Journal of Physical Chemistry and Functional Materials (JPCFM)

journal homepage: http://dergipark.gov.tr/jphcfum

Received: 28 July 2018 Accepted: 31 July 2018 Research Article

Effect of Bioceramic Coating Materials on Surface Hardness, Morphology and Coating Thickness

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Abstract

Stainless steel Rex-734 biomedical alloy (ASTM F1586) can be used as a new functional implant material with its extra ordinary corrosion resistance and material properties. In order to functionalize such material, Single Hydroxyapatite(HA) (S_1), Hydroxyapatite-SiO_2 (S_2), Hydroxyapatite-Ag (S_3) and Hydroxyapatite/Zr (S_4) dip coatings were executed on Rex-734 implant alloy. Different coating thicknesses for S_1, S_2, S_3 and S_4 groups were obtained 12.4, 10.9, 11.1 and 10.3 µm, respectively. From the morphologic SEM views, the better and crack free coating surfaces were found for HA/Zr (S_4) group. The average hardness values for single HA coatings were found to be 290 HV. In comparison with single coatings, HA/SiO_2 coatings caused lower hardness (261 HV) and higher values (312 HV) for HA/Ag double coatings, however, highest hardness was obtained (353 HV) for HA/Zr coatings.

Key Words: Hydroxyapatite, REX-734, Silica, Silver, Sol-gel, Zirconium.

1.Introduction

The main purpose of biomaterials is to perform or support the functions and general performance of damaged tissues. Among the metallic biomaterials used for this purpose, stainless steels stand out due to their superior tensile strength, fatigue strength and fracture toughness [1]. Stainless steels are widely preferred especially in orthopedic applications due to their low cost, corrosion resistance and superior mechanical properties [2,3]. However biocompatibility and corrosion resistance of stainless steels are insufficient in in-vivo conditions. Therefore, various studies are carried out in order to improve the biocompatibility and corrosion resistance properties of stainless steel. In these studies; it has been found that hydroxyapatite (HA) improves the biocompatibility of metallic implants and enhances the corrosion resistance due to its bubble-like structure and its superior biocompatibility properties. Therefore, coating of metallic implants with HA is recommended to increase the biocompatibility and the corrosion resistance of the metallic surfaces [4-11].

Calcium phosphates, in general, are very compatible with tissues and they are used as bone substitute in granular, powder or solid block forms. The most important of these compounds, HA, is almost identical to the mineral phase of bone and teeth. For this reason HA is used both as bulk and surface coating material [12,13]. However, the mechanical properties of HA are not sufficient to be used directly due to its brittleness for hard tissue applications where higher strength and fracture toughness requirements. Because of this, HA is generally preferred as coating material on the metallic implant surfaces to obtain bioactive biomaterials with high strength [14]. Such coatings are widely applied by various surface modification techniques e.g. Plasma Ion Implantation, Laser Melting, Laser Surface Alignment, PVD-CVD, Thermal Oxidation and Electrochemical Surface Modification. However, the application of these surface modification techniques is limited in complex processing procedures and coating-surface adaptation. Whereas the sol-gel method is an alternative method to achieve the objective coating properties [15]. One of the most important advantages of the sol-gel method is that the properties of the coating can be made functional by changing the particles to be added to the sol and the heat treatment parameters. Another fundamental advantage of this method is that homogeneous coatings can be achieved in desired coating thicknesses and the method can be applied at relatively low heat treatment temperatures [16]. The dip-coating method is commonly used in the coating of optical films and in the production of transparent layers [17]. The most important advantages of the dip-coating method are; allowing to coat complex shapes, obtain uniform and multi-layer coatings, controllable coating thickness, and obtain coatings with the same properties regardless of the geometry of the coating materials [18].

One of the main purposes in bioceramic coatings is to improve tissue-implant interaction. For this, various additives are used in order to improve the mechanical, corrosion and biocompatibility behaviours of the coating [19-22]. This study focuses on the effects of coating thickness and additives (SiO_2, Ag and Zr) on surface morphology and hardness of HA-based bioceramic coatings. There are similar studies in literature about the effects of additives on hardness in bioceramic coatings. For example; Ti6Al4V metallic surfaces were coated with HA/Ti6Al4V composite coatings by plasma spray method and the hardness value of the bioceramic coating was measured as 400 HV [23]. In another study, the effects of Mg^{2+} and Zn^{2+} metal ions on the morphological and sintering properties of HA coatings were investigated [24]. It has been observed that HA with metal ions gives better results in terms of hardness and compressive strength than pure HA. The Vickers hardness of pure HA was measured as 325 HV while the hardness increased to 380 HV with 1% Mg^{2+} addition and to 350 HV with Zn^{2+} addition in the same amount. HA/Al_2O_3-TiO_2 duplex coatings were executed on pure Ti implants by plasma spray method and hardness values were measured as 236 ± 16 HV on HA coated and 738 ± 12 HV on HA/Al_2O_3-TiO_2 duplex coatings [25].

1. Materials and Methods,

As the substrate material, the biocompatible REX-734 (ASTM F1586 Hard–HI, Sandwick) samples were used and chemical composition was shown in Table 1,. Four group coatings as Single-HA (S_1), HA/SiO_2 (S_2), HA/Ag (S_3) and HA/Zr (S_4) were applied on Rex-734 alloy substrates by using the sol–gel method. XRD-SEM-EDX characterization analyzes of the coated surfaces were carried out and the coating thicknesses were measured. The hardnesses of the coated surfaces were measured to determine the effect of the additives on the hardness and the measurements were interpreted. The flow-chart has been presented in Fig. 1 about the preparation of the sol-gel coatings.

Table 1. Chemical composition of REX-734

REX-734 Chemical composition (%)								
C	**Cr**	**Cu**	**Mn**	**Mo**	**N**	**Nb**	**Ni**	**Si**
0,031	20,68	0,13	4,12	2,27	0,38	0,28	9,59	0,47

1.1. Sample Preparation and Pre-Processing

As substrate material, 8-mm diameter cylindrical Rex-734 (ASTM F1586 Hard–HI, Sandwick) was used and REX-734 samples were cut in the sizes of 8x20 mm. Samples were machined sensitively performed with 1-mm SiC cutting discs. In order to increase surface roughness and surface area, SiO_2 particles was applied onto the sample surfaces with a compressor before surface coating. The surfaces were ultrasonically cleaned to provide adequate surface cleaning were pre-treated in the HNO_3 solution to enhance coating efficiency [26].

1.2. Surface Coating

Following the pre-processing, four different bioceramic coatings were applied on Rex-734 alloy substrates. Sample groups and coating type are given in Table 2.

Table 2. Sample groups and bioceramic coatings

Scpecimen groups	Substrate	Coatings
S_0	REX-734	Control (Uncoated)
S_1		HA
S_2		HA/SiO_2
S_3		HA/Ag
S_4		HA/Zr

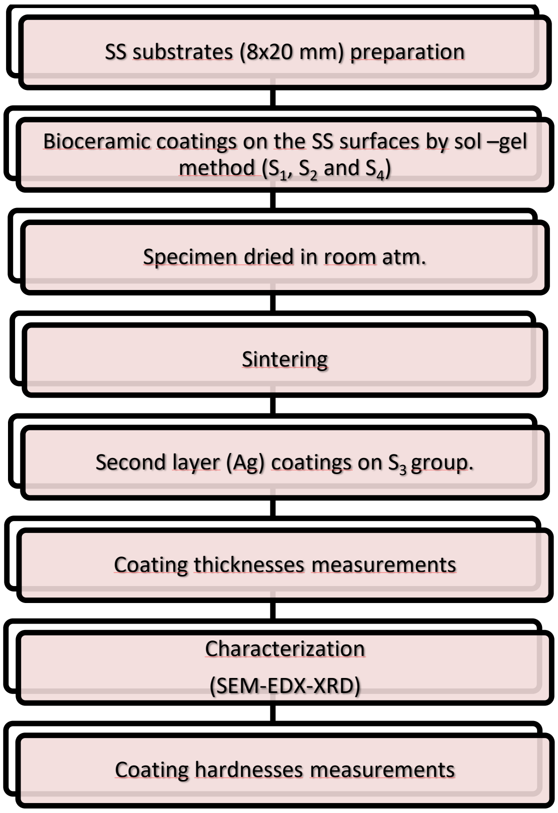


Fig. 1. Flow-chart of experimental process

For coating processes, distilled water-based sols (HA, P_2O_5, KH_2PO_4, $NaCO_3$) were prepared and the sol was ultrasonically homogenized until a homogeneous gel was obtained. The samples were coated by two seconds of immersion periods and kept under room conditions for 24 hours then they were subject to pre-drying at 130 °C in the furnace. The samples were sintered at 750 °C for 120 min in a vacuum environment. For samples of group S_2 and S_4, 10% (mol); SiO_2 and 10% (mol) Zr were added to the HA-based coatings, respectively. Samples of group S_3 are duplex coated, unlike other groups. In group S_3, firstly, the sample was coated with HA, sintered, and then the second layer with Ag (10 mol %) was coated. 0.5 M $AgNO_3$ solution was used for Ag duplex coating.

1.3. Characterization Analysis

The surface morphologies of the coatings were examined by using scanning electron microscope, SEM (JEOL JSM 7001F) and Analysis spectra of displayed regions (EDX) were detected by using Oxford INCA System X-ray spectrometer. For XRD analyses, XRD device (Bruker D8 Advance) with a Kα tube was used and the analyses were performed with a pitch rate of 0.02° between 10° and 90° at a wavelength of 1.5406 (λ).

1.4. Coating Thickness Measurements

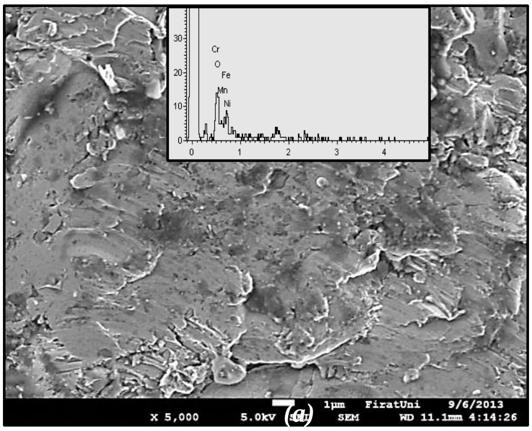
Coating thicknesses were measured from the cross section of the samples by using an optical microscope (OM, Nikon Ecupse MA200) with a magnification of x1000. Measurements of coating thickness from different regions were performed by using optical images and mean coating thickness values were then determined. Coating thickness measurements were verified by micro-meter measurements as well as optical measurements. For micro-meter measurements, an electronic micro-meter with a sensitivity of 0.001 mm was used and uncoated specimens and coated specimens were measured separately, and the difference was considered as the coating thickness.

1.5. Hardness Measurements

The hardness measurements of the bioceramic coatings were performed with a Vickers indenter (136°) (0.098 - 98 N/0.01 - 10 kgf) hardness test machine (Emco test, Durascan). A load of 2.94 N (300 gr) was applied to the specimens for 10 seconds and the indenter mark was imaged by Nikon Ecupse MA200 optical microscope, diagonal lengths of mark was determined and finally Vickers hardness values were determined. Mean values were calculated by performing six measurement for each group.

2. Result and Discussion

SEM examinations indicated that a compact structure was provided in bioceramic coated and sintered samples. From the SEM views shown in Fig 2a-e, it can be observed that the coatings exhibit crack-free and porous-like structure (Fig. 2). Such porous-like structures may provide preferable osteointegration properties between the tissue and implant since the development of the tissue may preferably lead to directing into the pores. The EDS analysis results given in Table 3 show that Fe-Cr-Mn and Ni exist on the uncoated sample surfaces. In contrast, when the HA bioceramic coating was applied, the Fe-Cr-Mn-Ni ratios of the substrate were significantly decreased and presence of HA appeared with Ca-P peaks. Similarly, the results of EDS analysis with Ca-P peaks of samples S_2, S_3 and S_4 showed that Si, Ag and Zr additions appeared on the surface after sintering. In the XRD analysis results, only Fe-Ni peaks were obtained in the uncoated sample and after coating with HA-based bioceramic coatings, as shown on spectra HA peaks were clearly detected on all coatings (Fig. 3). Although Ag and Zr peaks were not detected in the XRD analysis, the presence of the additives was supported by the EDS quantitive elemental analysis as given in Table 3.



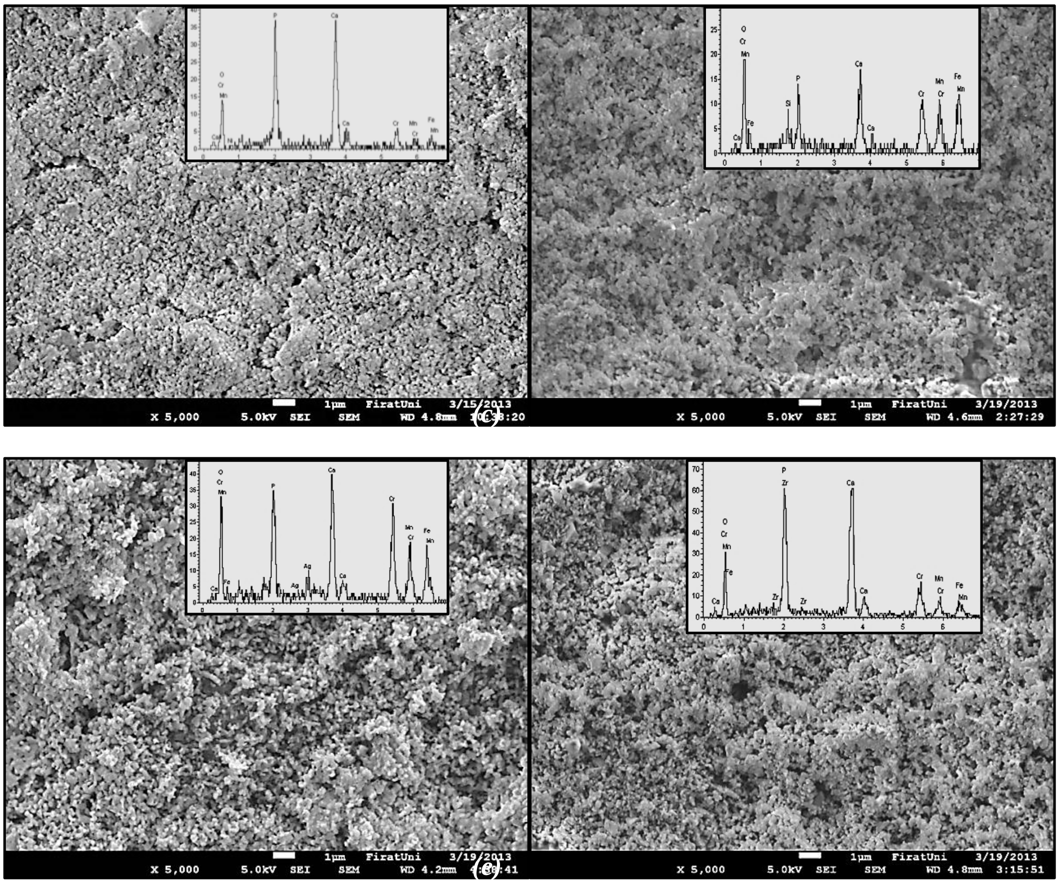


Fig. 2. SEM views and EDS spectrums of uncoated/coated specimens, (a) uncoated, (b) HA coated, (c) $HASiO_2$ coated,

(d) HA/Ag coated and (e) HA/Zr coated.

When the coating thickness measurement results are examined, it is seen that the bioceramic coatings have similar thickness values between 10 - 15 μm as comparatively shown in Fig. 4. Differences in hardness values were determined, although all of the coatings made HA-based and had similar thickness values. In the literature, HA hardness is given as 600 HV as block material [27]. However, in this study the hardness of the HA coatings was measured as about 300-350 HV. This difference may be due to the porous structures of the coatings. Furthermore, crack formation may occur due to the thermal expansion difference between the metallic substrates and the bioceramic coatings, during the sintering process [28]. These cracks may be another cause of the decrease in hardness values. In addition, the hardness value was measured as 290.2 HV in Single-HA coatings. A reduction of about 10% (261,4 HV) with the addition of SiO_2 was determined and an increase of about 7% (312,7 HV) with Ag duplex coatings was measured. The highest value (353,2) with highest increase about 22 % was achieved with the Zr addition as shown (Fig. 5)

Table 3. Result of EDS analysis of uncoated/coated specimens.

	EDS quantitative elemental analysis results									
Sample	**Element (% Atom)**									
	O	**P**	**Ca**	**Fe**	**Cr**	**Mn**	**Ni**	**Si**	**Ag**	**Zr**
S_0	37,59	-	-	33,97	12,30	11,44	4,70	-	-	-
S_1	65,97	13,03	15,12	1,80	3,16	0,83	0,09	-	-	-
S_2	61,82	6,68	5,81	11,76	6,34	5,80	-	1,80	-	-
S_3	59,25	8,12	9,44	6,22	10,6	5,12	-	-	1,26	-
S_4	64,43	11,99	14,02	2,48	3,99	2,00	-	-	-	1,09

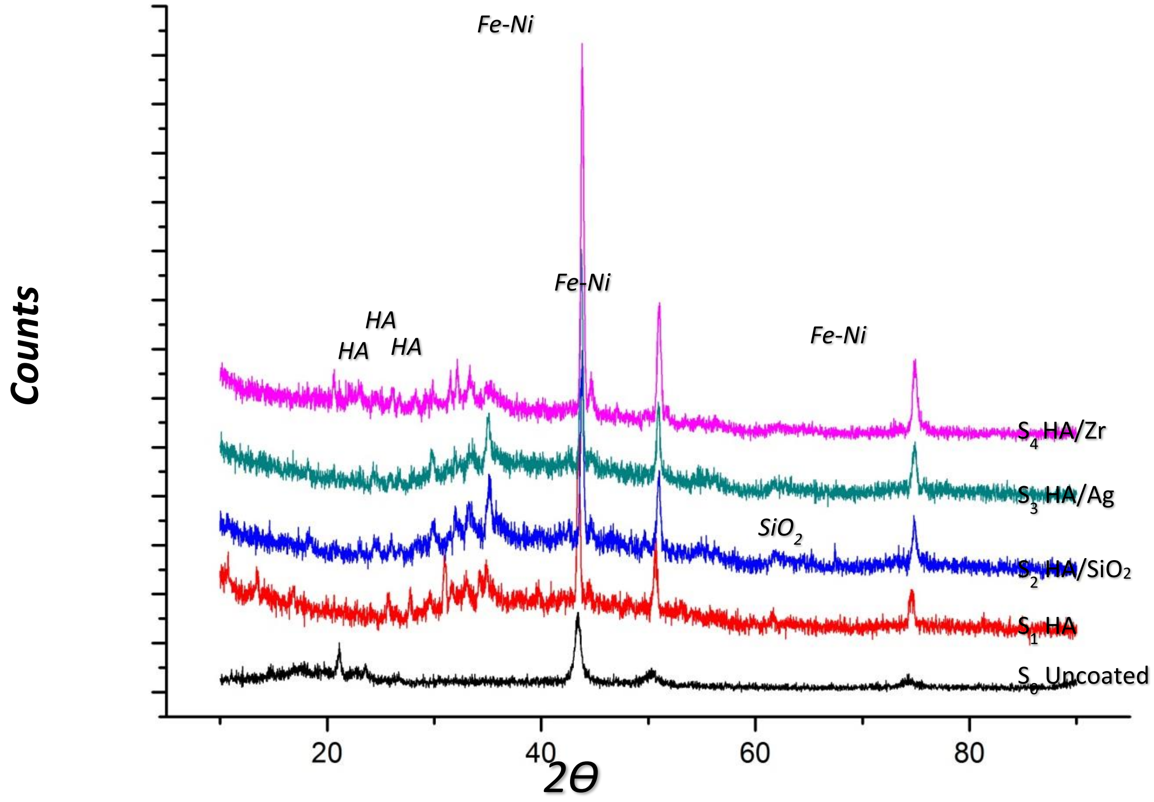
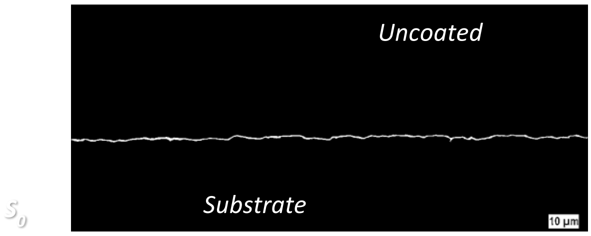


Fig. 3. XRD patterns of uncoated/coated specimens



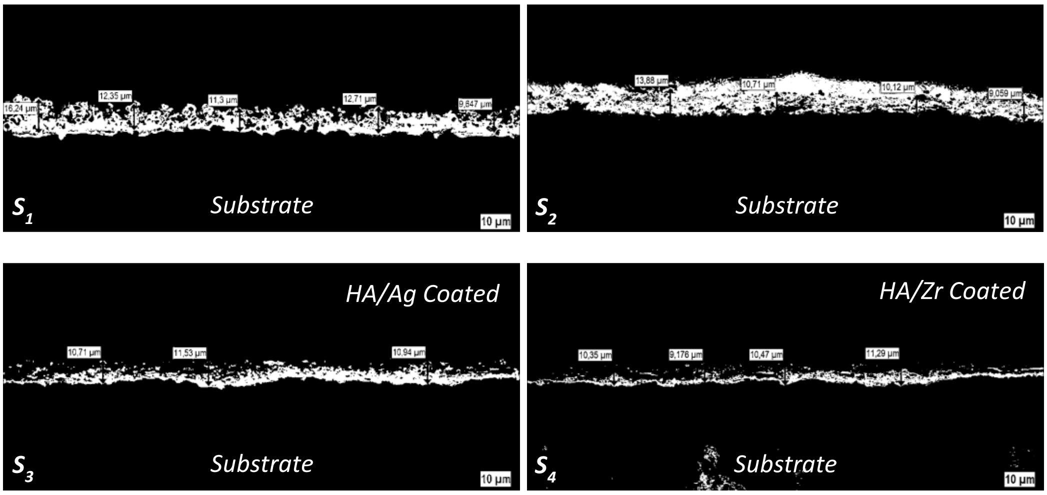


Fig. 4. Cross-section views of bioceramic coatings (X500)

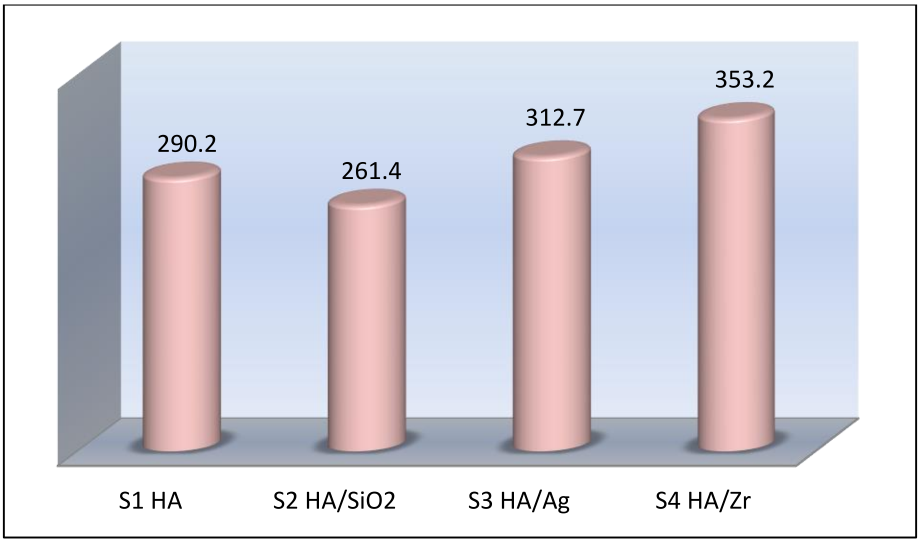


Fig. 5. Comparison of Hardness results for various bioceramic coatings.

Conclusions

- Crack free and porous Bioceramic coatings were achieved in four groups.
- Bioceramic coatings were characterized and validated via EDX and XRD analysis.
- 10-12 µm coating thicknesses were measured in fabricated Bioceramic coatings.
- SiO_2 addition caused about 10 % decrement in coatings, as Ag addition caused 7 % increment.
- Zr addition provided the highest hardness by % 22 increments in Bioceramic coatings

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