Review on Nanocoating for Bio-Implants

S.Aravind[1], M.Gokul Prabhu[2], D.Kaushik[3], K.L.Senthil Kumar[4]

[1,2,3] U.G Scholar, Department of Mechanical Engineering, Sri Ramakrishna Engineering College, Coimbatore–641022, Tamil Nadu, India
[4] Assistant Professor(Sr.G), Department of Mechanical Engineering, Sri Ramakrishna Engineering College, Coimbatore–641022, Tamil Nadu, India.

---***---

Abstract - *The aim of this paper is to study and review on Nanocoatings for Bio-Implants. In this paper, a detailed study on materials used for coating with respect to its mechanical and metallurgical properties was carried out. The bonding strength of the coating material was studied based on its adsorption property. Similarly, the corrosion behaviour and life of the implants were also studied through the SEM, XRD, SEM and TEM.*

Key Words: **Nanocoatings, Bio-Implants, Materials, Adsorption.**

1. INTRODUCTION

Nanocoating is an application where nano structures build a consistent network of molecules on a surface. Nano coating is hydrophobic , oleo phobic surface layer that repels water, oil, dirt, and other dry particles. Superhydrophobic coatings are used in dry surface application. These naturally occur in some plant leaves, such as the lotus leaf, and some insect wings. High hydrophobicity eco-friendly nano coating can be applied onto objects to make them waterproof for the long-term. The product is anti-corrosive or oxidation, anti-icing, UV resistance, high temperature resistant and also resistant to chemical compound. It has self-cleaning capabilities when it rains and can be used on a variety of surfaces.

Nano coatings do not change the colour of the surface to which they are applied. They are invisible to the naked eye. This entails the chemical process where the surface can be designed to become (super) hydrophobic or hydrophilic for example. Nanocoating is a growing line and some of its applications are already in use whereas many more, with great potential, are being researched on.

Nanotechnology is a great technology that deals with structures measuring less than 100 nanometres. A nanometre is one-billionth of a metre. This is the size of a football in relation to the earth, or the breadth of a hair split 80,000 times. Nanotechnology is used in robotics, sensing technology, process technology, biotechnology and medicine, among other areas.

In the recent years some investigations which exploit the biomorphic ceramics as new scaffold for bone implants were studied. Implantation of bone autograft or allograft is a known strategy for the treatment of large bone defects. Tissue engineering is trying to solve this problem by development of bone substitutes using cells and bio-scaffolds. Whereas, most of them have relatively poor mechanical strength and cannot meet the requirements for many applications. Hence, there is a need to fabricate new scaffolds with improved mechanical properties and biocompatibility.

1.1 Coating Properties

- Highly effective dirt-repellent, non-stick coatings resembling glass-ceramic or Teflon.
- Hydrophilic, conductive, coloured, transparent or decorative ("soft feel") and corrosion-proof coatings.
- High adhesion thanks to the coating's chemical bond with the workpiece's surface (unlike a conventional PTFE coating).
- High chemical and temperature resistance (up to 600°C).
- Diffusion barrier for certain metal ions.
- Can be cleaned with very little effort.

1.2 Applications of Nanocoatings

- Anti-corrosive coatings
- Water proof and non-stick coatings
- Antibacterial coatings
- Thermal Barrier coatings
- Anti-abrasion coatings
- Self-healing coatings
- Anti-reflection coatings
- Anti-graffiti coatings

2. LITERATURE REVIEW

Magnesium and its alloys are recently found important in the field of bone repairing for their ideal mechanical performance and excellent biocompatibility. Magnesium-based materials have good biological performance[1] in the physiological environment. They are non-toxic materials and can probably benefit tissue growth. Moreover, the mechanical properties of magnesium-based materials, such as density, strength and elastic modulus, are much closer to that of natural bones compared with stainless steels or titanium alloys. Generally, degradable magnesium alloys must have a moderate corrosion rate to ensure that the implanted fixture last for at least 12 weeks[2]. Some possible coating technologies available for magnesium and its alloys, including microarc oxidation (MAO), electrophoretic deposition (EPD), sol–gel, anodicspark deposition (ASD) and their combinations.

Huijun Yu[3] analysed that Micro-arc oxidation (MAO) is a simple, controllable and efficient electrochemistry method that can prepare protective ceramic coatings on magnesium and its alloys. The properties like thickness, microstructure, roughness and composition of the MAO coating is controlled easily by adjusting the voltage, current density, duration and the electrolyte concentration. The structure characteristics and element distributions of the coatings are investigated by XRD, TEM, SEM and EPMA. The MAO[4] samples are immersed in SBF for 7, 14 and 28 days respectively to check its behaviour. The corrosion behaviour of the samples in SBF is investigated by potentiodynamic polarization curves. The corrosion products is characterized by EDS and FT-IR. The MAO coated ZK61 alloy samples showed excellent corrosion resistance and bioactivity. As a result it is found that the applied voltage has a great effect on the relative amount and crystallinity of MgO and Mg2SiO4. The surface of the MAO coatings on the ZK61 alloy is found to be porous. The roughness increases with the decrease in the applied voltage. The inner of the coating is much denser, so it has fine bond to the substrate. Thus the MAO method demonstrates a great potential in the preparation of degradable and bioactive orthopedic magnesium-based implants.

ZhijieMa and HuiXie[5] suggested that the porous silicon carbide (SiC)[6] is best suited due to its excellent physical and chemical properties, such as strength, resistance to oxidation and corrosion. The apparent densities of SiC foams can be controlled between about 0.4 and 1.3g/cm^3, with corresponding compressive strengths ranging from about 13 – 60 MPa and flexural strengths from about 8–30 MPa[7]. Hence they come to know that the SiC can be used in repairing complex shape and long weight-loading bone defects. Tantalum (Ta) attracts much attention for biomedical applications due to its good biocompatibility and chemical stability. Tantalum is used in clinical practices and found in a wide range of diagnostic and implant applications such as radiographic marker, vascular clips, endovascular stent, cranioplasty plates, and orthopedic and dental implants. The combination of the excellent mechanical properties and low density of the biomorphic SiC scaffold is used as a base material for implants. By chemical vapor deposition (CVD) process the bioactive metallic tantalum coating is deposited on the surface of porous SiC. The morphology and phase composition of tantalum coating is characterized by SEM, EDS and XRD. The cell adhesion test is employed with pre-osteoblast to evaluate the cytocompatibility of Ta coating. The MC3T3-E1 cells has shown good adhesion and spreading on the surface of Ta coating, which indicates excellent bioactivity and cytocompatibility and they concludes that porous SiC scaffolds with Ta coating appears to be quite interesting material for bone substitutions, combining the characteristics of both materials into a new product as that enhances the mechanical and biochemical properties.

P Layrolle[8] analysed that Calcium phosphate(CaP) coatings, especially those made with hydroxyapatite(HA,Ca10(PO4)6(OH)2), are applied on titanium implants to improve its bone-integrative properties[9]. Calcium Phospate is similar in composition as the bone mineral, and able to achieve an early and functional bone apposition on the implants. CaPs are also similar in composition to the mineral part of bones and teeth. CaPs are salts of the phosphoric acid H_3PO_4 and thus it can form compounds that contain $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} ions. The surface of titanium implants is generally grit-blasted with alumina ceramic(Al_2O_3) particles.

Titanium has high surface roughness[10] that ensures good mechanical interlocking of CaP coatings on metals , improving bonding strength and shear resistance. Atmospheric plasma spraying (APS) is the widely applied method to deposit HA coating onto titanium alloy prostheses. The method consists of injecting the ceramic HA particles into a high-temperature (>10000^{o}C) and high-velocity (>800 m/s) plasma torch. The HA particles partly melts and are projected on the surface of the titanium implants where they condense and fuse together forming a coating. The plasma-spraying method is highly effective for coating orthopedic prostheses, as CaP layers having a thickness of 50–100 mm are produced within minutes. In the Electrochemical Deposition process (ELD), electrochemical reactions near the electrode induce local pH increase and thus CaP precipitation on the titanium implant. The ELD process is carried out in supersaturated or metastable CaP solutions and is based on the electrolytic decomposition of water.

A platinum electrode (acts as anode) and the titanium implant (acts as cathode) are connected to a current generator. The local pH rise leads to an increase in the relative supersaturation of the electrolyte and the precipitation of CaP on the titanium surface. There are some drawbacks in plasma-sprayed HA coatings[11], and hence a new coating is developed method inspired by the natural process of biomineralization known as biomimetic method. This method involves the heterogeneous nucleation and growth of bone-like crystals on the surface of implant at physiological temperatures and pH conditions. The problem of low saturation of SBF is overcome by increase in calcium and phosphate concentrations by bubbling a weak acid gas, namely, carbondioxide. The biomimetic approach is found to have four main advantages: (i) it is a low-temperature process applicable to any heat-sensitive substrate including polymers; (ii) it forms bone-like apatite crystals having high bioactivity and good resorption characteristics; (iii) it is evenly deposited on porous or complex implant geometries; and (iv) it can also incorporate bone-growth-stimulating factors. The aim of the author is to provide metal implants with surface biological properties for the adsorption of proteins, the adhesion of cells, and the bone apposition.

Table-1: Ionic composition of Simulated Body Fluids

Ionic Composition of Simulated Body Fluids	
Ionic Concentration	SBF
Na^+	142
K^+	5
Mg^{2+}	1.5
Ca^{2+}	2.5
Ca^-	147.8
HCO^{3-}	4.2
HPO_4^{2-}	1
SO_4^{2-}	0.5
pH	7.4

Yashan Feng[12] found that the poor corrosion resistance of biodegradable magnesium alloys is the dominant factor that limits their clinical application. To deal with this challenge, a fluoride coating was prepared on Mg-Zn-Ca alloy as the inner coating and then hydroxyapatite (HA) coating as the outer coating is deposited on fluoride coating by pulse reverse current electrodeposition (PRC-HA/MgF_2).

To make a comparative study, the microstructure and corrosion properties of the composite coating with the outer coating is fabricated by traditional constant current electrodeposition (TED-HA/MgF_2) is also investigated. Scanning electron microscopy (SEM)[13] images of the coatings shows that the morphology of PRC-HA/MgF_2 coating is dense and uniform, and gives nano-rod-like structure. When compared with that of TED-HA/MgF2, the corrosion current density of Mg alloy coated with PRC-HA/MgF2 coatings decreases from $5.72x10^{-5}$ A/ cm^2 to $4.32x10^{-7}$ A/cm2, and now the corrosion resistance increases by almost two orders of magnitude and PRC-HA/MgF2 coating is dense and uniform and the surface presents nano-rod-like structure with the rod diameter ranging from 50 nm to 80 nm.

In immersion tests, samples coated with PRC-HA/MgF_2 coating always shows the lowest hydrogen evolution amount, and could induce deposition of the hexagonal structure-apatite on the surface rapidly. The corrosion resistance and the bioactivity of the coatings can be improved by adopting double-pulse current mode in the process of preparing HA coating[14] on fluoride coating, and the PRC-HA/MgF_2 coating is worth of further investigation and it has greater potential to be used as biological materials.

William R. Walsh[15] suggested that rapid and stable fixation at the bone-implant interface is regarded as one of the primary goals to achieve clinical efficacy, regardless of the surgical site. Although mechanical and physical properties of polyetheretherketone (PEEK) provide advantages for implant devices, but the limitations of hydrophobic nature and the lack of direct bone contact still remains. The author examined the effects of a plasma-sprayed titanium coated PEEK[16] on the mechanical and histologic properties at the bone-implant interface.It is made as a preclinical laboratory study.

Polyetheretherketone and plasma-sprayed titanium coated PEEK implants is placed in a line-to-line manner in cortical bone and in a press-fit manner in cancellous bone of adult sheep using an established ovine model[17]. Shear strength has been assessed in the cortical sites at 4 and 12 weeks, whereas histology was performed in cortical and cancellous sites at both time points. As a result, the titanium coating dramatically improved the shear strength at the bone-implant interface at 4 weeks and continued to improve with time compared with PEEK. Direct bone on-growth in cancellous and cortical sites is achieved using a plasma-sprayed titanium coating on polyetheretherketone. The author concludes that the direct bone to implant bonding can be achieved on PEEK in spite of its hydrophobic nature using a plasma-sprayed titanium coating.

Xiang Li[18] experimented on porous tantalum (Ta), produced using chemical vapor deposition (CVD) onto a vitreous carbon. Ta film is deposited on porous Ti_6Al_4V scaffolds using CVD technique. Digital microscopy and scanning electron microscopy indicated that the Ta coating evenly covers evenly the entire scaffold structure. Through X-ray diffraction analysis, author found that the coating consisted of α and β phases of Ta. Mesenchymal stem cells of a goat is seeded and cultured on the Ti_6Al_4V scaffolds with and without coating. The tetrazolium-based colorimetric assay exhibits better cell adhesion and proliferation on Ta-coated scaffolds compared with uncoated scaffolds. Now the porous scaffolds were subsequently implanted in goats for 12 weeks. Histological analysis reveals that the similar bone formation around the periphery of the coated and uncoated implants were formed, but bone ingrowth is better within the Ta-coated scaffolds. The in vitro experimental results reveals that Ta-coated scaffolds is found to have positive effects to MSCs in terms of adhesion, growth, and proliferation. According to the histological results, Ta-coated scaffolds has better biocompatibility and osteogenesis than

Ti_6Al_4V scaffolds, indicating that has potential for clinical use in orthopedics.

ZHOU Yue-bo[19] investigated that Ni-Cr nanocomposite coatings with different Cr particles contents can be developed by electrodeposition method from a nickel sulphate solution that contains different concentrations of Cr nanoparticle with an average particle size of 40 nm. The characteristics of the coatings is assessed by scanning electron microscopy(SEM) and microhardness test. The friction and wear performances of Ni-Cr nanocomposite coatings and pure Ni film is investigated and compared with the effect of the Cr content on the friction and wear behaviors to be emphasized. The results indicate that the microhardness, friction and wear behaviors of Ni-Cr nanocomposite coatings are closely related with Cr particles content. The author analysed that the content of Cr particles in Ni-Cr nanocomposite coatings increases with increasing concentration of Cr particles in the plating bath. The microhardness, friction and wear behaviours of Ni-Cr nanocomposite coatings are closely related with the particles content of Cr. The Ni-Cr nanocomposite coating with a lower Cr content of 4.0% shows somewhat increased microhardness and wear resistance when compared with that of pure Ni coating. The author finally discussed the effect of content of codeposited Cr nanoparticles on the wear resistance of the nanocomposite coating.

Woojune Hur[20] experimented that sustained release of alendronate, which is a drug known to inhibit osteoclast-mediates bone resorption and expedite the bone-remodeling activity of osteoblastscoated a bone plate already in clinical use with a blend of alendronate and a biocompatible polymer, azidobenzoic acid-modified chitosan (i.e., Az-CH) photo-cross linked by UV irradiation. The drug is released from the coating at an average rate of 4.03 μg/day for 63 days in a sustained manner. The effect on bone regeneration is examined by the plate that is fixed on an 8mm cranial critical size defect in living rats and the newly formed bone volume is quantitatively evaluated by micro-computed tomography (micro-CT) at scheduled time of over 8 weeks. At week 8 as a result, the group implanted with the plate enabled with sustained delivery of alendronate showed a significantly higher volume of newly formed bone (52.78 ± 6.84%) than the groups implanted with the plates without drug (23.6 ± 3.81%) ($p < 0.05$). The plate enabled with alendronate delivery also exhibits good biocompatibility on H&E staining, which was comparable to the Inion plate that was already in clinical use. The author finally suggested that a bone plate enabled with local, sustained delivery of alendronate is a promising system with the combined functionality of bone fixation and its expedited repair.

B. Bakin[21] suggested that the titanium(Ti) and its alloys are widely used as implant materials as it has excellent mechanical properties and corrosion resistance. It improves the bone bonding ability, titanium is generally coated with osteoconductive biomaterials such as CaP ceramics investigate the effect of Mg-substitution on corrosion and bioactivity properties of CaP coatings on Ti_6Al_4V substrates produced using electrodeposition technique. Chemical and morphological characterizations of the coatings is examined by using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Corrosion properties of the coatings were studied electrochemically by potentiodynamic polarization technique in simulated body fluid (SBF) at 36 ± 1 °C. The bioactivity properties[22] of the coatings investigated in SBF varies with the time of 1, 7 and 14 days. According to XRD analyses CaP coating (Mg-0) and Mg-substituted coatings (Mg-1, Mg-2 and Mg-3) are composed of brushite phase. Crystallinity degree of coatings progressively decreased with increasing Mg content. The author concludes that the Mg-substitution enhances the bioactivity properties but does not have an affirmative effect on corrosion properties of the coatings.

3. CONCLUSIONS

Through this study, the titanium alloy and magnesium alloy is found to have more mechanical properties when compared with any other metals. Calcium and phosphates can be selected as a coating material since it is non-toxic and has material composition as like bone. The coating is processed through pulse reverse electro deposition method as it is more efficient. This results in increased life span of the implant.

REFERENCES

[1]. Y.F. Zheng, X.N. Gu, F. Witte, Biodegradable metals, Mater. Sci. Eng. R 77(2014) 1–34.

[2]. X.N. Gu, N. Li, Y.F. Zheng, et al., In vitro degradation performance andbiological response of a Mg–Zn–Zr alloy, J. Mater. Sci. Eng. B-Adv. 176 (2011)1778–1784.

[3]. Huijun Yu, Preparation of Si-containing oxide coating and biomimetic apatite induction on magnesium alloy, journal homepage: www.elsevier.com/locate/apsusc.

[4]. M. Razavi, M. Fathi, O. Savabi, D. Vashaee, L. Tayebi, Regenerative influence of nano structured bredigite (Ca7MgSi4O16)/anodic spark coating on biodegradable AZ91 magnesium alloy implants for bone healing, Mater. Lett.155 (2015) 97–101.

[5]. Zhijie Ma, A novel Tantalum coating on porous SiC used for bone filling material, journal homepage: www.elsevier.com/locate/matlet.

[6]. Mahboobeh Mahmoodi and Lida Ghazanfari, Fundamentals of Biomedical Applications of Biomorphic SiC, Properties and Applications of Silicon Carbide, Prof. Rosario Gerhardt (Ed.), ISBN: 978-953-307-201-2, InTech, 2011.

[7]. Wu Lin, Xu Xing-xiang, Li Bo,et al.,Biocompatibility of silicon carbide foam. Chinese, J.Mater.Res.22(1)(2008)58–62.

[8]. P Layrolle, Calcium Phosphate Coatings, 2017 Elsevier Ltd. All rights reserved.

[9]. Leon, B.;Jansen,J.A. Thin Calcium Phosphate Coatings for Medical Implants; Springer: NewYork,2009.

[10]. Lavenus, S.;Ricquier,J.C.;Louarn,G.;Layrolle,P. Nanomedicine (Lond.) 2010, 5, 937–947.

[11]. European Spine Implants Market 2008-2010 In Avicenne Market Reports, 5^{th} edn.,2009.

[12]. Yashan Feng, Characterization and corrosion property of nano-rod-like HA on Fluoride coating supported on Mg-Zn-Ca alloy, journal homepage: http://www.keaipublishing.com/en/journals/bioactive-materials.

[13]. R.C. Zeng, L. Sun, Y.F. Zheng, H.Z. Cui, E.H. Han, Corrosion and characterisation of dual phase Mg-Li-Ca alloy in Hank's solution: the influence of microstructural features, Corros. Sci. 79 (2014) 69-82.

[14]. H.R. Bakhsheshi-Rad, M.H. Idris, M.R. Abdul-Kadir, Synthesis and in vitro degradation evaluation of the nano-HA/MgF 2 and DCPD/MgF 2 composite coating on biodegradable Mg-Ca-Zn alloy, Sur. Coat. Tech. 222 (2013) 79-89.

[15]. William R. Walsh, Plasma-sprayed titanium coating to polyetheretherketone improves the bone-implant interface, The Spine Journal(2015).

[16]. Kersten RF, van Gaalen SM, de Gast A, Oner FC. Polyetheretherketone (PEEK) cages in cervical applications: a systematic review. Spine J 2013.

[17]. Bertollo N, Da Assuncao R, Hancock NJ, Lau A,WalshWR. Influence of electron beam melting manufactured implants on ingrowth and shear strength in an ovine model. J Arthroplasty 2012;27:1429–36.

[18]. Xiang Li, Tantalum coating on porous Ti6Al4V scaffold using chemical vapor deposition and preliminary biological evaluation, journal homepage: www.elsevier.com/locate/msec

[19]. ZHOU Yue-bo, Fabrication and wear properties of co-deposited Ni-Cr nanocomposite coatings.

[20]. Woojune Hur, Bioabsorbable bone plates enabled with local, sustained delivery of alendronate for bone regeneration, journal homepage: www.elsevier.com/locate/jconrel

[21]. B. Bakin, Bioactivity and corrosion properties of magnesium-substituted CaP coatings produced via electrochemical deposition, journal homepage: www.elsevier.com/locate/surfcoat.

[22]. S. Durdu, M. Usta, A.S. Berkem, Bioactive coatings on Ti_6Al_4V alloy formed by plasma electrolytic oxidation, Surf. Coat. Technol. Xxx (2015) xxx-xxx.