Medicine, 19(5), pp.1953-1961.

Sami, A. and Nabeel, k., 2008. Hydroxyapatite coating improved corrosion resistance of 316L stainless steel used for surgical implants applications. Eng. And Tech., Vol.26, No.8.

Sajjad, J., Mehdi, M.A. and Jamaliah, I., 2012. Comparative study on bioactive coating of Ti-6Al-4V alloy and 316 l stainless steel. Metallurgical and Materials Engineering, 18(2), pp.145-158.

Todd, R.C., Lightowler, C.D.R. and Harris, J., 1972. Total hip replacement in osteoarthrosis using the Charnley prosthesis. British medical journal, 2(5816), p.752.

Vincent J.F.V., 1991. Strength and fracture of grasses", J. of Mat. Sc.q, 26: pp.1947-1950.