Materials Research Express

OPEN ACCESS

PAPER

Adhesiveness of TiO$_2$ PVD coating on electropolished stainless steel 17–4 PH orthodontic bracket

S Supriadi$^1$*, B Suharno$^4$, N K Nugraha$^2$*, A O Yasinta$^2$ and Dhyah Annur$^2$

1 Mechanical Engineering Department, University of Indonesia, Depok 16424, Indonesia
2 Metallurgy and Materials Engineering Department, University of Indonesia, Depok 16424, Indonesia
E-mail: sugeng@eng.ui.ac.id

Keywords: SS 17–4 PH, orthodontic bracket, electropolish, PVD, TiO$_2$, coating

Abstract

Performance of stainless steel 17–4 PH as the orthodontic bracket can be improved by titanium dioxide (TiO$_2$) coating. In order to produce a good quality of the coating layer, the substrate had to be smooth and free from any contaminants. The electropolishing method was used to clean bracket’s surface from oxides substances which formed during sintering by reducing its surface roughness. Bath temperature and electropolishing time were varied to 30 °C and 70 °C, for 15 and 25 min, respectively. Those differences in electropolishing condition would affect the final surface’s roughness of the substrate. The atmosphere during PVD was controlled using oxygen and argon gases with the flowing rate ratio of 10:90 sccm and 50:50 sccm, and these gases would affect TiO$_2$ coating mechanical properties. The lowest roughness of 0.99 μm and the highest roughness of 2.85 μm were obtained after electropolishing. The coating quality on the substrates with different roughness was assessed through coating adhesivity on the substrate by micro Vickers qualitatively. The results showed that the TiO$_2$ coating layer on the substrate with a lower roughness had better adhesivity rather than on the substrate with higher roughness.

1. Introduction

Aiming oral beauty and healthy, fix orthodontic bracket is currently preferable to treat malocclusion. However, a patient with orthodontic treatment often encounters dental problems such as enamel demineralization, or white spot lesions [1–3]. Patient’s oral environment and complex shape of the orthodontic bracket may induce the proliferation of pathogen microorganisms such as Streptococcus mutans and Lactobacillus acidophilus [4]. Among biomaterials, stainless steel is the most frequently chosen material for orthodontic bracket [5–7]. Despite its cost-effective and high corrosion resistance, the biocompatibility of stainless steel has remained an issue; hence it can cause an allergic reaction due to toxic metal ions dissolution such as nickel and chromium [7, 8].

Biocompatibility and antibacterial properties of stainless steel can be improved by surface modification such as titanium dioxide (TiO$_2$) coating. TiO$_2$ offers high chemical stability, corrosion resistance, and antibacterial properties [2, 9]. Recently, several techniques have been developed for metal surface coating; such as ion implantation [10], sol-gel method [11], chemical vapor deposition (CVD) [12], and physical vapor deposition (PVD) [13, 14]. Among them, PVD especially using magnetron sputtering offers excellence feature since it can modify the material’s surface properties without affecting the bulk’s properties [15].

It is essential to induce a strong adhesion of the thin film and the substrate to achieve a durable TiO$_2$ coating on stainless steel. A detachment of TiO$_2$ coating in orthodontic bracket might be dangerous for the patient. Several factors that could affect coating adhesiveness are substrate cleanliness, substrate roughness, contamination, excessive stress on the substrate’s surface, and bond strength between the coating layer and the substrate [16]. One factor that affects coating adhesiveness the most is substrate roughness [17]. Clean and smoother surface of the substrate provides better adhesion on the coating properties [18]. Thus, surface polishing is generally conducted before the coating process.
Due to irregular surface and small size of the orthodontic bracket, mechanical polishing and chemical polishing might be less effective than electropolishing. Electropolishing can be used to remove contaminants and to obtain the finer surface finish of the metal in a significantly shorter time [19]. Electropolishing is influenced by the type of the electrolyte and processing condition such as temperature and duration of the process [19]. Accordingly, this study is conducted to observe the effect of the electropolishing process as a pretreatment of TiO₂ coating on stainless steel orthodontic bracket which produced by metal injection molding (MIM) method. Bath temperature and electropolishing time were varied to show the relationship of the surface roughness and the adhesiveness of TiO₂ coating on stainless steel 17-4 PH orthodontic bracket.

2. Experimental method

2.1. Materials and manufacturing procedures

The material used to make the orthodontic bracket specimens in this study is 17-4 PH stainless steel feedstock which produced from Ryer, Inc. The orthodontic bracket was manufactured using the MIM method. Detailed MIM processing parameter was described in the previous research [20]. Afterward, each specimen was subjected to solvent debinding and thermal debinding which was described elsewhere [20, 21].

The as-sintered products were then polished mechanically using Kyngty mini tumbler to remove oxide layers that formed after the sintering process. After that, the brackets were subjected to electropolishing process. The electrolyte used for this process consisted of 60% H₃PO₄ + 20% H₂SO₄ + 10% H₂O + 10% Glycerin. The voltage and current density used were 5V and 0.7 A respectively. Carbon graphite was used as a cathode, and the bracket was used as an anode. There were four variation process in the electropolishing process; 30°C for 15 and 25 min, and 70°C for 15 and 25 min. Variation on the temperature was chosen according to the previous research [22]. These conditions are selected to observe effect of lower and higher electropolishing temperature on coating performance.

After electropolishing, TiO₂ was coated on bracket’s surface by Physical Vapor Deposition (PVD) magnetron sputtering method. Voltage and bias voltage used was 50 V and 50 V respectively, and the deposition time was 30 min. Two kinds of gases were used: oxygen and argon. The flow rate ratios of oxygen and argon (O₂: Ar) used in this study were 50:50 and 10:90 sccm.

2.2. Characterization

Macroscopic photographs of bracket’s surface were taken with Dynolite Microscope. The roughness of bracket’s surface was measured with Acretech Surfcom. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were carried out to observed surface morphology and also elemental composition. Coating adhesiveness was measured quantitatively via micro Vickers using a load of 50 gf and 10 s dwell time, to find composite hardness value and the indentation depth. SEM characterization was also done to observe coating adhesiveness qualitatively by inspecting the indentation mark on bracket’s surface.

3. Results and discussion

3.1. Electropolishing surface treatment on SS 17-4 PH sintered bracket

Electropolishing process aimed to remove the oxide layer, to lower the roughness of the brackets and to increase the bracket’s brightness until the mirror-like finish. Figure 1 showed the comparison of brackets with different surface, the as-sintered (figure 1(a)), mechanically polished (figure 1(b)) and electropolished at 30 °C for 25 min (figure 1(c)). The as-sintered bracket showed a surface covered by an oxide layer in dark and blackish colour, while the mechanically polished bracket showed lessened black oxide layer but showed many scratches. In contrast, the electropolished bracket showed a cleaner, bright and an oxide-free surface.
During electropolishing, the electrolyte colour transformed from transparent into yellowish green (figure 2). It happened due to a dissolution metal ion phenomenon from the anodic surface during electropolishing. The metal ions were Fe$^{3+}$, Cr(IV), Ni$^{2+}$, and Ni$^{6+}$, the yellowish color was from Cr(IV), and the green color was from Mo(IV) [23].

The viscous layer would play a crucial role in the electropolishing by giving Ohmic resistance to the metal surface. In the rough surface, there would be a height difference of the surface between the peak and the valley. The viscous layer would also give a different thickness, which promoted the different ohm resistance, resulted in a lower resistance of the peak area and a higher resistance on the valley area. As a consequence, when the electrical current flowed, the peak area would be dissolved faster because the electrical current was higher [24]. This mechanism makes the rough surface becoming a smooth surface.

3.2. Effect of electrolyte temperature and electropolishing time towards the surface roughness of SS 17-4 PH orthodontic bracket

Macro photos of the bracket’s surface are depicted in figure 3. According to figures 3(a)–(b), some scratches were found on the bracket after mechanical polishing, but scratches on the bracket decreased significantly or entirely removed after electropolishing at 30 °C for 15 min (figures 3(c)–(d)). When the electropolishing time reached 25 min, it reduced the surface roughness and also increased the brightness (figures 3(e)–(f)). In contrast, electropolishing at 70 °C for 15 and 25 min (figures 3(g)–(j)) tend to increase the surface roughness.

More detailed analysis on the surface roughness of the orthodontic bracket is shown at the figure 4. and table 1. The orthodontic bracket is compared with the commercial bracket and also the mechanically polished bracket. It was shown that the commercial bracket had the lowest surface roughness (0.63 μm). Likewise, the surface roughness measurement showed that different processing temperature and time in the electropolishing process gave a different surface roughness. The lower surface roughness was reached by electropolishing process in the low temperature (30 °C), while the higher surface roughness was obtained by electrospinning process in the high temperature (70 °C). Furthermore, this result indicated that the electropolishing process in 30 °C would give a better surface roughness than the mechanically polished bracket (1.48 μm).

Further, the microstructure of the bracket’s surface was observed in the SEM and shown in figure 5. From figures 5(a)–(b), the mechanically polished bracket was full of scratches. The scratches were formed because of the friction of the bracket with the abrasive media (metal buckshot). Additionally, porosity was also detected at the surface as a defect of the sintering process [23]. After electropolishing, the scratches on bracket’s surface were fully removed as shown as figures 5(c)–(f). However, some porosity remained on the surface. SEM images revealed the electropolishing at 30 °C produced a smoother surface than the electrospinning at 70 °C. Moreover, increasing electropolishing time from 15 min to 25 min was proven to decrease the surface roughness and also to reduce the size of the porosity.
Figure 3. Bracket’s surfaces comparison with different surface treatments (a)–(b) mechanically polished, Electropolished (c)–(d) 30 °C for 15 min, (e)–(f) 30 °C for 25 min, (g)–(h) 70 °C for 15 min (i)–(j) 70 °C for 25 min.

Figure 4. Bracket roughness comparison.
On the contrary, electropolishing at 70 °C showed a tendency of increasing surface roughness by creating more porosity and also deeper porosity. Moreover, some pitting initiation areas were shown after electropolishing at 70 °C for 15 min. When the electropolishing time was increased for 25 min, the bigger and deeper pitting hole was formed.

Figure 6 showed chemical composition of bracket’s surface after being mechanically polished and electropolished. After mechanically polished (figure 6(a)), oxygen content on bracket’s surface reached 21.2 wt%. Conversely, electropolished reduced the oxygen content up to 4.8 wt%, 5.8 wt% and 3.7 wt% (figures 6(b)–(d)). This decline of oxygen content more likely means the electropolishing process could remove the oxide layer from the bracket’s surface. In another study, the electropolishing can be done in two steps to form passive layer which might increase the oxygen content [25], however this study only focus on levelling and flattening the surface before the PVD coating process.

EDS analysis also detected phosphor (P) in the electropolished bracket. Phosphor could be traced because the electrolyte used in this process contained H₃PO₄ and might form an oxide compound on bracket’s surface [26]. The electropolished bracket (at 70 °C for 25 min), also showed the trace of Chlorine (Cl₂) about 0.2 wt%.

| Electropolishing parameter (Temp–Time) | 30 °C- 15 min | 30 °C- 25 min | 70 °C- 15 min | 70 °C- 25 min |
|---------------------------------------|--------------|--------------|--------------|--------------|
| Ra (μm)                               | 1.12         | 0.99         | 2.71         | 2.85         |

Table 1. Surface roughness ($R_a$) of each electropolishing parameter.

Figure 5. SEM characterizations bracket’s surfaces from different surface treatments: mechanically polished (a)-(b), electropolished at 30 °C for 15 min (c), electropolished at 30 °C for 25 min (d), electropolished at 70 °C for 15 min (e), and electropolished at 70 °C for 25 min.
Contamination of Cl₂ may also be caused by the use of H₃PO₄ which contained 2ppm of Cl₂. Further, Cl₂ could lead more pitting formation on bracket’s surface in the electropolishing especially in high temperature.

3.3. Electropolishing mechanisms on different temperature and time

SEM and EDS characterizations from the electropolished brackets show how the processing temperature and time in the electropolishing influenced the surface roughness. In this study, electropolishing at 30 °C would create a smoother surface, electropolishing at 70 °C would increase the surface roughness.

There were two primary mechanisms of electropolishing macro polishing and micro polishing [27]. Macro polishing was aimed to level the rough surface which had different heights; the process was removing the big sized molecules >1 μm from the surface. Micro polishing was intended to increase the brightness and polish the surface to create a mirror like-finish. The process was to remove small sized molecules <1 μm from the surface. The roughness of the electropolished bracket at 30 °C for 15 min was higher than 25 min. When the electropolishing time was 15 min, the process that might be happened was macro polishing only, but when the
Electropolishing time was 25 min, both processes had happened so that the roughness would be lower and the brightness would be higher.

Figure 7 illustrates the electropolishing mechanism that happened at 30 °C. It was shown that before the electropolishing, the surface full of scratches, indicated by some high peaks and rough holes. After the electropolishing process, the sharp peaks became flattened and a prolonged electropolishing time made the holes smaller.

Electropolishing at high temperature was much more complex and could increase the surface roughness. In high temperature, the viscous layer would not be formed uniformly nor evenly because of thermal motion which influenced by high temperature. Metal ions and accepot ions molecules would not be able to make a stable layer but could only form clustering on the metal surface. The viscous layer would be formed inhomogeneously. Hence, it would make a significant difference in metal dissolution and roughness [22].

High temperature would also cause oxygen evolution on the anode because as temperature increased there would be an increase in current density [24]. Oxygen bubble would form on the anode and moved toward electrolyte. Because there was a difference of surface tensions between the viscous layer and the electrolyte, the bubble would burst and destroy the viscous layer. This phenomenon is called 'Broken Bubble Tunneling Effect' (BBTE) [28]. The area of the destroyed viscous layer would only be covered by a thin viscous layer metal, making it susceptible to be locally attacked with electric current and dissolve faster; hence it would form a lot of small pitting holes.

Figure 8 showed the mechanism of electropolishing at 70 °C. The first stage of electropolishing is the formation of a non-stable viscous layer and the bubble on top of the viscous layer. Later, the bubble burst and destroyed the viscous layer, resulting in pitting formation. The longer the process, more bubbles would be formed, and the BBTE effect would be worsened causing the pitting holes would be more in-depth and broadening.

3.4. Effect of bracket surface roughness on TiO2 coating adhesiveness

After the electropolishing, all the brackets were coated with TiO2 via physical vapor deposition (PVD) method. The differences on oxygen gas flow used in this study, 50 and 10 sccm, slightly affected the mechanical properties of the TiO2 layer formed on the bracket. The PVD process which used a higher oxygen flow rate would produce slightly lower hardness TiO2 layer. It was because the higher oxygen rate which has higher deposition energy would produce bigger TiO2 crystal [29]. The resulted image of the substrate and the coating is depicted in figure 9.

Figure 9 showed the PVD has successfully coated TiO2 on the stainless steel surface. The thickness of the coating was 15.6 ± 6.6 and 8.2 ± 1 μm for 50 and 10 sccm oxygen flow rate respectively.

The adhesiveness of TiO2 coating was assessed quantitatively and qualitatively by micro Vickers. The quantitative assessment would be measuring the coating hardness of TiO2, while the qualitative evaluation would be analyzing the indentation made on the surface of the orthodontic bracket after micro Vickers testing. The evaluation of coating adhesion was based on the proposed model in the literature [30], by assuming the substrate and the coating as a composite material. Two requirements must be fulfilled to do the coating assessment. First, the thickness of TiO2 film should be more than 0.2 μm [30]. Second, the penetration depths is suggested of the order of 0.07–0.2 times the coating thickness. Below that range, hardness value represent the intrinsic coating hardness [31]. Over that range represents coating and substrate hardness or called as composite hardness.
The indentation depth according to the graph in figure 10 showed the lowest value was 2.14 μm, and the highest value was 2.8 μm. The indentation depth in this study is more representative for the specimen with 50:50 O2:Ar flow rate. For specimen with 10:90 O2:Ar flow rate, the indentation was deeper than 0.2 of the coating thickness. It means, the plastic deformation of the substrate might also affected [30]. According to ratio between penetration depth and coating thickness two conditions shows similarity in hardness value.

Adhesiveness of the coating layer correlates with composite hardness (Hc) [31]. Composite hardness is the hardness of coating and substrate mixture. The higher Hc of material would in line with a higher critical load of the scratch test. High critical load suggests the coating has high adhesiveness. In this study, surface roughness (Ra) (as shown in table 2) were compared to Hc and also the indentation depth (figures 10(a)–(b)). When the surface roughness is high, the Hc would be low. The highest Hc of TiO2 with 50 and 10 sccm oxygen flow rate was 410.71 HV and 419.99 HV respectively, which coated on the smoothest surface with 0.99 μm roughness.
While the lowest Hc for TiO2 coating, in the 50 and 10 sccm oxygen flow rate were 242.47 and 245.81 HV (Ra = 2.85 μm), which coated on the roughest surface. The results indicated that the composite hardness of coating would be higher if the substrate surface were smooth [32].

Qualitative assessment was performed based on the analysis of the indentation crack in the coating layer, following the criteria from the previous research [32]. Typical indentation cracks on each specimen and their analysis were summarized in table 2 and figure 11.

From figures 11(a)–(b), the electropolished surface at 30 °C for 15 min figure 11 a showed modes of delamination and weak radial crack. While, figures 11(c)–(d), the indentation showed no evidence of crack delamination. Moreover, from figures 11(e)–(f), the electropolished surface at 70 °C for 15 min, it showed some cracks, which means a medium radial crack. Lastly, from figures 11(g)–(h), the electropolished surface at 70 °C for 25 min, the indentation cracks of TiO2 were big, deep, and also included delamination, showed a strong radial crack. In such a way, it can be concluded that the adhesiveness of the coating can be increased by providing a smooth surface.

The qualitative assessment of coating adhesiveness is in an agreement with the quantitative assessment whereas smoother surface would result in better adhesiveness of TiO2 coating. On the rough substrate, the surface had different contour and different heights, there was ‘peaks’ and ‘valleys’ along the surface. If the rough
surface was coated, the peaks area would give localized stress concentration to the layer which would make coating layer easily deformed and detached from its substrate [33]. Therefore, electropolishing process should be optimized for a better coating process.

4. Conclusion

Electropolishing could be used to clean SS 17-4 PH orthodontic bracket and to reduce the surface roughness. However, the electropolishing temperature should not be too high. The higher temperature of electropolishing is increasing the possibility to get such a rough surface. The most effective condition to achieve smooth and bright surface is to electropolish the brackets at lower temperature in an extended period, in this study at 30 °C.
for 25 min. Surface roughness also correlates with coating adhesion, if the surface roughness increased then the adhesion of coating would be decreasing.

**Acknowledgments**

This research was financially supported by Universitas Indonesia through Hibah QQ 2019.

**ORCID iDs**

S Supriadi [https://orcid.org/0000-0001-8153-4036](https://orcid.org/0000-0001-8153-4036)

N K Nugraha [https://orcid.org/0000-0003-2479-6771](https://orcid.org/0000-0003-2479-6771)

**References**

[1] Liu J, Lou Y, Zhang C, Yin S, Li H, Sun D and Sun X 2017 RSC Advances, 7 43938–49
[2] Cao S, Liu B, Fan L, Yue Z, Liu B and Cao B 2014 Appl. Surf. Sci. 309 119–27
[3] Shah A G, Shetty P C, Ramachandra C, Bhat N S and Laxmikanth S 2011 The Angle Orthodontist. 81 1028–35
[4] Baby R D, Subramaniam S, Arumugam I and Padmanabhan S 2017 Am. J. Orthod. Dentofacial Orthop. 151 678–84
[5] Fatani E J, Almutairi H H, Alharbi A O, Alnakhli Y O, Divakar D D, Alkheraif A A and Khan A A 2017 Microb. Pathog. 112 190–4
[6] Zhang M, Liu X, Shang H and Lin J 2019 Surf. Coat. Technol. 362 381–7
[7] Deguchi T, Ito M, Obata A, Koh Y, Yamagishi T and Oshida Y 1996 J. Dent. Res. 75 1491–6
[8] Elia N 2019 Materials, 12 407
[9] Yuan X-S, Wang Y, Cao L, Cao B-C and Liang J 2015 Corrosion 71 784–94
[10] Thamigajaul K, Elayaraja K, Magudapathy P, Mudali U K, Nair K G M, Sudarshan M, Krishna J B M, Chakraborthy A and Kalkura S N 2013 Ceram. Int. 39 3027–34
[11] Curkovič L, Ćurkovič H O, Salopek S, Renjo M M and Segota S 2013 Corros. Sci. 77 176–84
[12] Hausbrand R, Bolado-Escudero B, Dhont A and Wielant J 2012 Corros. Sci. 61 28–34
[13] Zalnezhad E, Sarhan A A and Hamdi M 2013 The International Journal of Advanced Manufacturing Technology 68 415–23
[14] Perez A, Billard A, Rebére C, Berziou C, Touzain S and Creus J 2013 Corros. Sci. 74 240–9
[15] Zalnezhad E, Hamouda A, Faraji G and Shamshirband S 2015 Ceram. Int. 41 2785–93
[16] Koski K, Holsä J, Enroult J and Rouzaud A 1996 Surf. Coat. Technol. 80 195–9
[17] Takadoum J and Bennani H H 1997 Surf. Coat. Technol. 96 272–82
[18] Navabpour P, Ostovarpour S, Tattershall C, Cooke K, Kelly P, Verran J, Whitehead K, Hill C, Raulio M and Priha O 2014 Coatings. 4 433–49
[19] Lin C-C and Hu C-C 2008 Electrochim. Acta. 53 3356–63
[20] Supriadi S, Suharno B, Hidayatullah R, Maulana G and Baek E R 2017 Solid State Phenom. 266 238–244
[21] Supriadi S, Ferdian D, Maulana G, Hidayatullah R and Suharno B 2018 Mater. Sci. Forum. 266 200–208
[22] Lin C-C, Hu C-C and Lee T-C 2009 Surf. Coat. Technol. 204 448–54
[23] Suharno B, Ferdian D, Saputro H R, Suharno L P, Baek E R and Supriadi S 2017 Solid State Phenom. 200–208 231–237
[24] Yang G, Wang B, Tawfik K, Wei H, Zhou S and Chen G 2017 Surf. Eng. 33 149–66
[25] Stables M, Sevior R, Bowfield A, Unsworth P and Weightman P 2008 Report on the Current Surface Characterisation Research Project for the UKRF Cavity Development Programme [https://pdfs.semanticscholar.org/08c3/05de98b258e8f2c2f9cbccc227892e6735889.pdf?_ga=2.33343948.73450200.1561474921-183541690.1561474921](https://pdfs.semanticscholar.org/08c3/05de98b258e8f2c2f9cbccc227892e6735889.pdf?_ga=2.33343948.73450200.1561474921-183541690.1561474921)
[26] Nazneen F, Galvin P, Arrigan D W, Thompson M, Benvenuto P and Herzog G 2012 J. Solid State Electrochem. 16 1389–97
[27] Pendyala P, Bobji M and Madras G 2014 Tribology Letters. 55 93–101
[28] Lee S-J, Chen Y-H and Hung J-C 2012 Int. J. Electrochem. Sci. 7 12495–12506 [http://www.electrochemsci.org/papers/vol7/712495.pdf](http://www.electrochemsci.org/papers/vol7/712495.pdf)
[29] Jonsson B and Hogmark S 1984 Thin Solid Films 114 257–69
[30] Puchi-Cabrera E 2002 Surf. Coat. Technol. 160 177–86
[31] Ichimura H and Rodrigo A 2000 Surf. Coat. Technol. 126 152–8
[32] Sivitski A 2010 Sliding Wear of PVD Hard Coatings: Fatigue and Measurement Aspects (TUT Press.)
[33] Subramanian C, Strafford K N, Wilks T P, Ward L P and McMillan W 1993 Surf. Coat. Technol. 62 529–35