I J C T A, 9(37) 2016, pp. 213-220

Surface Modification of 316L Stainless Steel with Hydroxyapatite for Dental Implants

N. Bliss Shiny[*] and S. Gnanavel[**]

Abstract: Biomaterials has various degrees of compatibility in a harsh environment in a living organism. Due to this surface modification of biomaterial systems are required. Here surface modification is done using RF magnetron sputtering method with in vitro study. Dental implants stability and functionality is focused here. The 316L Stainless Steel (SS) and other biocompatible alloys can exhibit good potentials and bone bonding properties of the ceramic by coating. Hydroxyapatite powder was synthesized, using a wet chemical technique. The precursors used were DiAmmonium Hydrogen Phosphate (DHP) and Calcium Nitrate Tetrahydrate (CNT). A white precipitate was formed when the mixture was allowed to be stirred overnight and strictly maintaining the pH at 10.8 with 0.1 N Ammonium Hydroxide (AH). The further process of characterization was done with Field Emission Scanning Electron microscope (FESEM), X-Ray Diffractometry (XRD), Energy Dispersive X-ray Spectroscopy (EDX) and Fourier Transform Infrared Spectrometer (FTIR). The results confirmed the presence of hydroxyapatite powder of size ranging from 300 to 400 nano meters. Hydroxyapatite was coated on the 316L SS with the help of RF magnetron sputtering technique. In vitro analysis using Simulated Body Fluid (SBF) was also done. Surface modified dental implant will have improved material properties low corrosion resistance, good osseointegration.

Index Terms: RF Magnetron Sputtering, 316L Stainless Steel (SS), Hydroxyapatite, Field Emmision Scanning Electron Microscope (SEM), X-Ray Diffractometry (XRD), Energy Dispersive X-Ray Spectroscopy (EDX), Fourier Transformed Infrared Spectroscopy (FTIR).

1. INTRODUCTION

Implant materials such as titanium, stainless steel, cobalt and their alloys are widely used in orthopedic and dental application because of their excellent strength, toughness and low rate in vivo corrosion [1]. Surface modification of implants reduces implant failure like, metal fatigue, unsuccessful osseointegration, fixation, load bearing, biomechanical failures involving fracture, screw loosening specially in single tooth restoration and breakage of prosthesis [2], [6]. 316L Stainless Steel (SS) has wide range of application due to its good general corrosion resistance and because of economical choices. Materials like Nickel and Chromium could leach toxic metal ions [3], [1]. These 316L SS may prone to pitting corrosion when it enters a halide environment hence to avoid this surface modification can be done on the surface of the SS implants [3]. The coating could be done through many process of coating were RF magnetron sputtering technique was found to be good. Since it overcome the problems such as delamination. By using a very low pressure it can also avoid oxidation i.e., removing contamination due to oxygen absorption [4]. The other methods in surface modification have disadvantages in the application of alloys and refractory metals. The basic advantages of RF magnetron sputtering technique are high deposition rate, ease of sputtering any metal, alloy or compound, high film purity, ability to coat heat sensitive substrate and more [5]. Hydroxyapatite is the emerging bioceramics the greatest substitution for bone which gives bone tissue bonding. On basis of crystallographic study and chemical studies synthesized hydroxyapatite are the same [7]. Hydroxyapatite coated implants

[*] Department of Biomedical Engineering, SRM University, Kattangulathur, Kancheepuram-603203, India. *9677871169, Email: n.shinyson@gmail.com*

[**] Department of Biomedical Engineering, SRM University, Kattangulathur, Kancheepuram-603203, India. *7810032558, Email: gnanam06@gmail.com*

shows improvement in various mechanical properties like osteoconductivity, osteoinductivity improves the performance of bone regeneration. Wet chemical methods of synthesis were known to be the easy way to synthesis [8]. This study focused on the surface modification of 316L stainless steel and an in vitro study of the sample which shows the osseointegration of the implant metal were studied.

2. SYNTHESIS AND SURFACE MODIFICATION

A. Materials and Methods

The raw materials which was used for the synthesis of hydroxyapatite are 0.4 mol DiAmmonium Hydrogen Phosphate ($(NH_4)_2 HPO_4$) and Calcium Nitrate Tetrahydrate ($CA(NO_3)_2$) precursors, 0.1 M Ammonium Hydroxide (NH_4OH) for maintaining the pH, Distilled water Ethanol and Acetone. Synthesis through wet chemical technique, surface modification of 316 stainless steel by RF Magnetron Stutterer and In vitro study in SBF Fluid.

B. Synthesis of Hydroxyapatite

There are various process through which hydroxyapatite could be synthesized such as electrophoretic deposition, sol-gel preparation, hydrothermal preparation, combustion preparation and wet chemical technique were wet chemical precipitation technique is used most popularly and widely. This is known to be the simple process for synthesis of hydroxyapatite. All the apparatus has to be washed and cleaned with acetone before using them.

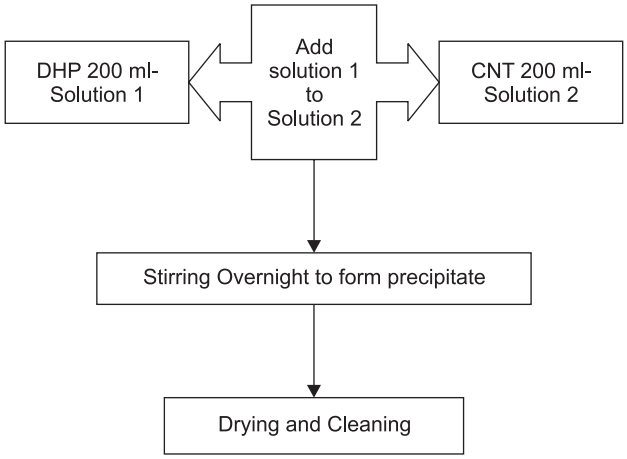

Figure 1: Flowchart of Synthesis Procedure

DHP solution was prepared for 200 ml with pH of 4. CNT solution was also prepared for 200 ml with pH of 7.4. Add DHP solution slowly to the CNT solution using a pipette. The solution has to be stirred well at room temperature and also maintaining the pH at 10.8. Precipitate could be found initially at a lower rate allowing the stirring overnight will yield the precipitate. The precipitate obtained has to be cleaned with distilled water and ethanol. This has to be dried using a hot air oven at 80^o Celsius. To focus on the grain size the reaction time and temperature has to be strictly followed.

C. Surface Modification

The coating was done using a RF magnetron sputtering technique. The discharge was produced using HHV technologies RF/DC Magnetron Sputtering System Model 12-MSPT. The pressure in the cylinder was kept at 25 (L/min), and other parameters as Mass Flow Control (MFC) to be 100%. The pressure levels at different stages are Pressure 1 at 2×10^{-2} to 4.4×10^{-2}, Pressure 2 at 1.6×10^{-2} to 5×10^{-2} and Pressure

3 at 4.1×10^{-3} to 1.7×10^{-3}. Temperature is another advantage of this technique was the whole process was done at room temperature. Sputtering can be done at a low pressure of 100 W-200 W to avoid oxidation. Coating thickness is directly proposition to time taken for the process. The 316 L stainless steel has to be polished and sonicated in sonicator bath before sputtering technique.

3. RESULTS

A. Characterization of Hydroxyapatite

1. *XRD:* X-Ray Diffractometry was done to analyze the crystalline nature of the compound. The Miller Indices value of the reflection panel is assigned with the *d*-spacing values of the peak observed from XRD spectrum. Analysis was done using powder *x*-ray diffraction with a scan range of 2θ and wavelength of around 1.5405 Å. JCPDS file no 2300273 was used to interpret the values of the XRD spectrum.

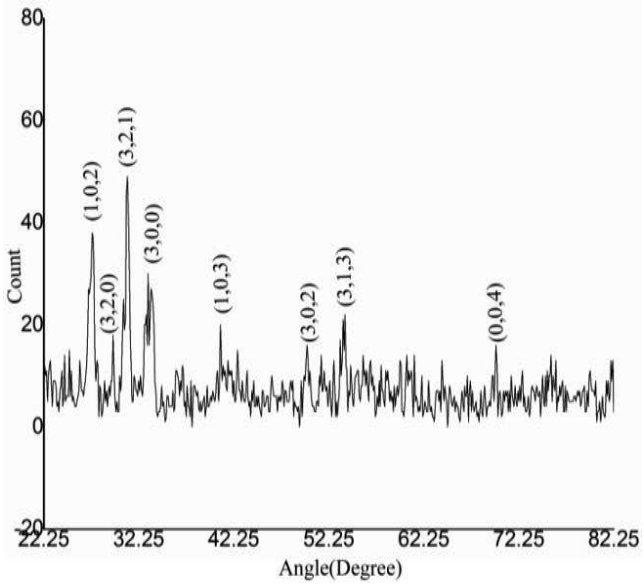

Figure 2: XRD Spectrum of Hydroxyapatite

2. *FTIR:* FTIR spectroscopy determines the functional groups of hydroxyapatite. The spectrum range for investigation was 400 cm^{-1} to 4000 cm^{-1}. The OH stretch hydroxyl group, carbonyl group and phosphate stretching groups were determined with the peak values in Figure 3. The stronger peak of ion stretching vibration was found at 3418.495 cm^{-1}. The peak 1634.991 cm^{-1} gives the carbonyl double bonded stretching group. The bending mode phosphate group was confirmed with the 563.422 cm^{-1} from the FTIR spectrum.

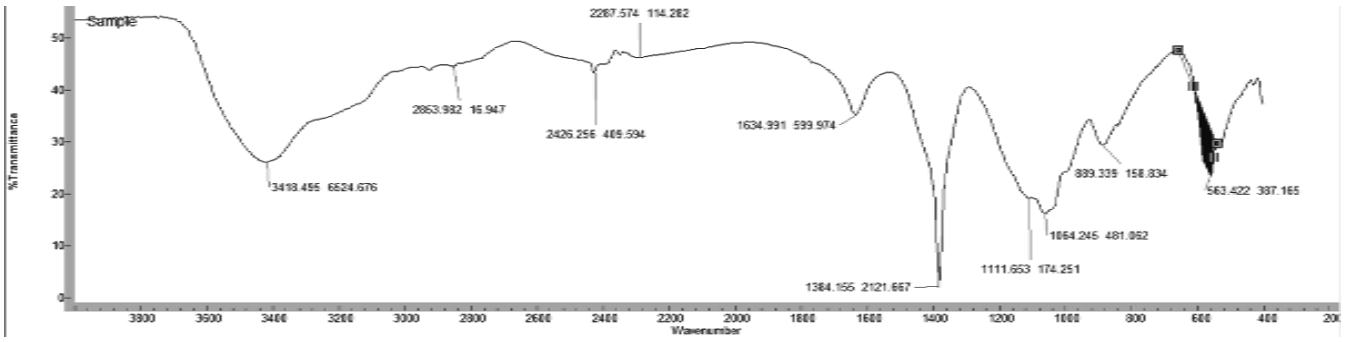

Figure 3: FTIR Spectrum of Hydroxyapatite

3. *FESEM:* Field Emission Scanning Electron Microscope was done to study the morphological details of hydroxyapatite. The shape, size and various morphological parameters could be determined using FESEM. From this Figure 4 we can know the shape of the particle to be as homogeneous and the size ranging from 300-400 nano meters which can give a good impact on the surface coating of 316L stainless steel. The particles are agglomerated and dense which is because of the high surface area to the volume ratio which is quite common in nano particles. The surface atoms exhibit stronger surface force which attracts the neighbor particle [9].

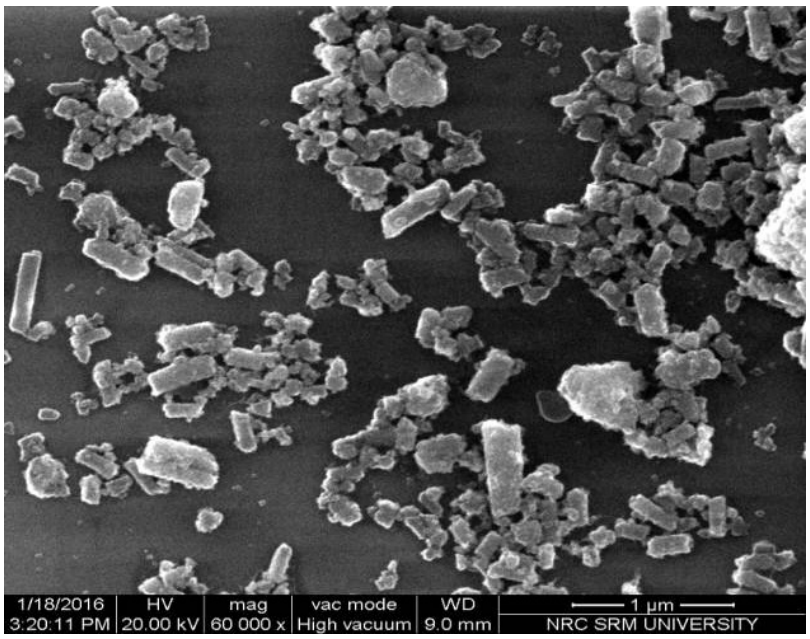

Figure 4: FESEM Image of Hydroxyapatite

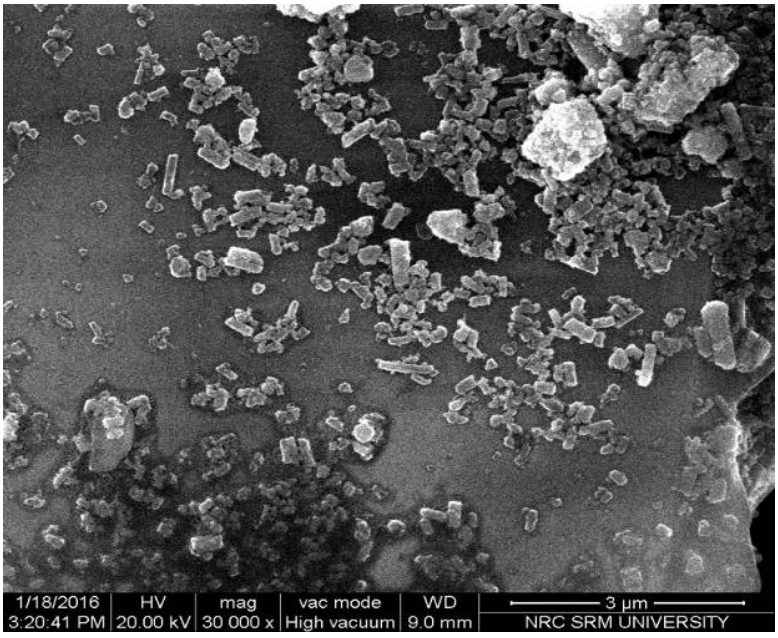

Figure 5: FESEM Image showing agglomerated particles

4. *EDS:* Energy Dispersive X-Ray Spectroscopy gives the detail on elemental composition. The elements present are tabulated in Table 2. Calcium, Phosphate and Oxygen are the major elements present in the EDS spectrum.

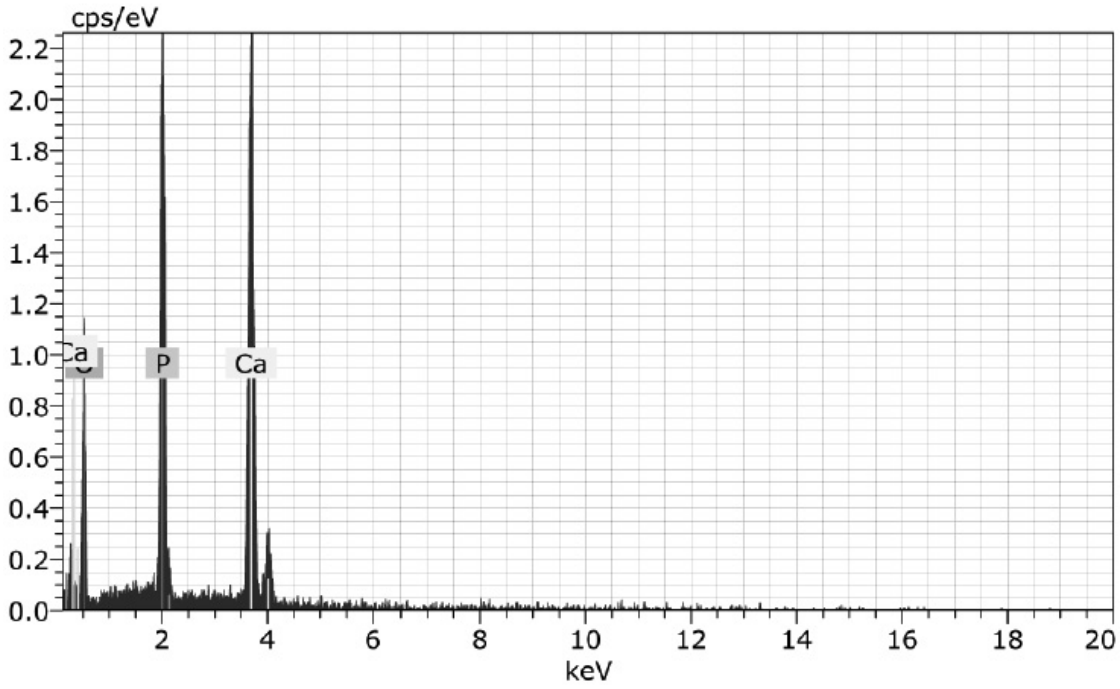

Figure 6: EDS Spectrum of Hydroxyapatite

B. Surface Modification and In vitro study

The surface treated samples were tested using biocompatibilty study. These studies were carried out with optical microscope and field emission scanning electron microscope. The sample was immersed in SBF solution for 2 days and images was taken under optical microscope. SBF solution is that which is equivalent to the human blood. During implantation the implant first comes in contact with the blood. The sample was washed using distilled water and examined under optical microscope at 500x magnification. The EDS spectrum of coated stainless steel shows the property of both the metal and hydroxyapatite in Figure 7.

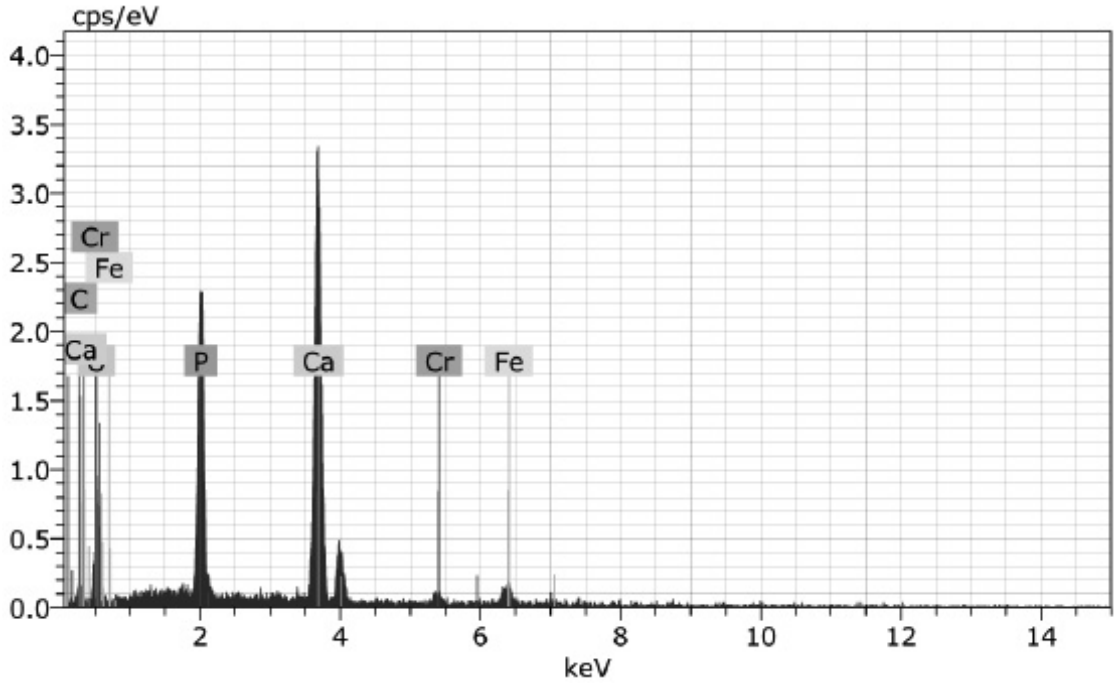

Figure 7: EDS Spectrum of Surface Modified Stainless Steel

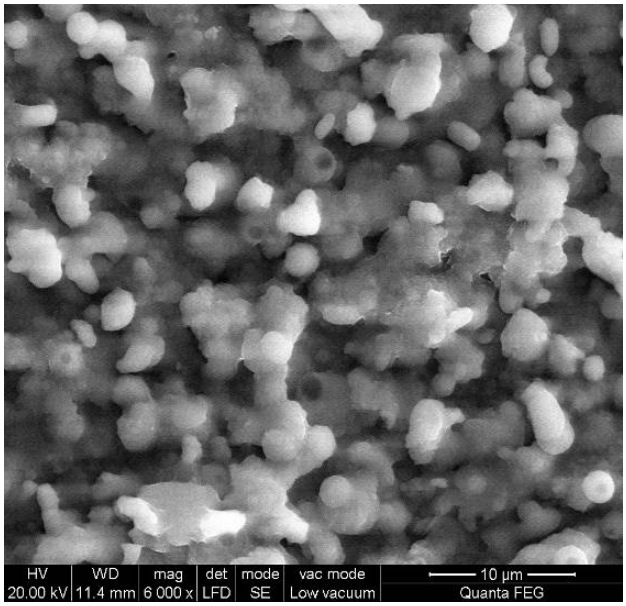

Figure 8: FESEM image of Surface Coated 316L Stainless Steel

Figure 8 shows how the hydroxyapatite has been coated on the surface the modified 316L stainless steel. Figure 9 gives the microscopic view of deposition calcium (Ca) and phosphate (P) on the coated surface of modified implant. The calcium and phosphate are the major bone constituents, which prove osseointegration by the enhanced apatite formation on the coated surface. Dip coating is the simple method to produce hydroxyapatite coating on stainless steel substrate [10].

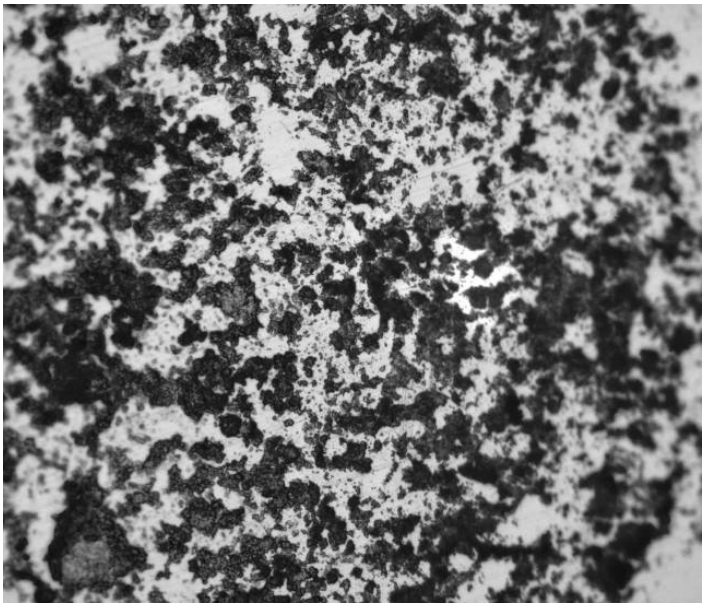

Figure 9: 500x magnification image of Ca and P Deposition

4. DISCUSSION AND CONCLUSION

The hydroxyapatite used for surface modification of 316L stainless steel was synthesized using wet chemical precipitation technique. In conclusion the characterization of hydroxyapatite shows the different elemental composition, morphology of hydroxyapatite with size from 300-400 nano meters and compound phase details. The synthesis of hydroxyapatite can be applied in orthopedics as well as dental applications. Surface modification was done using the RF Magnetron sputtering technique with best coating results on

deposition of hydroxyapatite on the modified hydroxyapatite coated surface. In this study we have focused on overcoming the dental implant failures by modifying the implants surface. The future work has a wide range of research on surface modification with other apatite which paves way for the application of surface modified implants in wider range.

Table 1
Miller Indices Values for Hydroxyapatite

(h,k,l) Values	*High Intensity Peaks*	*Scan Range*
(1,0,2)	29.5	2θ
(3,2,0)	31	2θ
(3,0,0)	33	2θ
(3,1,3)	49.8	2θ

Table 2
Elements Present in Hydroxyapatite

Elements Present	*Series*	*Weight (%)*
Oxygen	K-Series	14.57
Calcium	K-Series	1.43
Phosphate	K-Series	0.83

Application

Surface modified 316L stainless steel has greater application in the field of dentistry and orthopedics. In this study we focused our application on improvisation of dental implants. They show good cytocompatibilty and enhance bone contact and greater new bone appositions with surface compositing containing calcium and phosphate. Particularly calcium containing surface has improved properties [2]. These surface modified implants have various applications such as repair of large bone defects and tooth replacement. With its improved mechanical property and biocompatibility they show clinical success rate of 98% and less than 2% of failure rate [2]. Recent advancements of surface modification were drug delivery layers which can supply drugs to a desired target mostly bone surrounding regions.

Acknowledgment

The authors gratefully acknowledge the Nanotechnology Research Centre, SRM University, Kattankulathur for helping in sample preparation, characterization, surface coating and In vitro study.

References

1. Vamsi Krishna Balla, Mitun Das, Sreyashree Bose, G.D. Janaki Ram and Indranil Manna, "*Laser surface modification of 316 L stainless steel with bioactive hydroxyapatite*", Material Science and Engineering C, July 2013.
2. Jabr S. Al-Sanabani, Ahmed A. Madfa and Fadhel A. Al-Sanabani, "*Application of Calcium Phosphate Materials in Dentistry*" Vol 2013, pp. 12, May 2013.
3. Nguyen Dang Nam and Jung Gu Kim, Phan Huu Tai and Dae Ho Yoon, "*Corrosion Properties of RF-Magnetron-Sputtered TiN Coating Deposited on 316L Stainless Steel*", Journal of The Korean Physical Society, Vol 54, No. 3, pp. 1104-1108, March 2009.
4. Kun Mediaswanti, Cuie Wen, Elena P. Ivanova, Christopher C. Berndt and James Wang, "*Sputtered Hydroxyapatite Nanocoatings on Novel Titanium Alloys for Biomedical Applications*", InTech Open. chapter 2, May 2015.
5. S Swann, "*Magnetron Sputtering*", Phys. Technol. Pp. 67-75, 1988.

6. W. Chee and S. Jivraj, "*Failures in Implant Dentistry*", British Dental Journal 202, pp. 123-129, February 2007.

7. Amit Kumar Nayak, "*Hydroxyapatite Synthesis Methodologies: An Overview*," Vol. 2, No. 2, pp. 903-907, June 2010.

8. T.V. Thamaraiselvi, K. Prabakaran and S. Rajeshwari, "*Synthesis of Hydroxyapatite that Mimic Bone Minerology*," Trends Biomater. Artif. Organs, Vol 19(2), pp. 81-83, 2006.

9. Christoph Bantz, Olga Koshkina, Thomas Lang, Hans-Joachim Galla, C. James Kirkpatrick, Roland H. Stauber and Michael Maskos, "*The surface properties of nanoparticles determines the agglomeration state and the size of the particles under physiological condition*", Beilstein J. Nanotechnol., pp. 1774-1786, May 2014.

10. N. Ramesh Babu, Sushant Manwatkar, K. Prasada Rao and T. S. Sampath Kumar, "*Bioactive coating on 316L stainless steel implants*", Trends Biomater. Artif. Organs., Vol. 17(2), pp. 43-47, 2004.