Ceramics-Silikáty 66 (3), 289-295 (2022)
www.ceramics-silikaty.cz doi: 10.13168/cs.2022.0025

ADHESION BONDING OF HYDROXYAPATITE WITH ADDITION OF ZIRCONIUM OXIDE ON TI-6AL-4V ELI FOR ORTHOPAEDIC IMPLANT

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Submitted April 5, 2022; accepted May 22, 2022

Keywords: Cross-cut, Dip coating, Hydrophilic, Osseointegration, Titanium alloy

The lack of adhesion bonding of a hydroxyapatite (HA) coating layer on the surface of an implant material can cause the coating layer to peel off during implantation and will increase the risk of metallic ion release into the human body and may also to increase the inflammatory effect and slow down the osseointegration process. In order to increase the adhesion of HA coated Ti-6Al-4V ELI, zirconia (ZrO_2) was added into the coating layer. The coating process of the HA suspension with addition of ZrO_2 on Ti-6Al-4V ELI sample surfaces was conducted by using dip-coating method. The samples were then heated to 800, 900, and 950 °C. The coating layer properties were then examined using a light microscope. The improvement in the adhesion bonding was correlated by calculating the removed area on the layer using the cross-cut tape test method and calculating the contact angle of the coating. The low value of the removed area and contact angle of the coating indicated the adhesion coating is good. The test specimen with the ZrO_2 addition has a lower removed area than the test specimen without the ZrO_2 addition. The value of the removed area also correlates with the obtained layer contact angle. The test specimen with the ZrO_2 addition has a lower contact angle (hydrophilic coating) than the test specimen without the ZrO_2 addition. The adhesion of this strong hydroxyapatite layer is good for improving the osseointegration.

INTRODUCTION

Ti-6Al-4V ELI is an α+β type titanium alloy that is widely used for implant materials including those used for orthopaedic implants [1]. This alloy has excellent mechanical and biocompatibility properties. However, as other implant metals, it is less bioactive in supporting the osseointegration process surrounding the implant. Therefore, the Ti-6Al-4V ELI surface needs to be coated with high bioactive substance, such as hydroxyapatite (HA). However, HA coatings with a low adhesion strength can cause the coating layer crack and to peel off from the implant surface, which leads to implant failure [2, 3].

In addition to improving the bioactivity, HA coated Ti-6Al-4V ELI is also aimed at avoiding direct contact between the material and the hard and soft tissues in the body to minimise the metal implant corrosion and the metallic ion release as well. The previous work showed that the adhesion of the HA coating layer was quite low, and there were many spots where cracks were found, which could lead to osseointegration failure [3, 4]. It was also found that there were a lot of agglomeration and cracks on the surface of the Ti-6Al-4V ELI test sample coated with the nano commercial HA under variation of the voltage and processing time using the electrophoretic deposition (EPD) method. Such conditions occurred in the densification process of the coating at a sintering temperature of 900 °C [4]. However, the test sample treated under 8 volts for 5 minutes showed the best adhesion bonding at a sintering temperature of 800 °C. The coating is quite uniform with a surface coverage of 82.1 % and with an average thickness of 73.3 μm. However, such a coating layer is still not good enough for orthopaedic implant applications.

Other researchers have also reported a similar problem with the HA coating layer where the layer was too brittle and had many cracks at a sintering temperature of 900 °C [5]. The adhesion strength was tested using the cross-cut tape test and the authors concluded that the adhesion was not so strong when the sintering temperature was over 800 °C. The best sintering temperature to minimise the cracks was at 800 °C. A high sintering temperature, on the one hand, can strengthen

the coating density and reduce the porosity. On the other hand, it also causes cracking, which begins with particular layers peeling off. Therefore, a strong adhesion strength is necessary to avoid cracks on the surface of the coating.

The adhesion strength of the coating layer is also affected by the size of the HA particles. An HA coating layer with a larger size of the coating particles has a lower adhesion strength, and is also easier to crack during the sintering process [6]. In order to reduce the coating layer cracks during sintering process, Guraksin et al. [7] used the additive solvents KH_2PO_4, Na_2CO_3, and P_2O_5 to improve the mechanical properties of the HA coated Ti-6Al-4V. They did not find cracks at a sintering temperature of 800 °C, but did at 900 °C. During sintering, gas was trapped in the material as it had no time to escape before the liquid bridge or particle necking occurred, which made the porosity path tightly closed. The trapped gas pushed out in all directions and resulted in bloating, making the pressure in the porosity to be higher than the outside. The low adhesion of the surface of the composite material particles cannot withstand higher pressure, thus causing cracking.

In order to improve the adhesion strength of the HA coating layer, especially at high sintering temperatures over 800 °C, it is necessary to add another substance that has the potential to increase the adhesion bonding strength and reduce the cracks as well. Using particles, such as zirconium oxide (ZrO_2), it was found that the HA coating layer is difficult to crack when heated above 800 °C [8]. Zirconia has high fracture resistance because it can absorb energy during the transformation from a tetragonal structure to a monoclinic one [9]. The main purpose of the coating layer is to improve the adhesion bonding and, thus, create osseointegration [10]. Besides, the coating layer can also increase the mechanical properties to protect the metallic ion release during implantation. Thus, in this study, ZrO_2 is also used to improve such properties by applying a simple dip-coating method to coat the HA particles on the surface of Ti-6Al-4V ELI. The main goal is to get strong adhesion bonding and also to minimise the coating layer cracking during the sintering process.

EXPERIMENTAL

Materials

Ti-6Al-4V ELI plate with a thickness of 4 mm was cut-off to get samples having size 10 mm × 10 mm × 4 mm. The samples were then ground using 800 – 1500 mesh silicon carbide sandpaper, polished using alumina powder, and then cleaned using a solution of acetone, 70 % ethanol, 25 % nitric acid with a pH of 7.3, and washed with pure water for 30 minutes [11]. Subsequently, the square plates were immersed in a 1 mol NaOH solution for 1 hour [12]. A multi-frequency ultrasonic bath was used for the cleaning process. The drying was performed with a stirring hot plate for 5 minutes at 50 °C [11].

A commercial hydroxyapatite (Sigma Aldrich, USA) measuring 200 nm (nanometeres) was used as the main coating substance. While, ZrO_2 (XFNANO brand) with model number XFI01-3 and a purity of 95 % was used as the strengthening particles. The suspension was made with 4 grams of HA powder plus 0.8 grams of ZrO_2 (17 wt. % ZrO_2) and 4 grams of the HA powder plus 1.0 gram of ZrO_2 (20 wt. % ZrO_2) and mixed in 100 ml of ethanol at pH 4.0 using the addition of an HNO_3 solution [12]. Subsequently, the solution was homogenised with a magnetic stirrer for 1 hour, followed by sonication in an ultrasonic bath for 2 hours. The hydroxyapatite that was attached to the surface of the test specimen was then dried for 24 hours at room temperature.

Methods

The coating process was carried out using the dip-coating method, which is easy to perform and inexpensive [13]. Immersion was carried out with a withdrawal speed of 4 $mm \cdot s^{-1}$ based on the results of obtaining an even HA coating. The dwell time of the substrate in the suspension was 5 seconds [14-18]. During the dip-coating deposition, the HA and HA/ZrO_2 powders partially sedimented. Subsequently, the obtained coating was compacted by the sintering process at temperature variations of 800 °C, 900 °C, and 950 °C with a heating rate of 5 °C minute. It was further held for 2 hours to ensure an even temperature in the test specimen, followed by annealing for 24 hours using a GSL-1100 Vacuum Tube Furnace. The thickness was measured using Sanfix Thickness Gauges (μm), GM 280 series, while the surface coverage of the coating was measured using ImageJ [16].

Because the test specimens have small dimensions, it is impossible to measure the adhesion strength of the coating using a pull-tester. Therefore, the cross-cut tape test method was carried out to determine the adhesive bonding of the coating using the an ETOPOO Cross Cutter Adhesion test tool and Scotch brand transparent tape [4]. The line was made according to the ASTM D3359 standard [4], which specifies the cut lines and spacing between lines based on the film thickness: 6 lines, spaced 1 mm for thicknesses of 50 − 125 μm. Furthermore, the specimen was tested by making scratches on the test sample coating, followed by the installation of tape on all the scratched surfaces. The tape was pulled at an angle of 180° and the level of adhesion was tested on a scale of 0 – 5, where 0 indicated more than 65 % of the removed area and 5 indicated 0 % for the removed area. If the coating had good adhesion, the removed area had a value of 0 – 15 % [4].

Furthermore, the removed area of the coating was compared with the measurement of the contact angle

of the coating [19]. Good adhesion has a contact angle (ΘC) less than 900, in the sense that the coating is hydrophilic, the coating has good wettability. The test method was in the form of determining the liquid coating drop (Sessile Drop) angle, which was measured using ImageJ [19, 20]. The coating layer properties were then examined using a Stereo Olympus LG-PS2light microscope.

RESULTS AND DISCUSSION

Thickness and surface coverage of the coating

One of the factors of good coating adhesion is the presence of a thin layer with an even thickness on the entire surface [4]. The dip-coating method was used to obtain a thin and even coating layer. Due to this, measurement of the thickness and surface coverage of the coating test specimens was carried out before measuring the removed area of the coating. In general, the obtained coating is quite good, in the form of a thin layer which was evenly distributed over the entire surface of Ti-6AL-4V ELI. The hydroxyapatite and hydroxyapatite/ZrO_2 powder partially sedimented during the dip-coating deposition. The comparison of the thickness and surface coverage values of the coating is shown in Table 1 and Figure 1.

Table 1. The values of the hydroxyapatite coating thickness and surface coverage with the ZrO_2 additions at all the sintering temperatures.

Sintering Temperature (°C)	ZrO_2 (wt. %)	Thickness (μm)	Surface Coverage (%)
800	17	89.7	88.92
	20	87.4	88.93
	0 (without any addition)	85.6	89.05
900	17	92.5	91.14
	20	93.8	87.32
	0	86.1	90.27
950	17	95.3	87.48
	20	91.2	90.57
	0	88.4	86.85

Based on the calculations using ImageJ software, the surface coverage levels of the hydroxyapatite-coated implant materials are found to range from 88.30 ± 1.99 % to 89.58 ± 2.00 %. A coating is said to be good if it covers at least 90 % of the material surface [3,4]. Furthermore, the obtained coatings are thin, ranging from 87.57 ± 2.06 μm to 90.80 ± 4.12 μm. These findings are in accordance with the results of several previous studies stating that the standard thickness of the hydroxyapatite layer for implant materials ranges from 50 to 200 μm [5, 7].

Removed area of the coating

Because the test specimens have small dimensions, it is impossible to measure the adhesion strength of the coating using a pull-tester. Therefore, the cross-cut tape test method was carried out to determine the adhesive bonding of the coating using the ETOPOO Cross Cutter Adhesion test tool and Scotch brand transparent tape [4]. In this case, the improvement in the adhesion bonding was correlated by calculating the removed area on the layer using the cross-cut tape test method. The low value of the removed coating area indicated the adhesion coating was good.

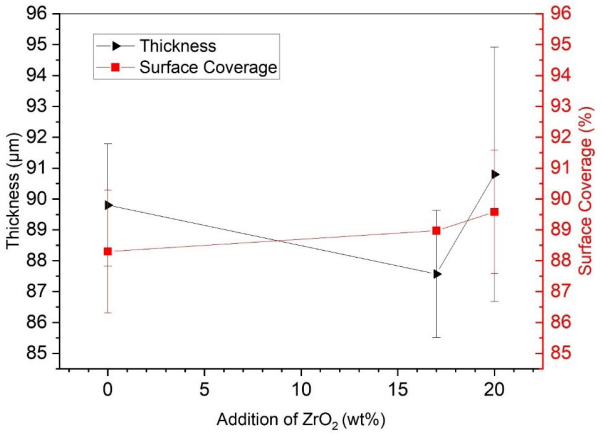


Figure 1. Thickness and surface coverage of the hydroxyapatite coating on the Ti-6Al-4V ELI treated with the different additions of ZrO_2 and sintering temperatures at 800, 900, and 950 °C.

Table 2. Removed area of the hydroxyapatite coating on the Ti-6Al-4V ELI treated by the addition of ZrO_2 and with the variation in the sintering temperatures.

ZrO_2 (wt. %)	Sintering Temperature (°C)	Removed Area (%)
17	800	3.75
20	800	2.25
0 (without of addition)	800	5.25
17	900	3.25
20	900	2.00
0	900	4.75
17	950	5.50
20	950	4.50
0	950	7.25

The removed area of the sintered coating layer with and without the addition of ZrO_2 is shown in Table 2. It can be seen that there was good adhesion of all the coating layers as indicated by the low removed area for all the specimens, which was distributed in a wide range of 2.00 – 7.25 % (less than 15 %) [4]. However,

the specimens with the addition of ZrO_2 has a smaller removed area than the test specimen without the addition at all the sintering temperatures of 800 °C, 900 °C, and 950 °C.

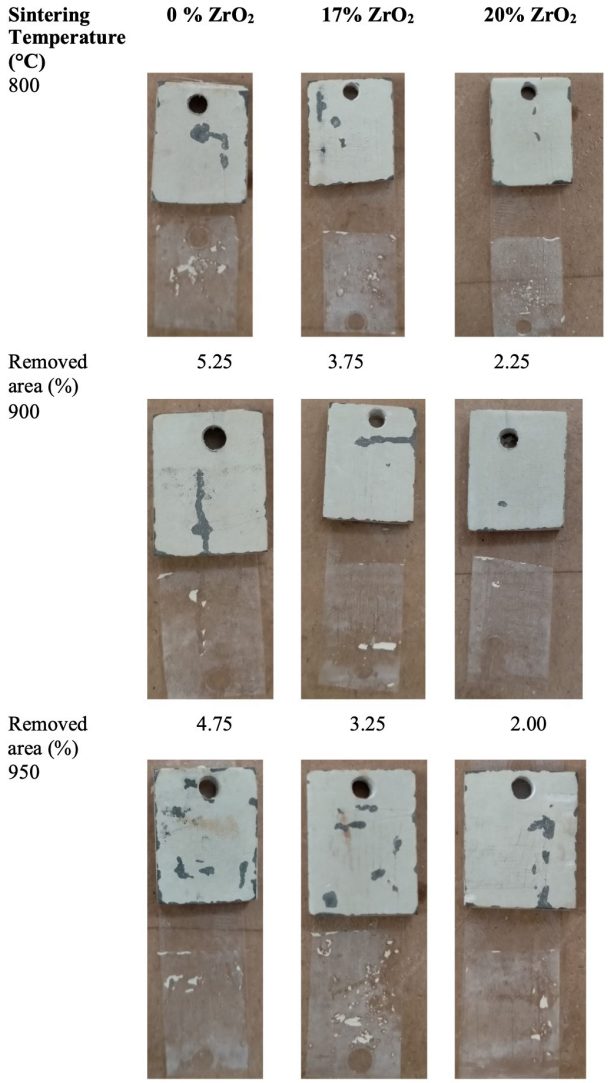


Figure 2. The removed area of the HA layer on the TI-6Al-4V ELI with the ZrO_2 additions at all the firing temperatures.

A line was made according to the ASTM D3359 standard [4]. Furthermore, the specimen was tested by making scratches on the test sample coating, followed by the installation of tape on all the scratched surfaces. The tape was pulled at an angle of 180° and the level of adhesion was tested on a scale of 0 – 5, where 0 indicated more than 65 % of the removed area and 5 indicated a removed area of 0 %.

The removed area is lower at 900 °C (4.75 %), because the percentage of removed area is at 4 on the scale (less than 5 %). The detachment of small flakes of the coating at the intersections of the cuts can be seen. The cross-cut area was not significantly greater than the 5 % affected area.

Contrary, the removed area is higher at 800 °C (5.25 %), and higher again at 950 °C (7.25 %). This is due to the percentage of the removed area is a 3 on the scale (5 to 15 %). The coating flaked along the edges and or at the intersections of the cuts. The cross-cut area was significantly greater than 5 %.

The removed area of the HA layer can be seen in Figure 2. The removed area of the coating with the addition of 20 % ZrO_2 is also lower than the addition of 17 % ZrO_2. This indicated that good results for the coating adhesion are obtained on the test specimen coating with the addition of 20 % ZrO_2 at a sintering temperature of 900 °C, where the removed area is 2 %. Meanwhile, with the variable sintering temperature, good coating adhesion was obtained at a temperature of 900 °C, followed by 800 °C and 950 °C.

From the picture above, there are visible cross-cut patterns in the coating, although there are some images that do not show the cross-cuts clearly, because the cut lines are too smooth. Admittedly, the dimensions of the substrate (10 mm × 10 mm × 4.0 mm) do not look the same. This is due to the difficulty in cutting the substrates whose dimensions are too small. This substrate was cut manually using a grinder with a saw blade.

The addition of ZrO_2 increased the adhesive of the Ti-6Al-4V ELI test specimens coated with hydroxyapatite. This is shown by the value of the low removed area when compared to the test specimens without the ZrO_2 addition. Good results with a value of 2 % removed area for the coating adhesion are obtained by adding 20 % ZrO_2 and sintering at 900 °C. Meanwhile, the adhesion of the test specimen coating without the addition of ZrO_2 had a removed area of 7.25 %.

This value was slightly better than the results of Gunawarman et al [4] using the EPD method, which had a removed area of 2.25 % at a voltage of 5V with a deposition time of 5 minutes. Furthermore, the amount of the ZrO_2 mass addition to the hydroxyapatite coating suspension also affected the adhesiveness. This showed that the addition of the ZrO_2 mass increases the adhesion of the coating. This is indicated by the value of the removed area at the addition of 20 % ZrO_2 (average 2.92 %), which is lower than the 17 % ZrO_2 (average 4.17 %).

The lower removed area of 2 % indicates that the adhesive bonding between the coating and the material is significantly high because ZrO_2 has good fracture resistance [4]. It also absorbs energy during the transformation from a tetragonal atomic arrangement to a monoclinic arrangement [9]. Also, the mineral can conduct good heat to the Ti-6Al-4V ELI because the coefficient of thermal expansion (CTE) of ZrO_2 (9.6×10^{-6} °C^{-1}) is very close to the CTE of Ti-6Al-4V ELI (8.6×10^{-6} °C^{-1}) [10]. The low CTE slows down the chemical reactions, which makes the coating to become crack resistant. Furthermore, ZrO_2 has corro-

sion-resistant properties because its electrons are neutral. It also has resistance to strong acids, such as sulfuric and nitric acid, which contributed to the corrosion resistance of ZrO_2 [20].

Contact angle of the coating

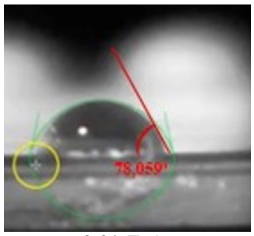
To further refine the analysis of the improvement in the layer adhesion bonding, this research also conducted a correlation approach to the wettability test method. In this case, the adhesion of the coating indicated by the value of the removed area is also compared with the value of the contact angle using ImageJ software. The low value of the coating contact angle indicates good adhesion. Materials with a special affinity for water, those it spreads across, maximising contact are known as a hydrophilic material [19]. Hydrophilic and hydrophobic materials are defined by the geometry of water on a flat surface, specifically, the angle between a droplet's edge and the surface underneath it. This is called the contact angle. If the droplet spreads, wetting a large area of the surface, then the contact angle is less than 90° and that surface is considered hydrophilic, or water-loving [19, 21]. Based on Table 3, the results show that the contact angle (Θ_C) of the coating is less than 90°. This shows that the coating is hydrophilic.

Table 3. Contact angle and removed area of the hydroxyapatite coating on the Ti-6Al-4V ELI treated by different wt. % ZrO_2 and variations in the sintering temperatures.

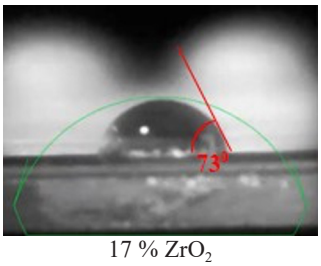
ZrO_2 (wt. %)	Sintering Temperature (°C)	Contact Angle Θ_C (°)	Removed Area (%)
0	800	79.315	5.25
	900	78.059	4.75
	950	80.130	7.25
17	800	74.135	3.75
	900	73.000	3.25
	950	75.815	5.50
20	800	61.120	2.25
	900	59.519	2.00
	950	63.015	4.50

The contact angle (Θ_C) of coating with the addition of ZrO_2 is lower than the test specimen without the addition. This shows that the coating with the addition of ZrO_2 has good adhesion compared to the test specimen without the addition of ZrO_2. The results of measuring the contact angle of the HA layer using ImageJ software can be seen in Figure 3.

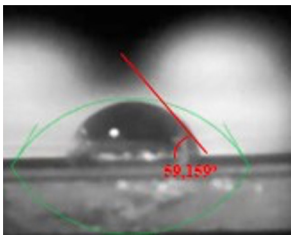
Good results are obtained with the addition of 20 % ZrO_2 with a value of Θ_C = 59.519°, followed by the addition of 17 % ZrO_2 (Θ_C = 73°) and without the addition of ZrO_2 (Θ_C = 78.059°). The value of the contact angle is less than 90° from this test specimen, which indicates the coating is hydrophilic and has good wettability. The comparison of the value of the removed area and the contact angle of the coating is shown in Figure 4.



0 % ZrO_2



17 % ZrO_2



20 % ZrO_2

Figure 3. The contact angle of the HA layer on the Ti-6Al-4V ELI with the ZrO_2 additions at all the sintering temperatures.

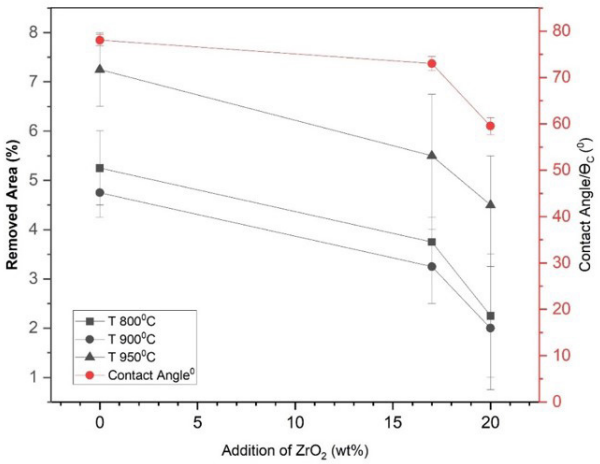


Figure 4. Removed area and contact angle of the hydroxyapatite coating on the Ti-6Al-4V ELI treated by the different wt. % ZrO_2 and sintering temperatures.

From the above picture, it can be seen that the value of the removed area is directly proportional to the contact angle of the HA layer. The value of the contact angle and removed area of the HA layer decreases when the test specimen has ZrO_2 added to the HA layer. Good coating adhesion has a small removed area and contact angle.

The HA layer with the addition of ZrO_2 has a lower removed area and contact angle compared to the test specimen without the addition of ZrO_2. This shows that the addition of ZrO_2 can improve the coating adhesion. The method of measuring the removed area and the contact angle of this layer is the first step in this research to see the correlation between the coating adhesion. Next, we will focus on researching the improvement in the adhesion of this layer with other methods.

Coating morphological characteristics

The adhesiveness of the coating, which is indicated by the value of the small removed area and the small contact angle of the layer, can also be seen from the surface photographs of the test specimen layer in Figure 5. The poor adhesion of the coating on the test specimen without the addition of ZrO_2, triggers the cracking on the coating surface. This occurs when the test specimen is heated to temperatures of 900 °C and 950 °C. On the other hand, no cracks were found in the test specimen with the addition of ZrO_2.

In Figure 5a-e, g, h, the test specimen heated at the sintering temperatures of 800 °C and 900 °C do not show any cracking in the coating, where an increase in the temperature gave a denser hydroxyapatite coating. However, a high sintering temperature can also cause the hydroxyapatite surface to crack because the titanium alloy passes through the α to ß transition temperature [9].

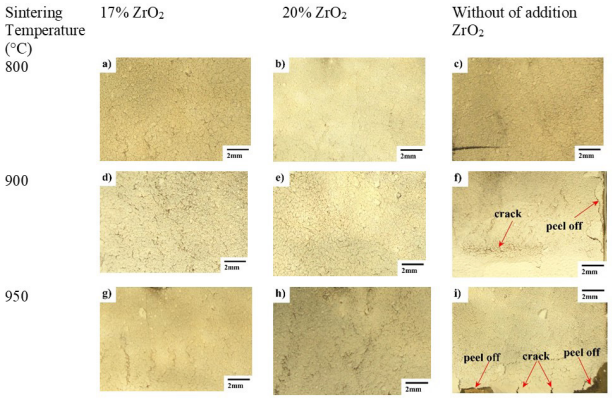


Figure 5. Surface photographs of the sintered hydroxyapatite coating layer on the Ti-6Al-4V ELI surface with the ZrO_2 additions at all the sintering temperatures.

These cracks are shown in Figure 5f, i, where the void coating and the loose bond at the interface (debonding) caused the coating to have micro-cracks [22], which were discovered in the test specimen coating without the addition of ZrO_2. This showed that sintering is required to obtain an increase in the adhesive strength between the coating on the surface of the material. Although high sintering temperatures can increase the coating compaction (densification) and reduce the porosity, it initiates the cracking by peeling off certain coating [22, 23].

The adhesion of the hydroxyapatite coating to the surface of the material is also affected by the sintering temperature. The results show that the coating adhesion at a sintering temperature of 900 °C is better than 800 °C as shown by the low removed area at 900 °C. Furthermore, an increase in the sintering temperature increases the coating adhesion because it hastened the diffusion of particles at the interface and triggered the diffusion of the bonding coating and material [4]. The coating adhesion is also influenced by the morphological characteristics of the thin layer and coating, while the hydroxyapatite accumulation on the surface (agglomeration) is minimal [24-26].

CONCLUSIONS

The addition of ZrO_2 to the hydroxyapatite coating layer increases the adhesiveness of the Ti-6Al-4V ELI surface coating. This is indicated by the lower value of the contact angle of the coating (hydrophilic) and smaller removed area as compared to those specimens without the ZrO_2 addition. With such surface properties of the hydroxyapatite coating layer, it is strongly expected to improve the osseointegration and reduce the inflammatory effect of the implants.

Acknowledgments

This research was funded by the Doctoral Dissertation Research Grant of the Ministry of Education, Culture, Research and Technology of the Republic of Indonesia with contract No. 104/E4.1/AK.04.PT/2021.

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