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MICROSTRUCTURAL, SURFACE ROUGHNESS AND WETTABILITY OF TITANIUM ALLOY COATED BY YZP-30WT.% TiO_2 FOR DENTAL APPLICATION

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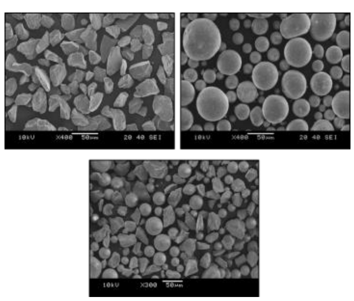
Graphical abstract



Abstract

Various roughness and surface topography of titanium coated ceramic material have been developed and used in clinical trials especially in a medical implant. The present work aimed to investigate the phase and microstructural of the yttria stabilized zirconia (YZP) coating reinforced titania (TiO_2) and its effects on wettability for dental implant application. Plasma spray technique was used to prepare the pure YZP and YZP-30 wt.% TiO_2 coatings. The titanium alloys coated with YZP/TiO_2 were investigated through scanning electron microscopy (SEM) analysis, roughness measurements, and contact angle analysis. The SEM analysis demonstrated a distinguished lamellae structure of YZP and TiO_2 in the coating. Instead of low wettability, the YZP-30 wt.% TiO_2 ceramic coating demonstrated high porosity and surface roughness (7.97±0.4 μm) than the pure YZP coating (7.06±0.9 μm) that is beneficial for cell growth and attachment.

Keywords: Coatings, zirconia, roughness, contact angle, dental implant

Abstrak

Pelbagai kekasaran dan mikrostruktur bagi titanium bersalut bahan seramik telah dibangunkan dan digunakan dalam percubaan klinikal terutamanya dalam implan perubatan. Kajian ini bertujuan untuk menyelidik kesan titania (TiO_2) ke atas ciri-ciri mikrostruktur salutan zirkonia separa stabil (YZP) untuk implan pergigian. Kaedah semburan plasma digunakan untuk penghasilan salutan tersebut. Mikrostruktur, komposisi fasa dan topografi permukaan masing-masing ditentukan melalui SEM, pengukuran kekasaran dan pengukuran sudut sentuh. Analisis mikrostruktur menunjukkan perbezaan ketara struktur lamellar bagi YZP dan TiO_2 di dalam salutan. Walaupun mempunyai sifat kebolehbasahan rendah, salutan YZP/TiO_2 mempamerkan sifat keliangan dan kekasaran permukaan yang lebih tinggi (7.97 ± 0.4 μm) berbanding salutan YZP (7.06 ± 0.9 μm) seterusnya amat bermanfaat bagi pelekatan dan pertumbuhan sel.

Kata kunci: Salutan, zirconia, kekasaran, sudut sentuh, implan pergigian

1.0 INTRODUCTION

Due to superior properties like excellent biocompatibility, good in bioactivity, and high corrosion resistance[1], titanium alloys have been utilised in a dental implant. Surface topography has been focused recently in order to explore the capability of biomaterials for bone apposition [2], bioactivities, and cell adhesion on the titanium alloys surface [3]. A study of producing a rough surface via a variety of surface treatments was carried out to improve the bone to implant contact of the dental implant [4]. Plasma sprayed was used to fabricate a coating layer on Ti alloys to retain the mechanical properties of the substrate as well as to get the advantage of the coating strength. A YZP coating is bioinert and has a higher bond strength compared to pure HA coating [5] leads to provide a good bone apposition and osseointegration of implant [6]. In order to improve the early cell response [3] and cell adhesion [7] of a dental implant, a surface modification by plasma spray was done. Two key issues still need to be addressed with regard to the use of plasma spray coatings for dental implants; crack and delamination. Another issue to be considered is the bioinertness of YZP. Bioinertness materials can be explained by the weak interaction between the surrounding living tissues and the materials surface [8, 9]. Normally, the failures of osseointegration, as well as implant failure, were caused by the lack of bioactivity of these materials. Hence, the selection of compatible materials is crucial in order to increase the bioactivity properties of the dental implant. High bioactivity is an important determinant for osseointegration or also known as direct structural and functional connection between the living bone and the surface of dental implants, especially for a long-term success.

There are so many approaches that aim to solve the problems of plasma spray coating defects and bioinertness materials. One of them is an additive method which adds bioactive layers onto a material surface. Kim *et al*. [10] found that the addition of bioactive calcium phosphate to zirconia implant surface resulted in a faster bone regeneration and a good osseointegration. The only problem with the additive method was adhesion problems between the layer and the implant [11].

In a recent study [12], new composite ceramics by adding bioactive materials to a zirconia matrix confirmed that materials combining zirconia and titania had better cell compared to pure zirconia or titania. Moreover, many researchers [13, 14] showed that the presence of TiO_2 induced in vitro bone-like apatite formation and stimulated in vivo osteoconductivity. Apart from that, the wettability of the surface is one of the crucial factors that affect cell attachment on the implant surface. The low contact angle indicated good wettability [15] and was favourable for implant surface [16-18] which may improve cell attachment as well as osseointegration. Surface wettability is characterised by measuring the hydrophilicity of the coating surface via water contact angle method. A previous study found that better wettability was achieved by roughening the surface and increasing the surface area [19]. The objective of this paper is to characterise and compare the morphological features and roughness value of the YZP and YZP/TiO_2 coating surfaces, in order to obtain the high-quality coated implants. The effect of TiO_2 content (30%) on the surface and wettability behaviour was also assessed. The main hypothesis of the study is by adding the TiO_2 to the YZP coating, it would result in a surface layer with morphological and other properties that are significantly better than the pure YZP coating layer.

2.0 METHODOLOGY

A commercial feedstock of zirconia partially stabilised with 3 mol % Y_2O_3 (YZP) and titania (TiO_2) powder (Inframat® Advanced Materials TM, USA) was used as the coating material. The mixed powders consisted of 70 wt.% YZP powders and 30 wt.% TiO_2 powders were prepared by milling and stirring in a ceramic jar with ethanol as the dispersant. The average after-milled powder size was found to be in the range of 45-90 μm. Titanium alloy (Ti6Al4V) plate (10mm x 3mm x 15 mm) was used as a substrate. Prior to plasma spraying, all substrate surfaces were pre-treated using alumina powder (24 mesh) grit blasting to provide a rough surface for better mechanical bonding between the coating and substrate. Zirconia partially stabilised (YZP) and titania (TiO_2) powders were then deposited on a substrate by using an atmospheric plasma spraying (APS) equipment (Sulzer Metco, Japan). After this the mixture of powder coating will be denoted as YZP/TiO_2 coating. The spraying parameters are summarised in Table 1.

In order to analyse the cross section area, the deposited coatings were sectioned by a diamond cutter; cold mounted in epoxy resin and polished up to 0.3 μm. The surface morphology and microstructure of both feedstock and as-sprayed coatings were observed by using SEM (JEOL, LA-6460, Japan). The SE mode with an acceleration voltage of 10-20 kV was selected for SEM analysis while the same magnification of x500 was selected for all the surface coatings for direct comparison. The phase composition was investigated by an XRD (Bruker, Germany) with CuK α 1 radiation operated at 40 kV and 30 mA. The scan rate of goniometer was set at 0.0058° s^{-1} over a 2θ range of 20-70°. The porosity was obtained according to a standard testing in ASTM E2109 [20]. The roughness measurements were obtained in microns using the mechanical profilometer (Formtracer SV-C3100) with measuring length = 8 mm and speed of 2.0 mms^{-1}. The contact angles were determined by a sessile drop method at 24 °C in an atmospheric pressure. The liquid used in the contact angle measurement was deionised water with a drop volume of 2 µL.

Table 1 Spraying parameters for as-sprayed YZP and YZP/TiO_2 coatings

Parameter	
Plasma gas/flow rate	Argon/42 L/min
Carrier gas/flow rate	Argon 7-8 L/min
Powder feed rate	10 g/min
Current	600 A
Spray distance	120 mm

3.0 RESULTS AND DISCUSSION

3.1 Phase Composition and Morphology

XRD pattern of both coatings was mainly composed by crystalline YZP. It is worth noting that the diffraction peaks of all the phases were constant sharp and high-intensity peaks. The crystallinity of YZP and YZP/TiO_2 coating was found to be 69.7% and 73.2%, respectively. XRD pattern of YZP coatings in Figure 1 is consistent with those of other studies [21, 22]. Tetragonal YSZ phase shows higher intensity compared to other compositions which proved that the YSZ as domain material in the coating. The X-ray diffraction peak of YZP/TiO_2 coating shows intense diffraction peaks at two values of 28.2° and 37.8° corresponding the rutile phase of the TiO_2 present on the surface of the substrate and similar observation was reported [7] for titanium dioxide film earlier. The peak of $ZrTiO_4$ also detected for YZP/TiO_2 coating thus proved the reaction occurred between YSZ and TiO_2 [23].

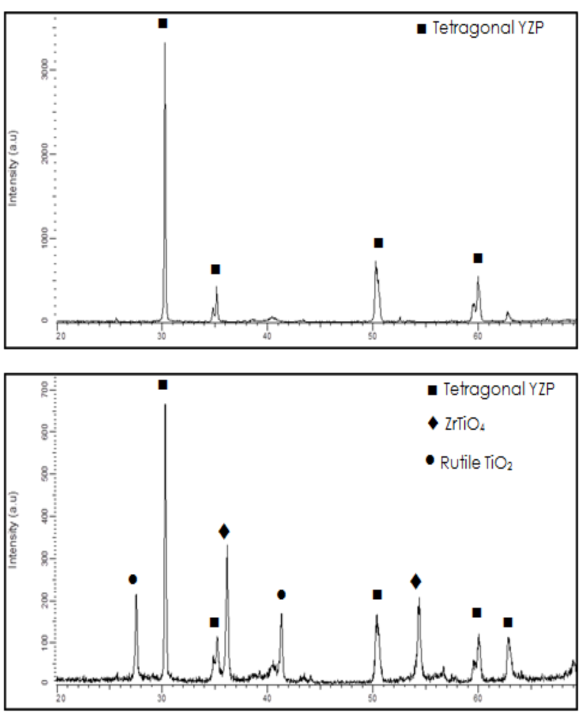


Figure 1 XRD patterns of YZP and YZP/TiO_2

As seen in Figure 2, starting powder of TiO_2 was angular and irregular in shape whereas YZP was spherical. Figure 3 shows the cross sectional of the plasma sprayed deposition. It was clearly noted that YZP coating displayed a typical rough microstructure with the presence of crack networks that were in agreement with previous findings [24].

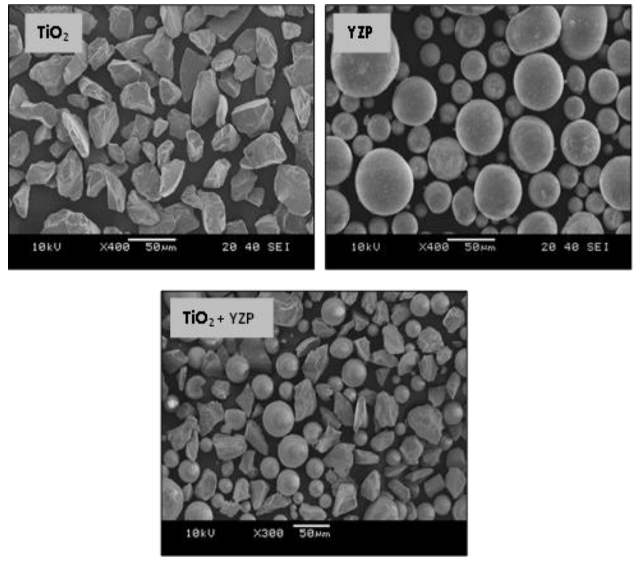


Figure 2 Morphology of a) TiO_2, b) YZP powder and c) mixture of both powders

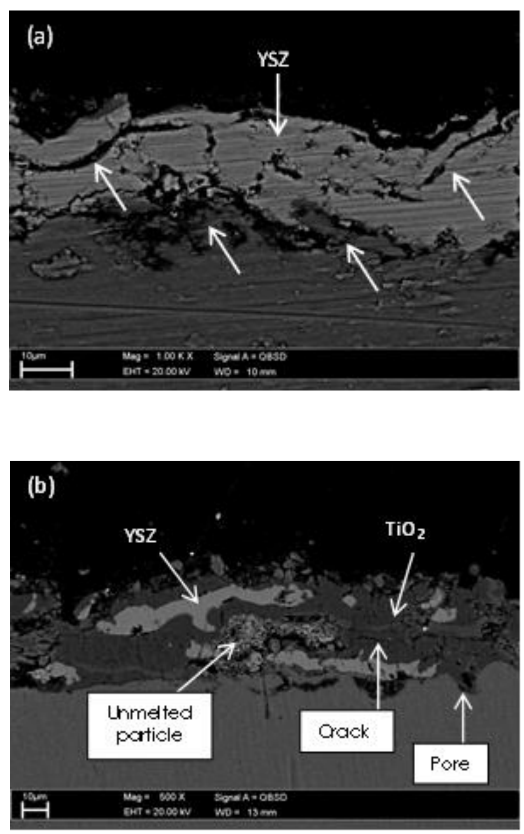


Figure 3 Cross section morphology of a) YZP coating b) YZP/ TiO_2 coating

As for YZP/TiO_2, the cross sectional view showed that the deposition was uniformly bonded onto the substrates with a thickness between 30 – 50 µm. Regardless of YZP/TiO_2 coatings; the surface microstructure is coarser (Figure 4b) and shows the presence of macro porosity and unmelted YZP particles. Additionally, the cross sectional view showed the presence of cracks (as shown by the white arrow in Figure 3a) and may cause the coating to become weak mechanically. The existence of these cracks might be caused by rapid solidification which was formed by the mismatch thermal coefficient [6] of YZP and TiO_2 (10.5 × 10^{-6}/K and 11.8 × 10^{-6}/K).

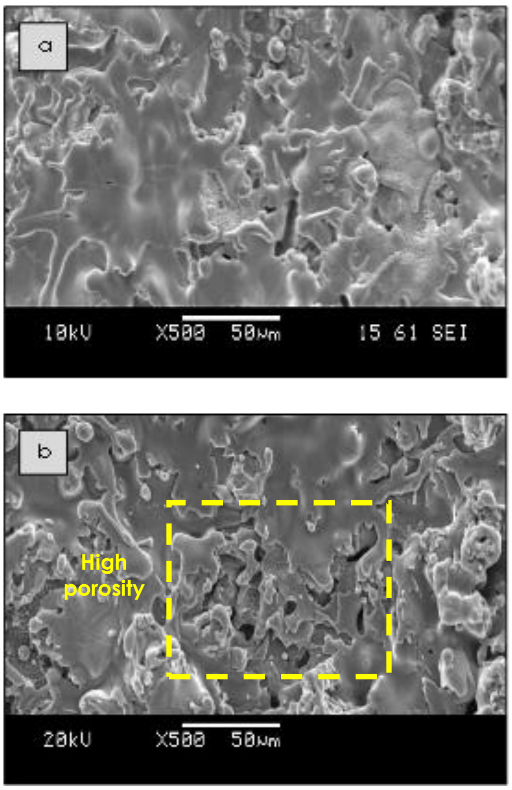


Figure 4 Surface morphology of a) YZP coating b) YZP/TiO_2 coating

On the other hand, the TiO_2 particles were completely melted along with unmelted YZP particles as depicted by the white particles embedded within the YZP/TiO_2 matrix as illustrated in Figure 2b. Generally, the long spray distance had frozen the semi-melted particles, thus, enough time for particles to melt before impinging onto the substrate was thought to be responsible for the unmelted particles [25]. Increasing the powder feed rate may cause unmelted particles to be conserved. Thus, some of the semi-molten or ought to melted powder particles were cooled before being impacted onto the substrate. Moreover, the high melting point for YZP (2,715 °C) compared to TiO_2 (1,843 °C) could be explained by the difficulty to reach complete powder melting.

3.2 Roughness

The measurements of surface roughness were carried out by using profilometer. It was found that YZP/TiO_2 coating possessed a rougher surface (is 7.98±0.4 µm) with a greater porosity of ~19% than the YZP (7.06±0.9 µm) alone. This can be clearly observed in Figure 4. According to Piconi and co-workers [8], significant micro-rough surfaces have the privilege in improving osseointegration for a 3-year term of dental implants. In fact, the roughness values were influenced by many factors such as the process of surface preparation, the presence of porosity, and cracks distribution within the coating. Based on the fact that the living cell tissue favoured the porosity between 1-10 µm [26], the present result suggests that the surface roughness of YSZ/TiO_2 coatings may improve the osteoblasts attachment as well as promote a good osseointegration.

Table 2 R_a and contact angle value

Composition	R_a (µm)	Contact Angle (°)	Porosity (%)
Ti alloys	0.12±0.3	20	-
YZP	7.06±0.9	90.1	~2
YZP/TiO_2	7.97±0.4	97.1	~19

3.3 Wettability

The behaviour of the surfaces analysed showed that wettability is reduced when TiO_2 was added. Both YZP and YZP/TiO_2 coatings exhibited hydrophobic surfaces with contact angles of 90.1° and 97.1°, respectively (refer to Figure 5). The YZP/TiO_2 coating exhibited a relatively less wettability but this surface was proper from the point of morphology. Previous studies [26, 27] claimed that a good osseointegration requires a proper surface topography with micropores with high surface roughness to support the cell attachment. This suggests that instead of low wettability, the YZP/TiO_2 ceramic coating demonstrated high roughness value, thus, beneficial for cell growth and attachment [16, 18]. The correlation between roughness and contact angle is displayed in Table 2. The current results are found to be in agreement with previous findings [28] with preferable properties of low wettability and high surface roughness. The topographical surface properties like roughness and wettability might modify the cell behaviour and alter the function of the cells in the initial mechanisms of osseointegration.

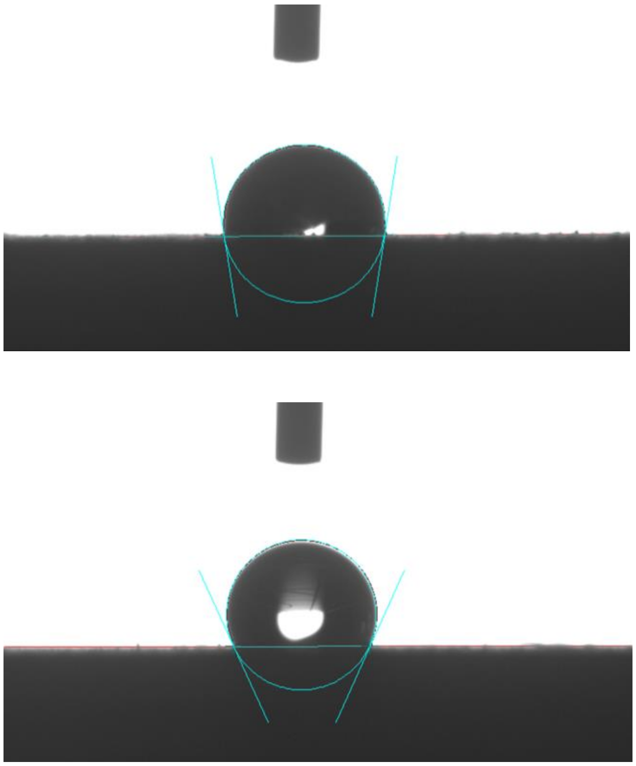


Figure 5 Water droplets of the coating surface a) YZP and b) YZP/TiO_2 coating

4.0 CONCLUSION

Plasma spray technique was successfully applied for the YZP- 30% TiO_2 coating on Ti alloy substrate. The XRD phase analysis revealed that both coatings constituted of highly crystalline YZP and TiO_2 phases. Even the chemical reaction between YZP and TiO_2 during the particle flight or coating formation is not clearly understood, but it seemed that the TiO_2 acted as a crack reducing agent for YZP and had a significant effect on the content of pore. The YZP/TiO_2 coating showed less wettability but the roughness value suggested that the surface may improve the osteoblasts attachment as well as promote a good osseointegration. However, further investigation is still needed to confirm the biocompatibility of these coatings. Still, these preliminary results might open the possibility of clinical applications in the dental industry.

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