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Bioceramic dip-coating on Ti–6Al–4V and 316L SS implant materials

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Abstract The focus of the present study is based on more economical and rapid bioceramic coating on the most common implant substrates such as Ti–6Al–4V and 316L SS used often in orthopedics. For ceramic dip coating of implant substrates, Hydroxyapatite (HA) powder, $Ca_{10}(PO_4)_6(OH)_2$, P_2O_5, Na_2CO_3 and KH_2PO_4 are used to provide the gel. Ceramic films on sandblasted substrates have been deposited by using a newly manufactured dip-coating apparatus. Sample characterization is evaluated by SEM and XRD analysis. A smooth and homogeneous coating films have been obtained and average of 20 MPa bonding strength has been achieved for both Ti–6Al–4V and 316L SS alloys after sintering at 750 °C under flowing argon. The level of importance of the process parameters on coating was determined by using analysis of variance (ANOVA). The current process appears to be cheap, easy, and flexible to shape variations and high production rates for orthopedic applications.

1 Introduction

In biomedical applications bioactive ceramic coatings are commonly used to modify the surface of the implant material and to create new surfaces with totally different properties with respect to the substrate. Dip coating is an alternative method for prosthetic devices used in orthopedics. Sol–gel process offers a number of advantages over other coating methods such as flexibility, control of coating morphology, chemistry and structure [1–4]. Moreover, if suitable additives are chosen, reduction in sintering temperature is also possible [5].

While metals or metal alloys meet many of the biomechanical requirements of orthopedic implants, the interfacial bonding between the metallic surface and the surrounding bone is poor to non-existent [2–5]. Thus analysis of those alloys provides convincing evidence that failure originates at the implant-tissue interface [6, 7]. One of the most common approaches to alleviate such problem has been the use of calcium phosphate, CaP coatings on to implant surfaces. During the past decade, calcium phosphate based ceramics have been used in many medical, orthopedic, and dental applications [8–13]. CaP materials such as hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, HA, has attracted considerable attention because of its close resemblance to the chemical and mineral components of teeth and bone. As a result of this similarity HA shows good biocompatibility with bone [14, 15], and this has led to the use of them as bioactive and for such tissue bonding materials.

Deposition of calcium phosphate coatings on implant materials are made by various methods, such as hot isostatic pressing, plasma or flame spraying, ion-beam sputter deposition, electrophoretic deposition, radio-frequency (RF), magnetron sputtering and sol–gel deposition [16–18]. Plasma spraying is a well understood and has most common usage for commercial aspects, but the control of its variables is quite complicated. Furthermore the extremely high temperatures (10,000–30,000 °C) used in the process can vastly affect the properties of the final coating and result in potentially serious problems. The most associated problems with the plasma spray method are addressed in

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[19]. These problems can be summarized as; substantial structural changes in coating and substrate material, vastly affects on the properties of the final coatings, internal cavities, difficulties in porous coating due to a line-of-sight process, lack of repeatability and homogeneity.

Hydroxyapatite coatings are used for cementless bioactive fixation to provide an enhanced quality of bone apposition and rate of fixation for long term prostheses [20]. However, through in vivo experiments they showed some instability and particulate debris reactions in the bone/coating/implant interface, which will reduce efficiency in the long term. The failure may be associated with coating thickness, as well as other chemical and physical properties [21, 22]. Some work dealt with synthesizing homemade hydroxyapatite powders [23–25] by using novel synthetic body fluid solutions via the self-propagating combustion method and using this sol–gel for a ceramic coating on Ti alloy substrates at 840 °C of sintering temperature. The citric acid combustion method has also been adapted to synthesize nanocrystalline HA powder throughout sol–gel [26]. Flexural strength and structural properties have been reported in this work. Milella et al. [27] achieved a bioceramic composite coating on a pure titanium substrate using dip-coating technique. Cameron et al. suggested the aging process of HA sol–gel solutions before coating [28]. HA coatings on Ti6Al4V substrates were prepared by a sol–gel method [29]. P_2O_5 solution was used and 14 MPa bonding strength was reported. In another work HA was coated onto a Ti substrate with the insertion of titanium (TiO_2) buffer layer by the sol–gel method. The biomimetic approach is one of the possible routes to obtain calcium phosphate coatings on metallic implants. A simple and rapid heating method was successfully developed for calcium phosphate coatings on Ti6Al4V deposited using sol–gel derived precursor [30]. Liu et al. [31] developed a water based sol–gel technique for coating of 316L stainless steel and it was, reported that despite some surface cracks occurred high bonding strengths were achieved. By the help of SBF-A solution and biomimetic bioreactor, a thin but uniform amorphous calcium phosphate coating was deposited on the Ti6Al4V and tantalum cylinders [32]. Costa and Maquis [33] used a surfactant acting as hydrophobic substrates and seashells as source of calcium. In their work to retain HA crystallization a SBF solution was used by immersion of substrates. Sol–gel deposition of HA have already been processed in the form of films and a polymerization routes have been presented in few works [34–37].

However, in relation to dip coating and sol–gel process, most work interested in producing homemade precursors, and/or none of the work dealt with high production rates and finding optimum sintering characteristics, biomechanical changes, surface analysis as whole for both common substrates. It is strongly believed that producing high amounts of HA or ceramic powders in research labs and using them in large scales for repeated deposition processes is hard task and so time consuming.

In this work, it was thought to be using a commercially supplied crystallized HA powders, together with other sol–gel chemicals and additives enables the process repeatability and high coating speeds at low temperatures coupling with high production rates. The bioceramic films, as thick as 15–20 μm, were deposited on both 316L and Ti6Al4V alloys by using a sol–gel process to achieve a fast and homogeneous coating and adequate bonding was achieved. For this, a sol–gel route was planned and so maintain the mechanical properties of the substrate. The surface morphology through SEM and XRD patterns has been evaluated and hardness, bonding stresses were determined with respect to sintering temperatures.

2 Experimental procedure

A sol–gel process is applied with controlled dipping and withdrawal rates for varying coating thickness. It involves simply preparing an adequate sol suspension by mixing HA with Ethanol (99.5%) in a 250 mL grinding jar and milling for 4 h. A fine and homogenized ceramic sol–gel is achieved using the biocompatible chemicals such as P_2O_5, Ca_2CO_3, $NaCO_3$, and a small amount of KH_2PO_4. A dipping system or apparatus is designed and manufactured (Fig. 1) allowing the substrate to be withdrawn with adjustable rates. The method benefits of simplicity, low cost, ease of control and reduced sintering temperatures due to small particle size and also additives, ability of homogeneous and smooth coating, on long and large orthopedic implants with good coverage and consistency. The prepared sol–gel suspension and the flow chart of the processes are tabulated in Fig. 2. By this processes common implants such as pedicle, intramadular, interference, and hip prosthesis, can all easily be coated in large scales by only varying the capacity of the dipping container.

2.1 Substrate preparation

The specimens (TST Medical Devices, Istanbul) machined from sheets and long bars to have dimensions of 8 mm diameter and 10 mm height for Ti–6Al–4V alloy rods and 2 × 10 × 20 mm (thickness, width, length) for stainless steel (316L) strips. Before dip coating process the Ti6Al4V and 316L substrates were sand blasted with silica beads of 50 μm particle size. The metal substrates were thoroughly washed with a detergent, then ultrasonically cleaned twice with acetone for 30 min and passivated in nitric acid (25%) overnight.

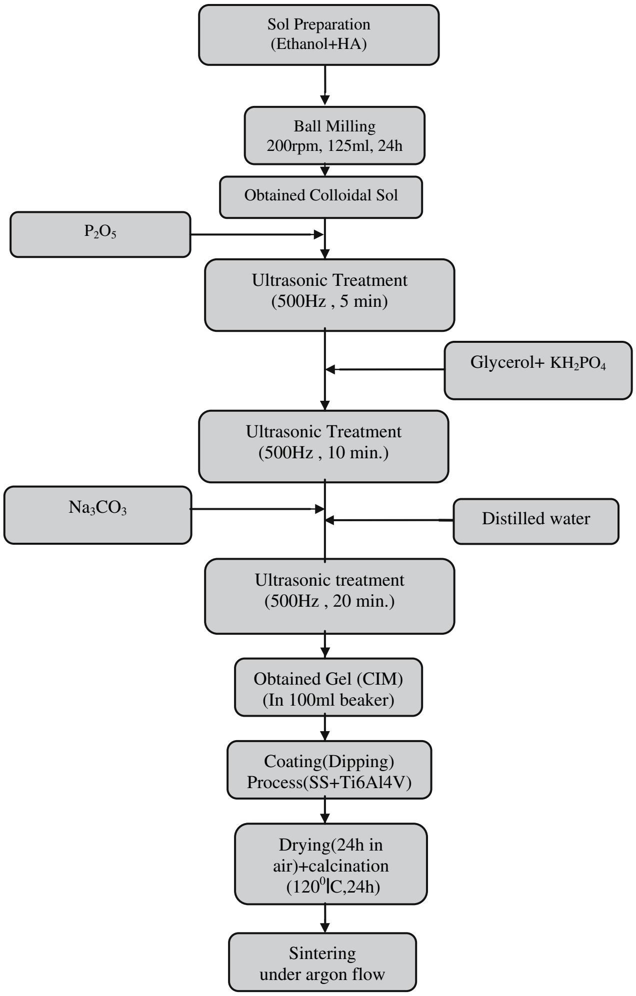

Fig. 1 Flow chart of the sol–gel procedure and dip coating

Fig. 2 Dipping apparatus

2.2 Sol–gel preparation

First, the ceramic sol–gel was prepared in 60 mL ethanol by adding HA (25 wt%), P_2O_5 (47 wt%), Na_2CO_3 (20 wt%), KH_2PO_4 (3 wt%) and trace amounts of glycerol (3 drops), 316L powder (5 wt%) and distilled water in a 125 mL container was also added during the homogenization process. In order to reach the final desired gelation, 20 mL distilled water to reduce the sintering temperature; KH_2PO_4 (3 wt%) was necessary to add into the slurry. It was also reported in [8] that P_2O_5 reacts with alcohol to form oxyalkoxide with liberation of water, which is in turn partially hydrolyzes the oxyalkoxide and phosphate precursors and these are responsible reactions in gelation process and the polymerization reactions thereby results in the gel. HA (25wt%) powders (Merck Gmbh) having an average particle size of 20 μm are used. The mixture of ethanol (min 99.8%, Sigma-Aldrich) and HA was wet blended continuously for 24 h in a grinder (Restch PM-400 at 400 rpm) and resulted in very homogeneous and finer HA particles (<5 μm) in the suspension. After obtaining such colloidal sol, few drops of glycerol (Merck), P_2O_5 (Sigma-Aldrich), 47% in wt, Na_2CO_3 (Sigma-Aldrich), 20% in wt, KH_2PO_4 (Sigma-Aldrich), (5% in wt), and 20 mL distilled water are used. The produced colloidal sol was mixed and homogenized with those of additives in appropriate amounts in a 100 mL glass beaker using a 500-W ultrasonic processor with a temperature controller (Cole-Parmer) and a titanium probe with a tip diameter of 1/2″. After adding the above chemicals and additives during the ultrasonic treatment for 30 min in total a gel was obtained, so called Cim, having a viscosity of 20 cp.

2.3 Coating process

The coating process took place using a newly manufactured belt-and-pulley-type apparatus as given in Fig. 2. In order to dip the substrates into the provided gel (Cim), the apparatus was designed and assembled in which having a two-way electronic switch, to descend and ascend the substrates in and out of the dipping suspension container. The thickness of coating was controlled by ascending and descending rates of the substrates. Ti and 316L stainless steel (SS) specimens are coated by ceramic films**.** The dipping process took place at constant dipping rates of 20 mm/s and 10 mm/s for thin and thick films, respectively. After coating, the samples have been dried in air for a day and were calcined in a furnace at 120 °C overnight.

2.4 Sintering

Subsequently, the dip coated substrates were sintered in a PID-controlled vertical, alumina tube furnace (Thermal Technology, Gmbh, Germany). The sintering procedure was carried out in flowing (5 L/min) argon-gas atmosphere at temperatures of 675, 750, 800 and 850 °C. The temperature deviation was at ±4 °C and peak soaking time was kept at 3 h and both heating-up and cooling-down rates are kept at 2 °C/min.

2.5 Bonding strength and hardness

In order to show the bonding strengths of the coatings; Ti6Al4V and 316L strips were machined to have dimensions of 2 × 10 × 100 mm and again subjected to the same routes of coatings. The films obtained by currently prepared sol–gel method and subjected to various sintering temperatures (675, 750, 800 and 850 °C). FM 73 toughened epoxy (TAI, Turkish Aerospace Industries Inc.) was applied on one side of the coated surfaces of the strips. The adhesive applied strip couples are subjected to a constant pressing and cured at the same time at 180 °C for 2 h. Afterwards, the pull-out tests were performed under increasing load at a crosshead speed of 1 mm/min using a tensile test machine (Autograph AG-100kN, Shimadzu, Japan) until shearing failure occurs. Averages of six specimens were tested for each sintering temperatures and coated substrates. The bonding strength of the adhesive FM 73 was 47 MPa. The failure mode is recorded gradually and the bonding strength is calculated as the load at failure divided by the coated bonded area and given in Fig. 3 for both Ti6Al4V and 316L substrate implants. Hardness tests took place on (EMCO-TEST M1C 010, Austria) by applying 0.3 kg indenter load for 15 s and the results are given in Fig. 4.

2.6 XRD and SEM analysis

Coating powders and surfaces are characterized by using (SEM, Jeol 6400), and X-ray diffractometry, XRD, by (Rigaku-2200D/Max) having the wave length of $\lambda = 1.5405$ Å (0.154 nm) and operated at 30 kV and 30 mA using monocromatized Cu–Kα radiation at scanning rate for 2θ of 1.5°/min and 0.1° of scanning step. X-ray diffraction patterns of the bioceramic coated surfaces are shown in Fig. 5 for Ti6Al4V and Fig. 6 for 316L substrates. The characteristic peaks of HA, TCP and CaO on the coated surfaces can be seen from diffraction pattern and SEM micrographs of the surface/cross section of coatings are shown in Fig. 7–10.

3 Results and discussion

The ceramic film coatings on both Ti6Al4V and 316L implant substrates were successfully applied with high speed and good repeatability. Through the chemical and homogenization processes, once the gel is obtained, then as many as substrates can be dipped and coated depending upon the capacity of the dipping or sol–gel container. If a longer container is chosen, long orthopedic implants such as long sized intramadular, kirtchen, shanz pins or femur stems can be coated the prepared gel, only by the help of a suitable dipping manipulator. If a large container is chosen and the sol–gel is prepared then again as many as dozens of small sized orthopedic implants such as pedicle and cortical screws can be dipped and coated.

Figure 3 illustrates the bonding strengths of the ceramic dip coatings of the Ti6Al4V and 316L substrates after sintering at different temperatures. The failure mode is evaluated by taking into account the average and standard deviation, (as indicated by the error bars) the bonding strength is calculated as the load at failure divided by the coated bonded area and the applied force and the bonding strengths were recorded. The average values of bonding strength increase with sintering temperature from 675 to

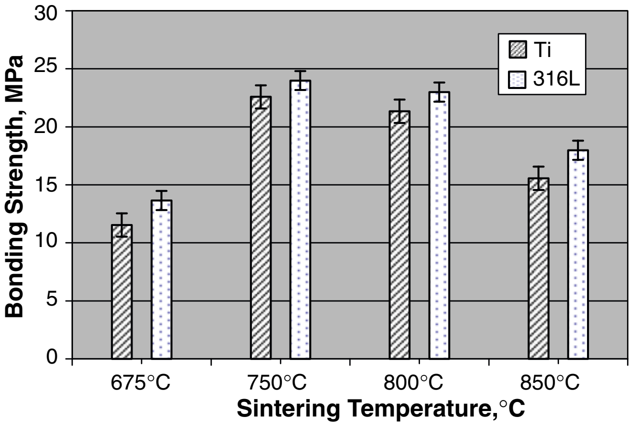

Fig. 3 The bonding strength of the coatings obtained for different sintering temperatures

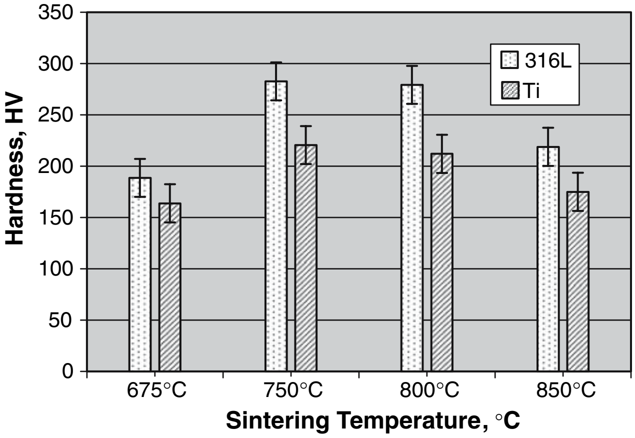

Fig. 4 Hardness of dip-coated surfaces for various sintering temperatures

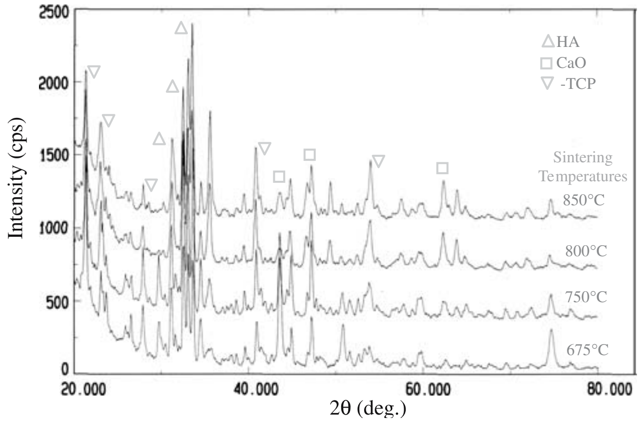

Fig. 5 XRD patterns of HA coated Ti6Al4V surfaces sintered at various temperatures

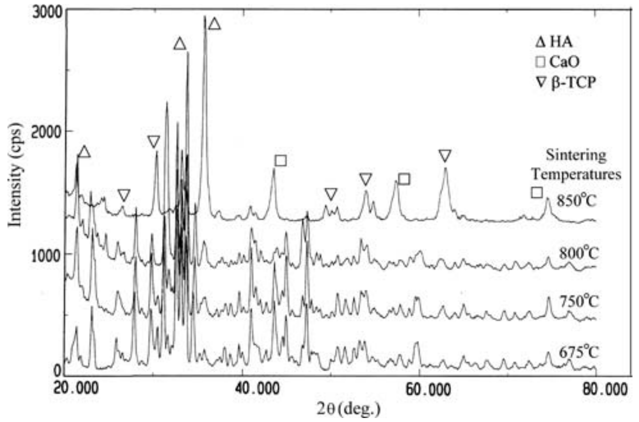

Fig. 6 XRD patterns of HA coated 316L surfaces sintered at various temperatures

750 °C, and then decrease between 800 and 850 °C. The presence of small pores and microcracks may be the factors resulting in a decrease in bonding strength. The bonding values for the thickness of 20–25°μm are about the same at sintering temperatures of 750 and 800 °C, however the bonding strength was found maximum (20–25 MPa) at 750 °C for 316L substrates. The films coated thinner than 25 μm showed crack-free and homogeneous distribution, however, the most undesired surface cracks occurred during thick coating at over 30 μm. Therefore in this work the coating thickness was kept less than 25 μm in average. The bonding strengths, in general, appeared to be lower for Ti6Al4V substrates, and much lower (10–14 Mpa) for the thicker coatings (25–40 μm) and the average bonding strength was about 17.5 MPa for both thin and thick coatings. The obtained bonding strength for the coatings, between 15 and 20 MPa, is high enough to keep the coated inorganic materials on substrates without peeling off during implantation and also could provide good fixation between bone and implant. This was proven in our previous in vivo work [1, 4]. As reported in there, we did not see any indication of peeling off during insertion process of coated screws. A relatively good bonding and surface feature of the underlying substrate were obtained in the current dipping method, and this is especially interesting in terms of sintering temperature as low as 750 °C. However it must be emphasized that for long term in vivo tests it is necessary to show degradability of such ceramic coatings, and this is our next task.

The Vickers hardness values of coated and sintered surfaces are shown in Fig. 4 for various sintering temperatures of 675, 750, 800 and 850 °C. As seen from the figure, there is an initial increase followed by a decrease with increasing sintering temperature. It is always desirable to lower the sintering temperature as low as possible, because high sintering temperatures cause significant phase changes in microstructure of substrate and so lowers the mechanical properties. Ti6Al4V has α–β transition at the temperatures of about 880 °C associated with a significant volume change that may cause surface cracks in the substrate. Therefore the sintering temperature throughout this work was kept below 880 °C. From the results it is seen that the minimum hardness values are obtained at 675 °C and despite both 750 and 800 °C of hardness values appeared to be close to each other, the maximum hardness is achieved at 750 °C of sintering temperature, and therefore it was used as optimum working temperature. It can be concluded from those figures that; the bonding tensile strength increases with increasing hardness and reaches to a maximum at the temperature of 750 °C.

Figures 5 and 6 both show XRD patterns of the coatings after sintering at various temperatures of 675, 750, 800 and 850 °C. As it can be seen from those figs, some peaks seen in between 20 and 50° of 2θ, represent the characteristic peaks of apatitic phase and also TCP according to JCPDS cards and these peaks slightly change with increasing sintering temperature. The intensity increase, however, for the substrate of 316L at sintering temperature of 850 °C this change becomes more noticeable due to high crystallization rates at high temperatures. From the both XRD patterns of the different sintering temperatures showed broad peak corresponding to the HA reflection, where the strongest peaks appeared to be at about 30–35° of 2θ angles. These peaks kept their position along 2θ angles but the intensity increased as the sintering temperature increased.

SEM micrographs of the coated surface morphologies were shown in Fig. 7a–d. In Fig. 7a due to low sintering temperature the coating material-HA appeared to be not sintered at all. However in Fig. 6b with increasing temperature (750 °C) coating gives better interconnected bonding and denser structure. In Fig. 6c although the bonding of HA powders showed good connection between powders it is seen that lower densification. Although in

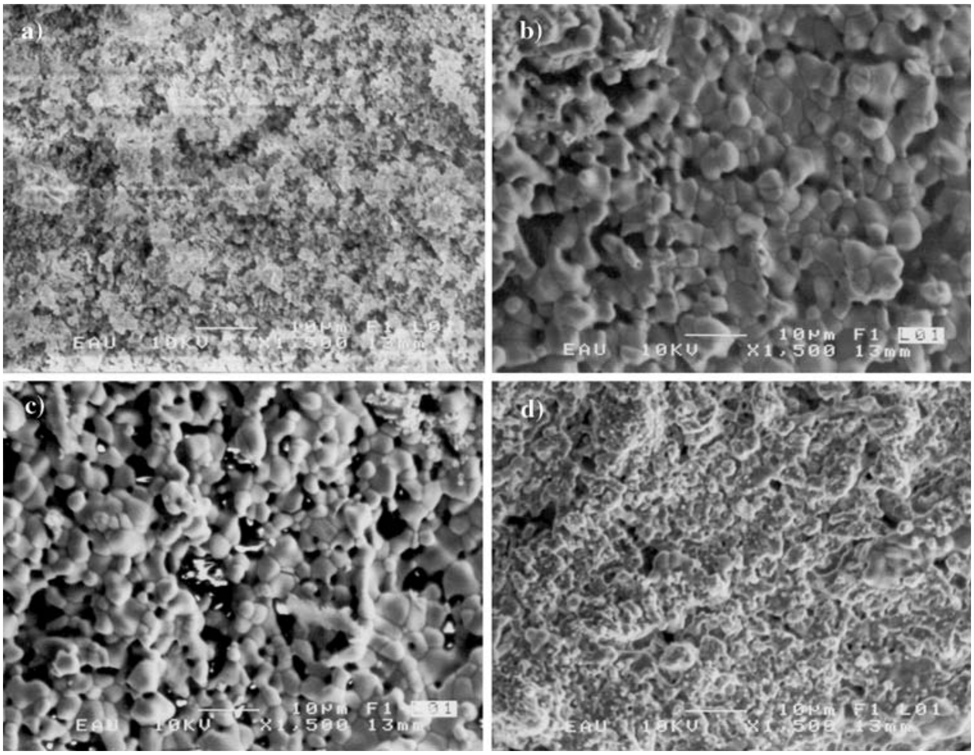

Fig. 7 SEM micrographs of HA coated Ti6Al4V substrate sintered at various temperatures; (**a**) 675, (**b**) 750, (**c**) 800, (**d**) 850 °C

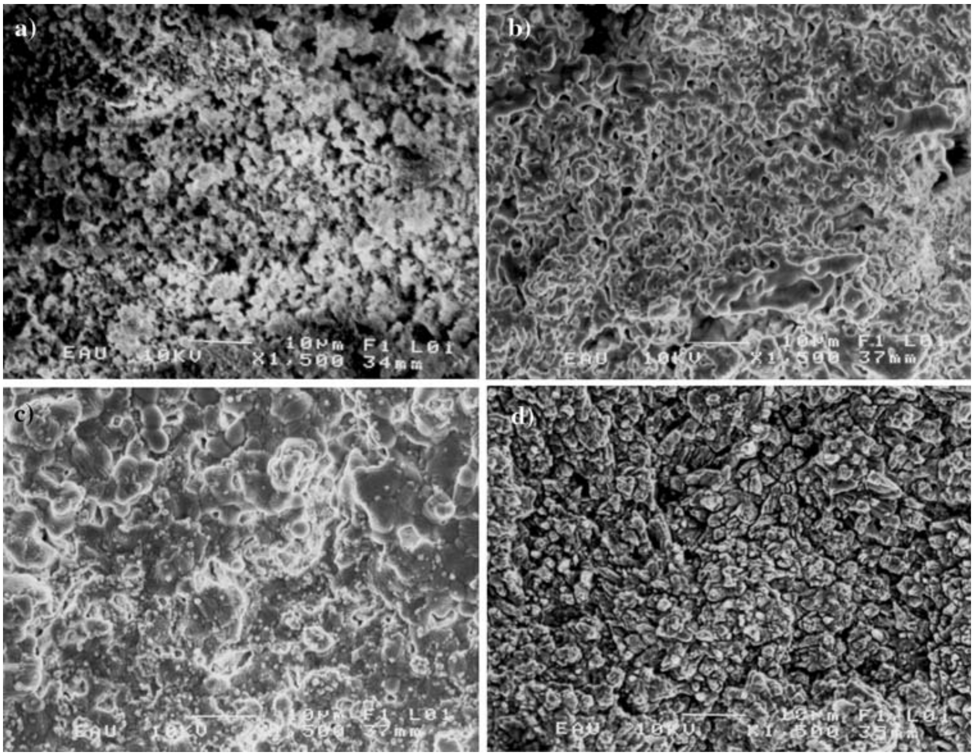

Fig. 8 SEM micrographs of HA coated 316L substrate sintered at various temperatures; (**a**) 675, (**b**) 750, (**c**) 800, (**d**) 850 °C

(Fig. 7d) shows lower bonding and densification in a comparison with others. Also Fig. 8d shows similar surface and lower bonding for the Ti6Al4V substrates. Better densification and interconnection between powder particles are obtained for 316L substrates in comparison with Ti6Al4V. The reason for this is may be due to similarity of the substrate e.g., SS with additive of 316L powder may cause the gel composition more similar to the substrate and so this makes the sintering easier, and resulting with better mechanical properties.

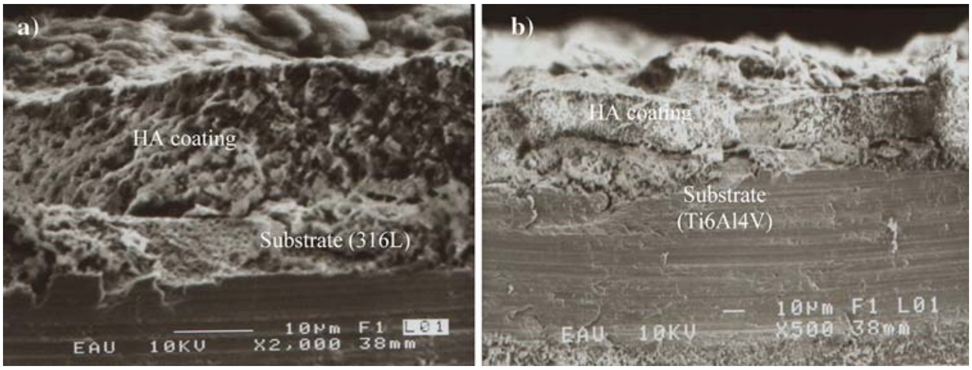

Fig. 9 SEM micrographs of (**a**) Coating cross section of (SS, sintered at 750 °C) (**b**) Coating cross section of (Ti6Al4V sintered at 750 °C)

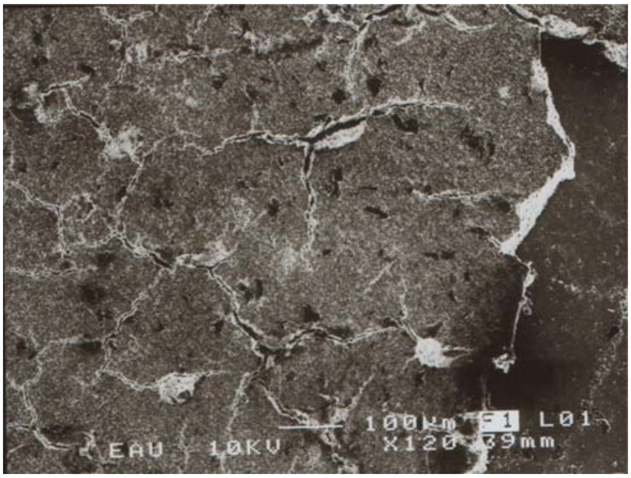

Fig. 10 Cracked surface of thick coating (>40 µm, 750 °C)

Figure 9a, b shows SEM micrographs of the surface films on both Ti6Al4V and SS substrates. An intersection is seen in (a) between the HA coating layer and substrate, and in the vertical cross-section 10–20 µm coating layers present. SEM micrographs showed that the hydroxyapatite layer is uniformly deposited with a relatively high bonding on those implant materials. At higher magnifications the coating surface showed cracks due to the shrinkage occurring during the drying and thermal processes (Fig. 10). Despite it was reported that this could supply points of “mechanical interlocking” [14] and so promoting osteointegration; in this work, unfortunately on the contrary, it was not the case. Some thick coatings, especially (>40 µm), exhibited severe surface cracks (Fig. 9) sometimes just after drying, but mostly seen after sintering processes, even though sintered at 750 °C. To overcome this problem, thinner coatings and/or some inorganic, biocompatible additives such as the amounts of phosphor pentha oxide and glycerol are to be determined and added into the sols. Furthermore multiple coating can also be considered may be to reduce or eliminate surface cracks [38]. However, the long term degradation of coating is our currently continuing work and the results will be submitted to be published soon.

Statistically, analysis of variance analysis (ANOVA) provides a decision at some confidence level as to whether the process parameters are significantly different [39]. Larger *F*-values indicate that the variation of the process parameter makes significant change on the tensile bonding strength (TBS). The results of ANOVA for this process is presented in Table 1 and 2, for both TBS and hardness, respectively. As seen in these tables the sintering temperature is the most effective parameter on some mechanical properties of the coating. The current analysis also showed that the experimental error was low (0.2 and 4.09%) and reliability limits are found to be as 99% for bonding and 95% for hardness.

Despite it was indicated that the dip coating would produce a rough surface [38], in fact, depending upon the particle size of powders and added gelation materials and their qualities, the dipping method appears to be producing a good and acceptable homogenous surfaces. However the repeatability and the quality of coating can be manipulated by careful treating of process parameter and the bonding strength can also be improved by sintering additives. In this work it was experienced and shown that, the use of sol–gel and dip coating method for deposition of bioceramic HA coating is simple, having good flexibility in using for various shapes of medical implant materials with a homogeneous smooth coating surfaces with high production rates, in comparison to other processing alternatives. Further work may require to show the variation of bonding with coating thickness, shape change and also application of process through long term in vivo applications, and in fact, this is our next task that will take place.

4 Conclusions

Cheap, easy, repeatable with high production rate of bioceramic coatings of the Ti6Al4V and 316L SS implant materials are achieved by using a dipping method. Among various sintering temperatures tested; the surface properties, hardness and bonding strengths showed better

Table 1 ANOVA variants analysis for bonding

Test parameters	Degree of freedom	Sums of Squares (SS_A)	Varians (V_A)	F_{A0}	% Distribution
Temperature (°C)	3	148.033	49.344	477.33[a]	95.17
Alloy	1	7.207	7.207	69.72[a]	4.63
Error	3	0.310	0.103	–	0.2
Total	7	155.55	–	–	100

[a] 99% Reliability limit

Table 2 ANOVA variants analysis for hardness

Test parameters	Degree of freedom	Sums of Squares of Areas (SS_A)	Varians (V_A)	F_{A0}	% Distribution
Temperature (°C)	3	8164.9	2721.6	14.68[a]	59.87
Alloy	1	4890.6	4890.6	26.39[a]	35.92
Error	3	556.1	185.4	–	4.09
Total	7	13611.6	–	–	100

[a] 95% Reliability limit

properties at 750 °C. Throughout SEM, XRD and biomechanical tests it was shown that a homogeneous and good bonding can be obtained for both substrate materials using commercial ceramic powders. According to ANOVA, the sintering temperature appeared to be the most effective parameter on bonding strength and hardness of the coating.

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