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A New Approach to Titanium-Hydroxyapatite-Bio Composite: Pressure-Assisted Coating on the Antibacterial and Electrochemical Properties of Ti6Al4V

Increase in stability and electrochemical performance

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This study aims to coat Ti6Al4V alloy with Ti-*x*HA (*x* = 2.5–10 wt%) mixture to improve its surface properties. A new approach using a powder metallurgical pressure-assisted sintering method was applied to the coating process. The *in situ* sintering and coating process was performed at 950°C for 45 min in a vacuum atmosphere of 10^{-4} mbar. A pressure of 50 MPa was applied during the sintering process. *Staphylococcus aureus* (ATCC® 29213™) and *Escherichia coli*

(ATCC® 25922™) cultures were used to determine the antibacterial activity of the sintered and coated samples. The electrochemical properties of the samples were studied by Tafel extrapolation and potentiodynamic polarisation tests. The results showed that the coating layer containing 7.5 wt% of hydroxyapatite (HA) increased the antibacterial property against gram-positive and gram-negative bacterial cultures. Furthermore, it was determined that the i_{corr} value of the material decreased and the corrosion resistance improved with an increasing HA ratio. In addition, no active-passive oxidation zone formation was observed up to 2000 mV in the HA-added samples.

1. Introduction

Titanium and its alloys are commonly preferred in biomedical applications due to their superior mechanical properties, high corrosion resistance, low density and biocompatibility (1). Pure titanium and Ti6Al4V alloy are the most commonly used titanium-based materials for orthopaedics and dental implant production. In particular, Ti6Al4V alloy is the best titanium alloy for its high chemical stability, mechanical properties and easy control of its microstructure (2). However, Ti6Al4V is a bio-inert material that limits the interaction between implant and bone and prevents the bone from growing into the implant. Moreover, insufficient natural antibacterial properties of pure titanium and titanium alloys can lead to infection after implantation. As a result, implantation may fail due to infection and revision surgery is required. This severe clinical problem urgently needs to be resolved in the medical field (3, 4). Studies show that the infection rate encountered in total knee and hip arthroplasty is between 0.5–5% and 0.6–16%, respectively (5). Considering the ever-increasing number of implantations, the number of patients suffering from infection is also increasing. Therefore, it is accepted in the medical field that developing new implant materials with enhanced antibacterial properties is vital (6).

Another problem that causes revision surgery, as well as problems caused by infection and inflammation, is the poor electrochemical properties of medical materials (7, 8). Corrosion-induced implant change in metallic materials is frequently encountered compared to ceramic and polymer-based materials. Titanium-based materials show better corrosion performance than other metallic biomaterial types due to the stable oxide layer formed on their surfaces. However, the titania thin film layer with a thickness of 2–7 nm does not provide the conditions to resist the aggressive character of corrosive body fluid (9). This situation reveals that the surface oxide film layer formed in pure titanium and titanium alloys should be strengthened.

Using a titanium alloy alone may cause revision surgery due to low bone-implant interface bond strength and insufficient antibacterial and electrochemical properties (10). Therefore, the use of bioactive materials is increasing daily to ensure bone neoformation and long-term stability. HA is the best choice among bioactive materials because its chemical and crystallographic structure is similar to bone minerals. On the other hand, HA is known to increase antibacterial activity (11). In addition, HA has superior corrosion resistance thanks to its ceramic nature (12, 13). However, HA's weak mechanical properties limit this material's use alone in implant production (14). Therefore, combining the bioactivity, antibacterial properties and high corrosion resistance of HA with titanium's superior mechanical properties and biocompatibility is considered a promising approach to producing excellent biomaterials for load-bearing applications.

In the literature reviews, it was observed that the most commonly used method for HA coating on titanium-based materials is thermal spraying. However, the high temperatures (1200–1400°C) applied in thermal spraying adversely affect the phase stability of HA (15). However, the inadequacy of applied coating techniques reduces the crystallinity of HA and leads to decomposition (16). Because of decomposition, the expected results cannot be achieved as HA loses its characteristic features. The simultaneous application of pressure and temperature to the particles in the die makes it feasible to produce coatings at lower temperatures compared to thermal spray. In addition, complex shaped parts may be coated using this method and this is one of the most essential advantages of powder metallurgy (17). To avoid this problem, in this study, Ti-*x*HA bio composite coating was made on Ti6Al4V by a pressure-assisted sintering technique, which differs from coating techniques used in commercial applications. In addition, the antibacterial and electrochemical properties of the produced material were examined in detail.

2. Sample Preparation and Methodology

In the research, Ti6Al4V particles served as substrate while pure titanium and HA powders were used as coating powders. Pure titanium powder was received from Alfa Aesar, HA powder from Nanography Nano Technology Inc and Ti6Al4V powder from Baoji RuiHong Metal Materials Co Ltd. The average particle diameters of pure titanium, Ti6Al4V and HA powders were measured as 25 µm, 75 µm and 55 µm, respectively. Scanning electron microscope (SEM) images of the powders were taken using a JEOL JSM-6060 scanning electron microscope and are given in **Figure 1**. It was noticed that pure titanium and Ti6Al4V particles were irregular while HA particles were spherical in form.

Pre-alloyed Ti6Al4V was used as the base material and a mixture of titanium and HA powders was used as the coating layer. In the mixing procedure, 50% of the glass jar was filled with 5 mm diameter zirconia balls and 25% with titanium and HA powders. The remaining 25% was placed as a space. The mixing operation was carried out in MSE-TEC ball mill at 315 rpm for 1 h. The hot press technique (DIEX VS150) was applied for both coating and *in situ* sintering of Ti6Al4V alloy with a composite mixture. First, Ti6Al4V alloy powders were filled into the graphite die and then the prepared coating biocomposite composition was included. The sintering and coating was carried out at 950°C, a pressure of 50 MPa was applied during the process and the sintering time was selected as 45 min. The schematic representation of the hot press process is given in **Figure 2**. **Figure 2** shows both the substrate and the coating layer, the image of the die during sintering and the resulting compact. The sintering and coating process was carried out under a vacuum of 10^{-4} mbar to prevent the oxidation of the particles. Five different compositions were used in the study (**Table I**) to investigate the effect of the HA content in the coating layer. X-ray diffraction (XRD) analysis was carried out using Rigaku SA-HF3 device. Copper-Kα beams used in the research at 40 V and 20 mA had a wavelength of 1.54 Å. In the analysis, 1° min^{-1} was selected as scanning speed and 10–80° as scanning area. Metallographic processing procedures were conducted prior to the characterisation techniques. For grinding, 320 grit, 600 grit and 1000 grit silicon carbide papers were utilised. Then, the polishing

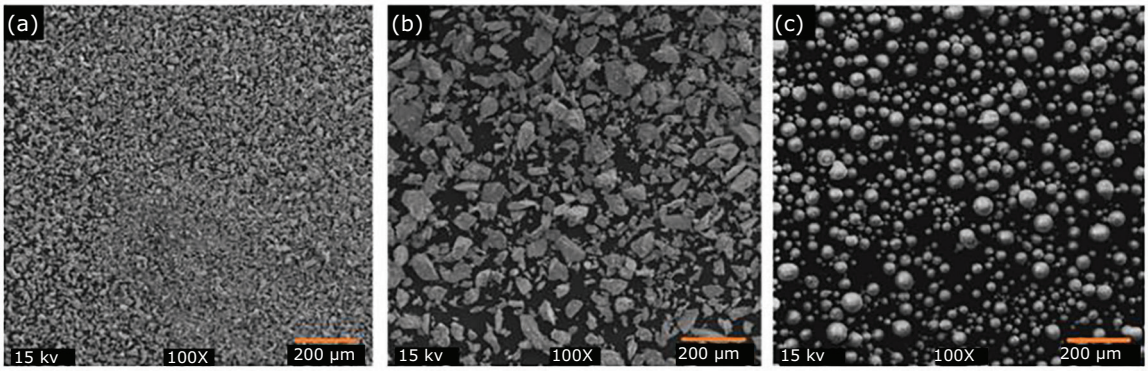

Fig. 1. SEM images of the powders used in the study: (a) pure titanium; (b) Ti6Al4V; (c) HA powder

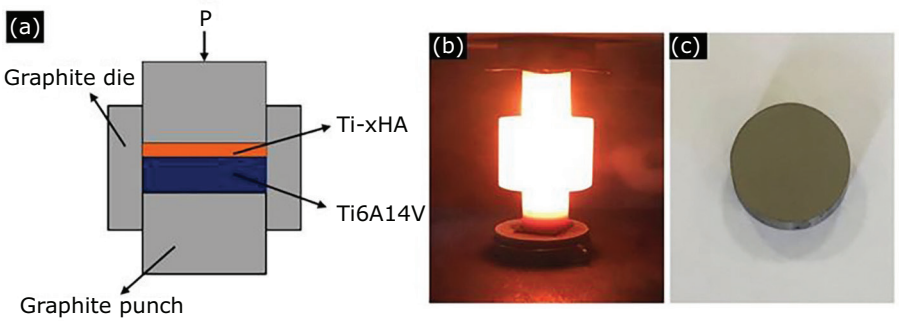

Fig. 2. (a) Schematic representation of the *in situ* coating process; (b) graphite die during production; (c) macro view of the sintered and coated sample

Table I Sample Codes and Chemical Composition of the Coating Layer

Substrate	Sample code	Coating layer, wt%
Ti6Al4V	Ti6Al4V	–
	Ti64-Ti	Pure Ti
	Ti64-Ti2.5HA	Pure Ti + 2,5 HA
	Ti64-Ti5HA	Pure Ti + 5 HA
	Ti64-Ti7.5HA	Pure Ti + 7,5 HA
	Ti64-Ti10HA	Pure Ti + 10 HA

procedure was carried out using 3–1 µm diamond polishing solutions. Finally, the samples were prepared for microstructural analysis by etching with Kroll reagent (2 ml HF, 6 ml nitric acid, 92 ml hydrogen trioxide). Optical microscope images of the polished and etched samples were taken using an OLYMPUS BX41M-LED microscope.

2.1 Antibacterial Analysis

Gram-positive *Staphylococcus aureus* (ATCC® 29213™) and gram-negative *Escherichia coli* (ATCC® 25922™) standard bacteria were used to determine the antibacterial activities of the produced samples. Bacteria were grown on Mueller-Hinton Agar (MHA) (Merck, Germany) medium. First, 34 g of powdered MHA medium was weighed and dissolved in 1 l of distilled water by heating. Afterwards, the medium was sterilised in an autoclave (Alp, Japan) at 121°C for 15 min. After waiting for cooling, it was poured into sterile plastic petri dishes under aseptic conditions. Petri dishes were allowed to cool at room temperature for one day. The bacteria was stocked at –80°C and started to work after being passaged at least two times. One day before the study, the bacteria were passaged into an MHA medium and incubated at 37°C for 18–24 h. Ultraviolet C (UVC) light was used during sterilisation. All surfaces of the samples were sterilised by UVC for 30 min in the Biosafety cabinet. All antibacterial analyses were carried out under aseptic conditions in a burner flame. According to the analysis, bacteria were first suspended in sterile saline (SF) solution and a turbidity equivalent to 0.5 McFarland turbidity (for *E. coli* at 600 nm optical density: 0.14, for *S. aureus* at 600 nm optical density: 0.08–0.1 absorbance) was obtained using a spectrophotometer (10^8 CFU ml^{-1}).

The obtained bacterial suspensions were diluted ten times in sterile SF and new suspensions containing 10^4 CFU ml^{-1} bacteria were prepared. First, 0.4 ml of the diluted suspension was taken with the help of an automatic pipette and left on the sterile samples. To determine the number of bacteria left on the samples, 20 µm of the diluted bacterial suspension were taken and left in the MHA medium, then inoculated on the surface of the medium with the help of a disposable sterile spatula (control cultivation at 0 h). Then, the samples and the control culture medium were incubated for 18–24 h in a 37°C oven with 90% humidity. In addition to these, a falcon tube containing 10^4 CFU ml^{-1} bacteria was also incubated under the same conditions (control cultivation 24 h) to determine the numbers of bacteria that did not contact the samples at the end of the incubation period and to compare them with the numbers of bacteria that came into contact with the samples. After incubation, the liquids on the samples were transferred to six 50 ml falcon tubes containing 3.6 ml of sterile SF. Similarly, the samples were transferred into falcon tubes with the help of sterile forceps and under aseptic conditions. Finally, pipetting and vortexing were applied to the samples inside the falcon tubes. After vortexing, 20 µl of liquid was withdrawn from the falcon tubes, left in an MHA medium and cultivated with a sterile spatula. In addition to these, 20 µl of liquid was taken from the tube, which was incubated under the same conditions (control sowing 24 h) and inoculated into the medium to control the number of bacteria at the end of the incubation period. All sowing procedures in the study were made on 3 MHA media with three repetitions. Then, the media were incubated for 18–24 h in an oven at 37°C. After incubation, all media were photographed using the imaging system (VersaDoc™, Bio-Rad).

2.2 Electrochemical Analysis

Different electrochemical tests were carried out to explain the biodegradation mechanisms of the samples. A three-electrode cell controlled by AMETEK brand VersaSTAT 4 model potentiostat/galvanostat was used. Obtained curves were processed with the VersaStudio program (version 2.42.3) and related results were calculated. While the produced samples were used as the working electrode, platinum was used as the counter electrode. Samples were soaked in simulated body fluid for 1 h before measurements. 0.9% sodium chloride solution (pH: 5.5) was used as simulated body fluid in the study. The i_{corr}, corrosion potential (E_{corr}) and R_p were determined by the Tafel

extrapolation method. The test was performed at 37°C with a scan rate of 1 mV s^{-1} between –250 mV and 250 mV (*vs.* SCE). Potentiodynamic polarisation tests were performed at a scanning speed of 1.0 mV s^{-1} between –200 mV and 2000 mV on HA-added coatings and HA-free samples to determine HA's effect on titanium dissolution. Before the experiment, the conductivity of the reference electrode and copper wire was checked with a multimeter. The area in contact with the solution (exposed to corrosion) of the samples in 0.9% sodium chloride electrolyte was set as 1 cm^2.

3. Results

3.1 Production of Biocomposite Coated Samples

For biocomposite coatings, the coating layer's thickness was selected as 200 µm (18, 19). Density measurements were carried out after coating and sintering. A density of 99.1% was obtained in the reference sample of Ti6Al4V produced by hot press. In the biocomposite coating layer consisting of pure titanium and HA coated on the Ti6Al4V alloy, the density values decreased with the increasing HA content. A density of more than 98% was obtained in all samples. High-density values are essential for the high strength of implant materials produced for load-bearing applications (20). **Figure 3** shows an optical and SEM cross-sectional images of the Ti64-Ti-*x*HA as an example. In order to produce biocomposite coatings in accordance with the standards, the coating thickness was targeted at 200 µm. When **Figure 3** is examined, no fracture growth was found between the substrate and the coating layer in any of the samples. The coating layer is clearly visible in the polished samples obtained after the metallographic processes were applied. It was determined that HA was homogeneously distributed in the coating. Additionally, when the coating thickness was measured, the target of 200 µm was reached. This is very important in terms of demonstrating the applicability of low coating thickness with pressure-assisted sintering method. On the other hand, as can be seen in **Figure 3(b)**, the base material consists of alpha and beta phases. The dark regions represent the beta phase, while the light regions are alpha phase. An interfacial layer can be seen between the coating and the substrate. When the SEM images of the coated layer in **Figure 3(c)** is examined, the interface formed between the coating layer and the substrate is clearly seen. In such cases, HA coatings establish only a mechanical bond with the substrate. The purpose of using a titanium-hydroxyapatite (Ti-HA) biocomposite structure instead of only HA in the coating layer used in the

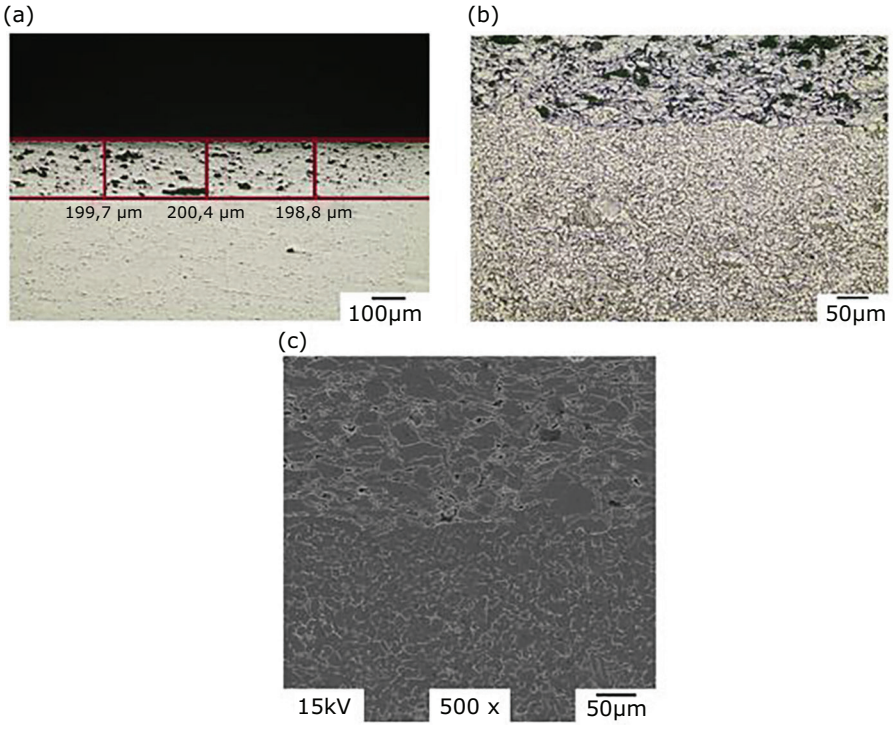

Fig. 3. Optical and SEM images of the samples: (a) polished Ti64-Ti5HA; (b) etched Ti64-Ti10HA; (c) Ti64-Ti7.5HA

study is to increase the base-coating integration and to prevent the coating from separating from the base material. At this point, the observation of interface formation confirms that a critical goal was achieved.

Another issue that has to be investigated in terms of coating quality in the study is the phase stability of HA. High temperatures (1200–1400°C) applied during the production of Ti-HA biocomposite negatively affect the phase stability of HA (21). High temperature causes the HA in the structure to decompose by decreasing the crystallinity. As a result of decomposition α–tricalcium phosphate or β-tricalcium phosphate (α-TCP or β-TCP), tetracalcium phosphate (TTCP), calcium oxide, amorphous calcium phosphate and oxyhydroxyapatite phases are formed (22). The biodegradable nature of TCP-type phase structures adversely affects the mechanical stability of HA. Low stability causes the ceramic reinforcement to dissolve quickly in body fluid (23, 24). Pressure-assisted sintering was used to prevent decomposition caused by high-temperature production. The simultaneous application of pressure and temperature to the particles in the die made it possible to produce coatings at lower temperatures compared to methods such as plasma spray, sol-gel, micro-arc oxidation and electrostatic spray deposition. XRD analysis results of the samples are given in **Figure 4**. Only α-titanium peaks were detected in the XRD analysis of pure titanium. On the other hand, after adding HA to pure titanium, characteristic peaks of HA (JCPDS card no:09-0432) (25) and titanium (JCPDS card no: 44-1294) (26) were observed in the XRD results. Only crystalline HA peaks in the HA-doped biocomposite coating layer indicate that HA has not undergone decomposition. Therefore, it is seen that production with pressure-assisted sintering allows production below the decomposition temperature.

3.2 Antibacterial Analysis

In order to evaluate the antibacterial analysis results, the bacterial colonies in the media were counted and the images of the formed colonies were taken. The antibacterial test results as a result of counting these colonies are given in **Table II**. It can be understood that the antibacterial effect of HA on *E. coli* was higher than that of *S. aureus*. On the other hand, the numerical results of the study with *E. coli* in **Table II** are visually supported in **Figure 5**. Samples shown in **Figure 5(a)** and **5(b)** were directly inoculated from the bacteria's own culture medium into the growth medium. In contrast, the samples in **Figure 5(c)**–**5(h)**, were diluted at a ratio of 1:10 as per the experimental protocol and thereafter inoculated into the growth medium. Hence, unlike **Figure 5(a)** and **5(b)**, these images show just 10% of the bacteria that would typically be observed. **Table II** containing the antibacterial analysis results was created by correcting this 1/10 difference. The numerical values specified in the second column of each bacterial culture are included. As a result, while the numbers in the **Figure 5(a)** and **5(b)** are the same as the numbers in **Table II**, the images in the **Figure 5(c)**–**5(h)** samples are 1/10 of the values

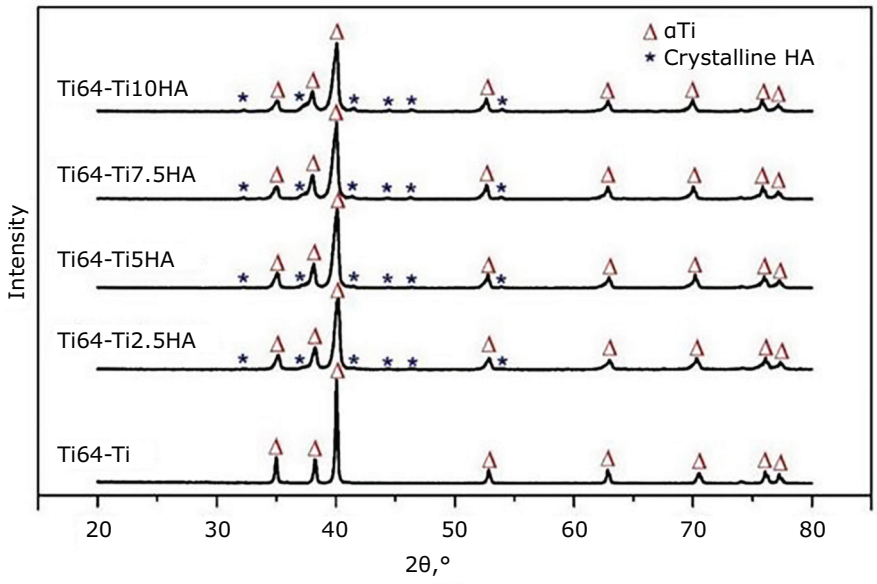

Fig. 4. XRD analysis results of the biocomposite coated samples

Table II Antibacterial Analysis Results

	***E. coli,* Number of colonies**		***S. aureus,* Number of colonies**	
Materials	20 µl	CFU ml^{-1}*	20 µl	CFU ml^{-1}
Ti6Al4V	440	22.000	WR**	WR
Ti64-Ti	1170	58.500	WR	WR
Ti64-Ti2.5HA	610	30.500	WR	WR
Ti64-Ti5HA	10	500	WR	WR
Ti64-Ti7.5HA	10	500	3150	3150
Ti64-Ti10HA	0	0	1860	157.500
Control (0 h)	267	13.350	375	18.750
Control (24 h)	1.322	66.100	73	3.650

*CFU/ml: The number of colonies forming units in one millilitre of liquid (CFU: Colony forming unit)
**WR: Widespread Reproduction

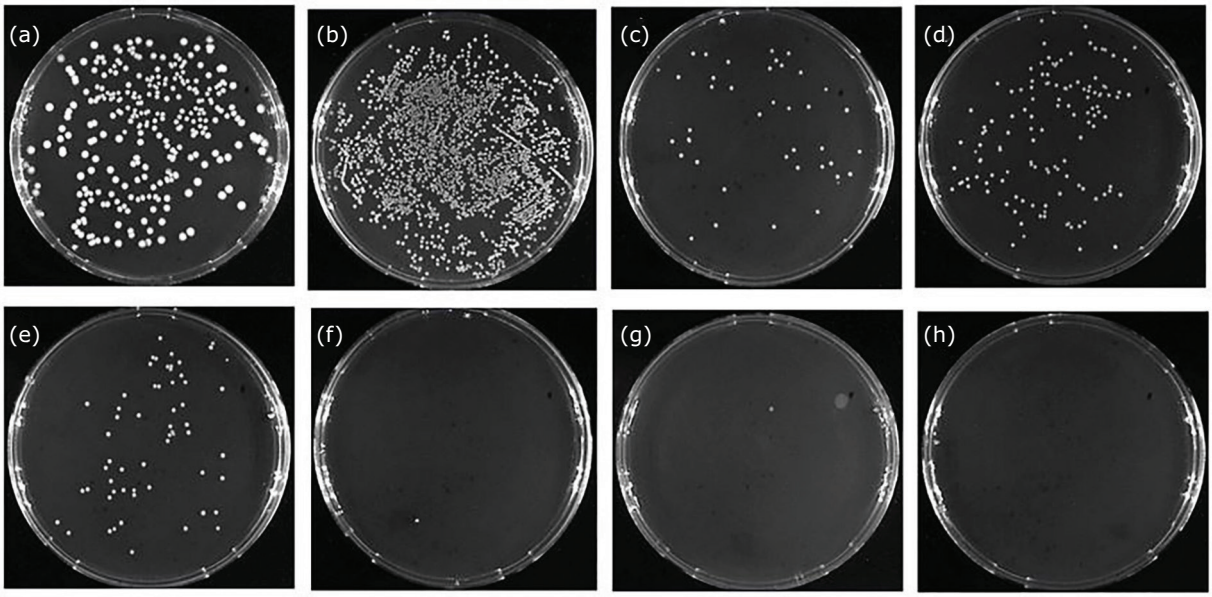

Fig. 5. Growth media images after antibacterial analysis with *E. coli*; (a) control sample 0 h; (b) control samples 24 h; (c) Ti6Al4V; (d) Ti64-Ti; (e) Ti64-Ti2.5HA; (f) Ti64-Ti5HA; (g) Ti64-Ti7.5HA; (h) Ti64-Ti10HA

in **Table II**. The number of colonies formed at the end of 18–24 h incubation of the control sample (24 h control) indicates the number of colonies typically formed by bacteria that did not encounter metal samples. The effect of metal samples on bacterial growth will realise the number of colonies that will form below or above this number.

Figure 5(c) and **5(d)** shows the growth media images of Ti6Al4V and Ti64-Ti, respectively. A high bacterial growth rate was detected in the reference samples after 24 h of incubation. On the other hand, in the growth medium of the Ti64-Ti2.5HA alloy, less bacteria grew than in Ti64-Ti and Ti6Al4V. As a result of increasing the HA ratio from 2.5 wt% to 5 wt%, there was a decrease in the number of bacterial colonies growing and only one bacterial colony was seen in the growth medium. The results of Ti64-Ti7.5HA and Ti64-Ti5HA samples were the same. 100% bacterial death was observed in the Ti64-Ti10HA medium. Therefore, Ti64-Ti10HA showed the best results for the antibacterial analysis with *E. coli*.

Figure 6 shows the images of the growth medium in which bacteria cultivation was carried out with *S. aureus*. When the growth media of Ti6Al4V alloy and Ti64-Ti were examined, a high bacterial growth rate was observed. This result revealed that the samples indicated did not have any antibacterial effect against *S. aureus* bacteria. There was no significant decrease in the number of

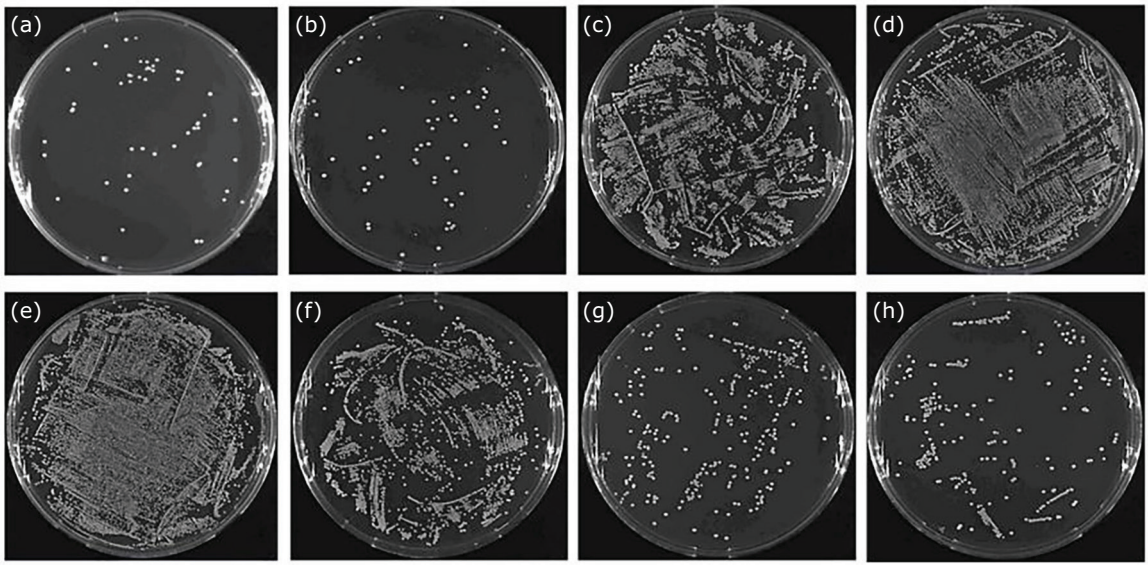

Fig. 6. Growth media images after antibacterial analysis with *S. aureus*; (a) control sample 0 h; (b) control samples 24 h; (c) Ti6Al4V; (d) Ti64-Ti; (e) Ti64-Ti2.5HA; (f) Ti64-Ti5HA; (g) Ti64 Ti7.5HA; (h) Ti64-Ti10HA

S. aureus in the Ti64-Ti2.5HA sample. Therefore, adding 2.5 wt% HA to the coating layer did not change the antibacterial properties of the material. There was a significant decrease in the Ti64-Ti5HA medium compared to the Ti64-Ti2.5HA sample. This decrease continued with the increase in the amount of HA in the coating content. Ti64-Ti10HA sample showed the highest antibacterial effect against the *S. aureus* bacterial culture. As seen in **Figure 6**, the samples produced could not provide a 100% effect on *S. aureus* bacteria compared to *E. coli*. This shows that the Ti-HA biocomposite coating is more effective in gram-negative than gram-positive bacteria. The results are compatible with the literature. Sato *et al.* (27) investigated the effect of Ti-HA containing 3 wt%, 6 wt% and 9 wt% HA on the biofilm structure formed by bacteria. It was stated that the produced samples showed antimicrobial effects against different bacteria (*E. coli*, *S. aureus*, *S. sanguinis* and *A. naeslundii*). On the other hand, it was stated that the materials did not show the same effect against all bacteria. Higher antimicrobial activity was observed against *E. coli* bacteria compared to *S. aureus* bacteria. Another study on a similar subject was done by Harwijayanti *et al.* (28) In the study, Ti-HA composite was sintered at 800°C for 3 h, 4 h and 5 h. Antibacterial activity test was performed using *E. coli* and *S. aureus* bacterial cultures on Ti-HA composites containing 20–30 vol% HA. It was stated that Ti-HA composites provided more effect against *E. coli* bacteria, similar to our study. The fact that the cell membrane of *S. aureus* bacteria is thicker than that of *E. coli* bacteria is the reason for this situation. Despite this, it was demonstrated in the study that HA also showed an antibacterial effect against *S. aureus* bacterial culture. Although it is currently seen that HA improves the antibacterial properties of titanium-based biomaterials, it has been demonstrated by studies that the addition of silver, zirconia, copper and strontium to the structure with HA leads to further development of this feature (21, 29–31).

3.3 Electrochemical Analysis

In order to examine the dissolution mechanisms of the produced samples, electrochemical tests were applied and cathodic and anodic polarisation curves were obtained in simulated body fluid. i_{corr}, E_{corr} and Rp values of the materials were determined by Tafel extrapolation method and their corrosion tendencies were compared with each other. It is also understood that the reaction is anodic or cathodic (32). It is stated in literature studies that the material becomes more prone to corrosion as the i_{corr} increases at a certain potential value (33, 34). To understand the dissolution mechanism of the titanium coating layer with and without HA content, the passivation properties of the materials were investigated by potentiodynamic measurements. As a result of the electrochemical experiments, the i_{corr} and E_{corr} values of the graphs of the samples were calculated based on the

above information. Polarisation resistance results were found by taking the slope of the linear region (E_{corr} ± 10 mV) in the potential-current curve. Rp is an indicator of resistance to dissolution and is inversely proportional to i_{corr} (35). The obtained values are given in **Table III.** The Tafel curves of all samples are shown in **Figure 7** on a single graph.

The highest i_{corr} value was seen in the Ti64-Ti sample. On the other hand, the i_{corr} value of the Ti6Al4V sample was lower than Ti64-Ti. In other words, the coating of Ti6Al4V with pure titanium led to a decrease in the corrosion resistance of the Ti6Al4V sample. The numerical values in **Table III** are also supported by the Tafel curves in **Figure 7**. It was observed that the Ti6Al4V curve shifted to the left compared to Ti64-Ti and had a lower i_{corr} value. On the other hand, the i_{corr} values decreased with the addition of HA to the coating layer. Therefore, in **Table III**, it has been seen that HA has a positive effect on the corrosion resistance of titanium. In general, it is a known fact that the corrosion resistance of ceramic materials is higher than metallic materials. In light of this information, it is expected that HA with ceramic characteristics will improve corrosion resistance when added to the metallic matrix. Literature reviews also show that HA increases the corrosion resistance of pure titanium and titanium alloys (13, 36). According to the Tafel extrapolation results, the lowest i_{corr} value was reached in the Ti64-Ti7.5HA sample. As the HA ratio increased from 7.5 wt% to 10 wt%, an increase in the i_{corr} value was observed. It is known that an increase in HA content in Ti-HA biocomposites leads to an increase in porosity in the structure. Increasing porosity affects the corrosion resistance negatively (37). This explains the decrease in corrosion resistance of the Ti64-Ti10HA sample. In **Figure 8** below, the potentiodynamic polarisation curves of the samples are given in the same graph for comparison purposes.

Table III Tafel Extrapolation and Linear Polarisation Resistance Test Results

Sample	$\dot{I}_{corr}$, µA cm^{-2}	E_{corr}, mV	R_p, ohm
Ti6Al4V	0.90	–283,55	4554
Ti64-Ti	1.20	–81,84	3289
Ti64-Ti2.5HA	0.81	–211,36	4785
Ti64-Ti5HA	0.77	–324,52	9984
Ti64-Ti7.5HA	0.65	–301,60	20364
Ti64-Ti10HA	0.74	–190,55	12014

It was determined from **Figure 8** that the Ti6Al4V and Ti64-Ti samples showed a typical oscillation potential. However, active-passive regions due to local oxidation were seen in these curves. A relatively smooth curve was formed in HA-added samples compared to Ti6Al4V and Ti64-Ti. Based on the curve types, it was observed that the addition of HA stabilised the passive film formed on the surface up to a potential value of 2000 mV.

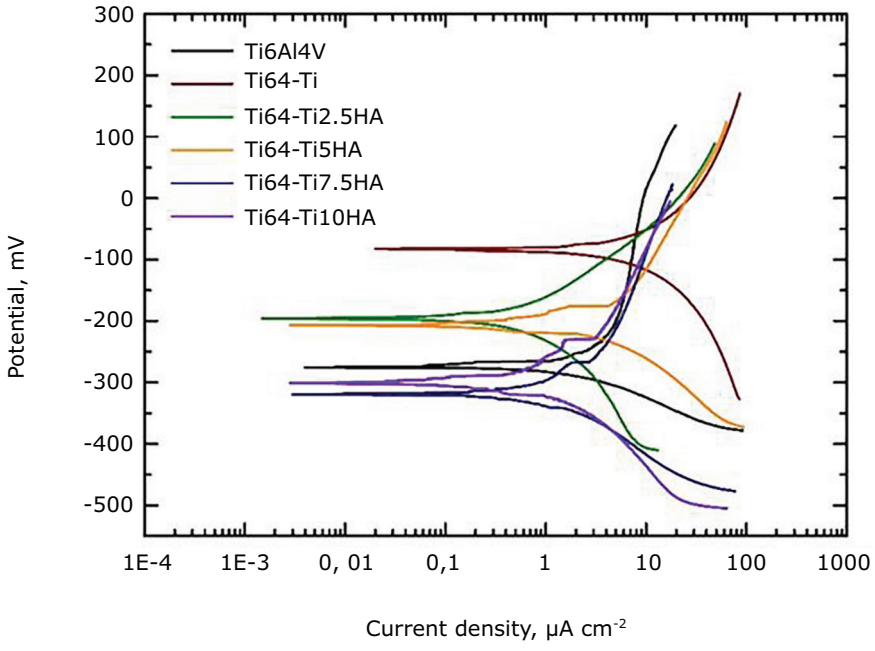

Fig. 7. Tafel curves of the produced samples

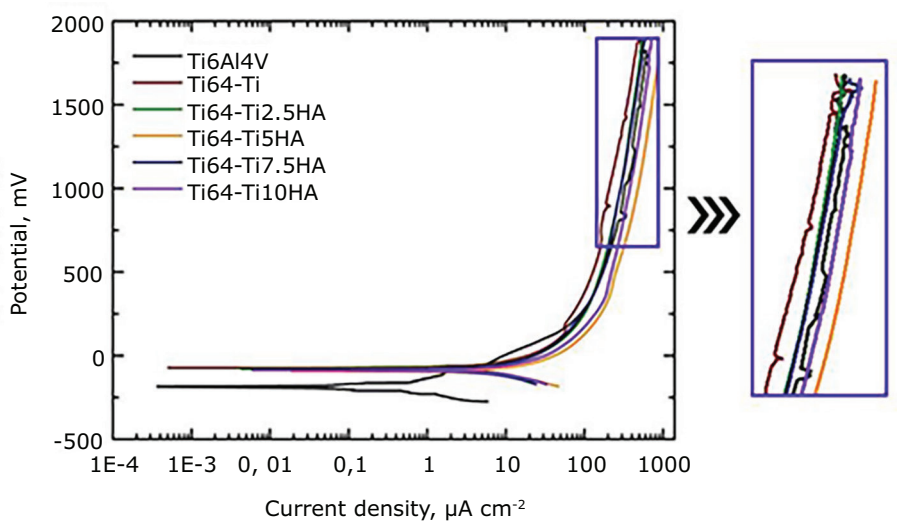

Fig. 8. Polarisation curves of samples taken in SBF

4. Conclusion

This study investigated the antibacterial and electrochemical properties of the Ti-*x*HA biocomposite coated Ti6Al4V alloy by pressure-assisted sintering. HA added samples were more effective against gram-negative *E. coli* bacteria compared to gram-positive *S. aureus* bacteria. It was determined that all *E. coli* bacteria were killed in Ti64-Ti10HA growth medium. In the study conducted with *S. aureus* bacteria, no antibacterial effect was observed until the addition of 5 wt% HA. As the HA ratio continued to increase, the number of bacterial cultures decreased. However, in the study conducted with *S. aureus*, no sample could provide 100% bacterial death.

The highest i_{corr} value was observed in the Ti6Al4V sample. As a result of the coating of the Ti6Al4V sample with titanium, the i_{corr} value decreased, so the corrosion resistance increased. However, a decrease in i_{corr} values was observed in direct proportion with the addition of HA. The lowest i_{corr} value was seen in the Ti64-Ti7.5HA sample. The i_{corr} value increased with the increase of HA addition from 7.5 wt% to 10 wt%.

Active-passive zones originating from local oxidation zones were detected below the potential value of 2000 mV in Ti6Al4V and Ti64-Ti samples. It was observed that HA inhibited local oxidation zone formation up to a potential value of 2000 mV in samples with the biocomposite coating layer. Therefore, the presence of HA led to an increase in the stability of the coating layer.

Although antibacterial properties were supplied in the material with the addition of 5 wt% HA, the electrochemical performance of this sample was not determined to be acceptable. Considering both electrochemical and antibacterial abilities, Ti64-Ti7.5HA sample was shown to have optimum properties. Both *S. aureus* and *E. coli* bacterial cultures did not survive on this sample surface. In addition, the lowest i_{corr} and the maximum linear Rp values according to i_{corr} and R_p values were achieved in Ti64-Ti7.5HA sample. The material's corrosion resistance decreased with the increase in the agglomeration of HA particles and porosity ratio in the coating layer with the increasing HA ratio. In this respect, 7.5 wt% HA applied to the coating layer led to an improvement in the antibacterial and electrochemical characteristics of the material compared to other samples.

As a result, Ti-HA biocomposites were coated by pressure-assisted sintering method different from the techniques in the literature and the effect of this new approach on material properties was evaluated. As a result of the simultaneous application of pressure and temperature, density values of 95% and higher were reached at lower temperatures compared to methods such as thermal spray. The decrease in the applied temperature caused the HA in the coating to maintain its stability. This indicated well on the electrochemical and antibacterial tests performed. In this respect, it was seen that innovative methods for biocomposite coatings are promising.

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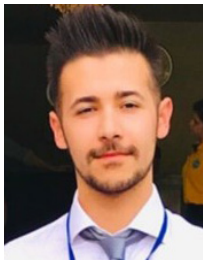

Onur Muratal had the opportunity to actively work with many ferrous and non-ferrous metal alloys (stainless steel, titanium, nickel, cobalt-chromium and aluminium) in the university laboratory. Especially powder production techniques and sintering techniques. Onur worked as an executive in many academic publications and projects on microstructural analysis, failure analysis and different metal alloys. He is currently working as a Materials Analysis and Development Senior Engineer at Toyota Toyotetsu Laboratory.

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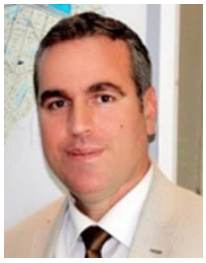

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