

Characterisation of surface modification on titanium alloys for dental implant application

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ABSTRACT – Titanium (Ti) and its alloys have been extensively applied as dental implant materials under load-bearing conditions due to their outstanding properties. The purpose of this paper is to investigate the effects of two types of surface modifications; acid etching and plasma spray coating on the surface finish of the titanium alloys. Acid etchings were carried out by varying the types of acids. In the plasma spray, a yttria stabilized zirconia (YSZ) was chosen as a coating material. All treated surfaces were characterised by an X-ray diffraction (XRD), a scanning electron microscope (SEM) and a roughness tester. It was noted that the coated surface with 7.78 μm was significantly rougher than the etched surface, ranging from 0.137 μm - 3.986 μm .

1. INTRODUCTION

Due to good properties in bioactivity, corrosion resistance [1] and biocompatibility titanium alloys has been utilised widely in dental implant industry. Topography is the favoured area that has been explored recently, especially for bone apposition and cell attachment around titanium implants [2]. Rough surface and micro pores have proved to enhance osseointegration rate [3]. An etching technique is carried out in removing the impurities or contaminants, which is also known as corrosion induced treatment that also produces the micropits on the surface for good mechanical adherence [4]. However, only a few types of acids can be successfully reacted on oxide surface which include hydrochloric (HCl), sulphuric (H₂SO₄) and fluoric (HF) [5]. On the other hand, plasma spray is used to deposit the alloys on the metallic substrate and at the same time, to take advantage of the coating strength and chemical reacting in cell growth. In this work, the YSZ coating is chosen for its bioactivity and it has higher bond strength compared to a pure HA coating [6], providing a good bone apposition and osseointegration of implant [7].

2. METHODOLOGY

In this work, two surface techniques were performed; acid etching and plasma spray. Disks of \varnothing 5

mm, 3 mm in thickness and plates of 15×10×3 mm of titanium alloys were prepared. Prior to the acid etching, a pre-treatment on the samples was performed [2]. The pre-treated disks were i) etched using a pure acid (H₂SO₄ or HF) and a combination of HCl+H₂SO₄ with an exposure time of 45 minutes for each treatment and ii) YSZ deposited by using an atmosphere plasma spraying (APS) equipment by Sulzer Metco, Switzerland. Optimum spray parameters are summarised in Table 1. The surface morphology of all samples was observed using the SEM and the phase composition via XRD was utilised. The roughness measurements were conducted by using a profilometer.

Table 1 Spray parameters for as-sprayed YSZ.

Plasma gas/flow rate	Argon/42 Lmin ⁻¹
Carrier gas/flow rate	Argon 7-8 Lmin ⁻¹
Powder feed rate	10 g/min
Current	600 A
Spray distance	120 mm

3. RESULTS AND DISCUSSIONS

3.1 Phase Composition

It was found that the XRD pattern of an untreated surface only consisted of high intensity peaks of titanium and its alloy. As for YSZ coating, the pattern was mainly composed by the crystalline YSZ with the presence of sharp and high intensity peaks. As for the etched surfaces, the peaks were due to the titanium hydride (TiH₂).

3.2 Surface Profiles

Figure 1 shows the surface morphologies with and without any acid etchants for 45 minutes exposure at room temperature. It was found that the H₂SO₄ etched samples experienced a grooved and non-uniform surface. A homogenous surface with sharp edges was observed after being exposed in a mixed acid involving HCl and H₂SO₄. An HF treatment had revealed a porous structure with irregular micropits which was beneficial for an osteogenesis [8]. The presence of micropits and micro-pores as in Figure 1 could enhance an early bone integration and the stability of the implant due to their

unique texture [4].

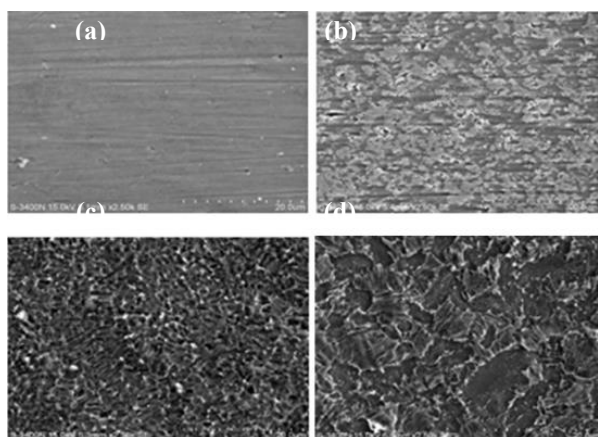


Figure 1 Surface morphologies of a) a controlled b) H₂SO₄ etched, c) HCl + H₂SO₄ etched and d) HF etched samples.

In Figure 2, the starting powder for the plasma spray is in a spherical shape form. The YSZ deposition exhibited rough surfaces with micro pores that mostly developed between splat boundaries. It was proven that the micro rough surface can improve osseointegration up to a 3 year period of a successful dental implant [9]. Typically, plasma spray coating surface is very porous. An open porosity of 15-40 % is believed to enhance the growth of bone cell inside the voids [10] on the surface for dental implants.

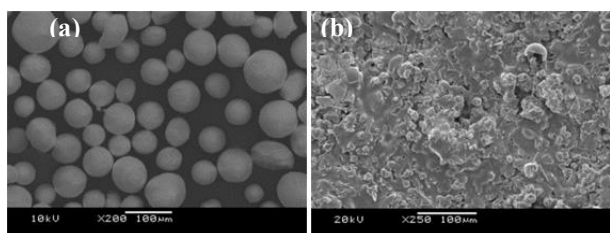


Figure 2 SEM micrograph of a)YSZ powders and b) deposited YSZ coating.

3.3 Surface Roughness

The original starting Ti alloys (without any surface modifications) was Ra = 0.124 μm. Table 2 shows the average roughness for all samples via these two techniques. The plasma sprayed YSZ coated surface had possessed the roughest surface providing a larger surface area that led to a higher survival rate of cell [11], better cell attachment and growth of osteoblasts [12]. As for the etching technique the roughness was also quite promising, particularly the HF etched samples.

Table 2 Average roughness for each type of modifications.

Surface modification	H ₂ SO ₄ etching	HCl + H ₂ SO ₄ etching	HF etching	YSZ coating
Roughness (μm)	0.137	0.161	3.986	7.78

4. CONCLUSION

It was strongly suggested that the etching process must be carried out with controlled condition involving temperature and concentration of the acid in order to obtain a compatible surface for a dental implant functionalities. Increasing the temperature may decreased the pore and roughness. As present result, dual acid etching (HCl + H₂SO₄) still cannot compete with single acid etching (HF) in term of roughness value, means the concentration act as control condition. However, a plasma spray method was preferred, resulting rougher surface than the etched ones.

5. REFERENCES

- [1] M. Browne and P. J. Gregson, "Effect of mechanical surface pretreatment on metal ion release," *Biomaterials*, vol. 21, pp. 385-392, 2000.
- [2] Y. Iwaya, M. Machigashira, K. Kanbara, M. Miyamoto, K. Noguchi, Y. Izumi, *et al.*, "Surface properties and biocompatibility of acid-etched titanium," *Dental Material Journal*, vol. 27, pp. 415-421, 2008.
- [3] M. Herrero-Climent, P. Lázaro, J. Vicente Rios, S. Lluch, M. Marqués, J. Guillem-Martí, *et al.*, "Influence of acid-etching after grit-blasted on osseointegration of titanium dental implants: in vitro and in vivo studies," *Journal of Materials Science: Materials in Medicine*, vol. 24, pp. 2047-2055, 2013.
- [4] X. Lin, L. Zhou, S. Li, H. Lu, and X. Ding, "Behavior of acid etching on titanium: topography, hydrophilicity and hydrogen concentration," *Biomedical Materials*, vol. 9, p. 015002, 2014.
- [5] A. Bagno and C. Di Bello, "Surface treatments and roughness properties of Ti-based biomaterials," *Journal of Materials Science: Materials in Medicine*, vol. 15, pp. 935-949, 2004.
- [6] H.-L. Huang, Y.-Y. Chang, J.-C. Weng, Y.-C. Chen, C.-H. Lai, and T.-M. Shieh, "Anti-bacterial performance of Zirconia coatings on Titanium implants," *Thin Solid Films*, vol. 528, pp. 151-156, 2013.
- [7] V. Sollazzo, F. Pezzetti, A. Scarano, A. Piattelli, C. A. Bignozzi, L. Massari, *et al.*, "Zirconium oxide coating improves implant osseointegration in vivo," *Dental Materials*, vol. 24, pp. 357-361, 2008.
- [8] P. T. de Oliveira, S. F. Zalzal, M. M. Beloti, A. L. Rosa, and A. Nanci, "Enhancement of in vitro osteogenesis on titanium by chemically produced nanopopography," *Journal of Biomedical Materials Research Part A*, vol. 80A, pp. 554-564, 2007.
- [9] S.-A. Cho and K.-T. Park, "The removal torque of titanium screw inserted in rabbit tibia treated by dual acid etching," *Biomaterials*, vol. 24, pp. 3611-3617, 2003.
- [10] E. Conforto, B. O. Aronsson, A. Salito, C. Crestou, and D. Caillard, "Rough surfaces of titanium and titanium alloys for implants and prostheses," *Materials Science and Engineering: C*, vol. 24, pp. 611-618, 2004.

- [11] Y. Hoon, S.-R. Noh, T.-Y. Im, E.-Y. Lee, H.-N. Jang, D. Dung Tran, *et al.*, "Comparison of surface roughness effects upon the attachment of osteoblastic progenitor MC3T3-E1 cells and inflammatory RAW 264.7 cells to a titanium disc," *International Journal of Oral Biology*, vol. 34, pp. 37-42, 2009.
- [12] F. Wang, L. Shi, W.-X. He, D. Han, Y. Yan, Z.-Y. Niu, *et al.*, "Bioinspired micro/nano fabrication on dental implant–bone interface," *Applied Surface Science*, vol. 265, pp. 480-488, 2013.