Research Repository UCD

Title	Wear resistance enhancement of the titanium alloy Ti6Al4V via a novel co-incident microblasting process
Authors(s)	Fleming, David, O'Neill, Liam, Byrne, Greg, Barry, Nicholas, Dowling, Denis P.
Publication date	2011-08
Publication information	Fleming, David, Liam O'Neill, Greg Byrne, Nicholas Barry, and Denis P. Dowling. "Wear Resistance Enhancement of the Titanium Alloy Ti6Al4V via a Novel Co-Incident Microblasting Process" 205, no. 21–22 (August, 2011).
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/5258
Publisher's statement	This is the author's version of a work that was accepted for publication in Surface and Coatings Technology. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Surface and Coatings Technology, 205 (21-22) 2011-08. http://dx.doi.org/10.1016/j.surfcoat.2011.04.076
Publisher's version (DOI)	10.1016/j.surfcoat.2011.04.076

Downloaded 2023-04-07T10:52:29Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)

© Some rights reserved. For more information

Wear Resistance Enhancement of the Titanium Alloy Ti6Al4V via a Novel Co-Incident Microblasting Process

David Fleming ^{a,*}, Liam O'Neill ^a, Greg Byrne ^b, Nicholas Barry ^b and Denis Dowling ^b

^a EnBIO, Fota Enterprise Park, Carrigtohill, Co. Cork, Ireland.

* Corresponding Author: Tel.: +353 (0)21 433 5339; fax: +353 (0)21 488 3618.

E-mail address: David.Fleming@cit.ie.

¹ Present Address: Centre for Advanced Photonics and Process Analysis (CAPPA), Cork Institute of Technology, Rossa Avenue, Bishopstown, Co. Cork, Ireland.

^b School of Electrical, Electronic and Mechanical Engineering, University College Dublin, Ireland.

Abstract

A study was undertaken to investigate the potential of a novel surface modification process to enhance Ti6Al4V wear resistance. The process consists of co-incident particle streams of abrasive and dopant materials which impact a substrate to create a modified surface. Al₂O₃ was chosen as the abrasive and Teflon, SiC and B₄C were investigated as dopants.

Al₂O₃-SiC and Al₂O₃-B₄C modified Ti6Al4V both exhibited increased surface hardness compared to the unmodified metal alloy. However, pin-on-disc tribometer measurements indicated that such hardening modifications exhibited no appreciable benefits in terms of wear resistance. On the other hand, Al₂O₃-Teflon modified Ti6Al4V demonstrated significantly reduced coefficients of friction and reduced wear rates under the same test conditions. Investigations suggest that although the Al₂O₃ abrasive is not incorporated into the coating, its presence is essential in order to achieve a wear resistant surface. Combinations of hard material (SiC or B₄C) modifications with a further layer of Teflon resulted in further enhancement of wear resistance as increased surface hardness was allied with similar low coefficients of friction.

In conclusion, a number of the surface modifications conducted have a beneficial affect on the wear resistance of Ti6Al4V. The process is also likely applicable to other metal/metal alloys such as CoCr, NiTi and stainless steels. Furthermore, the chemical-free nature and ambient temperature conditions concerned afford this process the potential to act as an attractive alternative to some of the more problematic high temperature approaches currently in use.

Keywords: CoBlast™, Ti6Al4V, wear, coefficient of friction, Teflon, silicon carbide, boron carbide.

1. Introduction

Titanium (Ti) and its alloys have been widely exploited in medical device manufacturing [1-9], automotive production [10], aerospace frame construction [1] and armoured material fabrication [11,12]. The superior specific strength [1-5] and corrosion resistance [1,2,4,5,10,13-17] of Ti-based alloys compared to many commonly available ferrous- and non-ferrous-based metals make them very attractive for such applications. One obstacle to even wider use of Ti-based alloys is the high energy cost associated with manufacture of high specification medical and aerospace grade materials [18,19]. Recently, however, a processing route for the commercial production of a lower grade of Ti (non-FDA approved material) has been developed [19]. This lower grade material should facilitate a wider adoption of the use of Ti, particularly in application areas outside of the medical device and aeronautical industries.

A number of authors have modified the surfaces of Ti-based alloys in order to enhance tribological properties via improving resistance to abrasive wear [4,20] and plastic shearing [4,21]. Johnson et al., for example, have improved the wear resistance associated with Ti6Al4V surfaces by using thermal oxidation to reduce the coefficient of friction to as low as 0.1 [10]. While this is a relatively low processing cost route for wear performance enhancement, it suffers the limitations as other thermal processes such as nitriding, carburisation and boriding, in that the high thermal stresses produced can lead to torsional twisting of substrates [4,22]. Similar problems are encountered with respect to thermal plasma coating techniques, as substrate surface structure damage can arise [23,24].

The recently developed CoBlast™ process, represented schematically in Figure 1, is a novel ambient temperature surface modification technique which enables application of coatings onto metal/metal alloy surfaces [25-27]. In this process, two compressed air streams, one containing an abrasive and the second containing the material to be coated, are directed at the same area on metal/metal alloy surface and the coating is deposited on the treated surface.

The use of this technique for the deposition of hydroxyapatite (HA) coatings has previously been reported [25-27], at which point it was shown that HA adhesion is enhanced by substrate roughening from abrasive particles. As the outermost oxide layer of the titanium substrate is removed the active titanium surface comes in contact with the HA particles resulting in formation of mechanochemical bonding [26, 27]. In this study the use of the CoBlast™ technique for the deposition of solid lubricant coatings, hard materials and combinations of both lubricant and hard metal coatings onto titanium alloy substrates is investigated for the first time. The solid lubricant coating investigated was Teflon, while the hard coating precursor powders studied were silicon carbide (SiC) and boron carbide (B₄C).

2. Materials and Methods

2.1 Ti6Al4V Surface Modifications

The titanium aluminium vanadium alloy substrate material investigated was Ti6Al4V. The deposition studies were carried out on 15 x 15 x 3 mm coupons cut from sheet material. These coupons were ground using P1200 grit SiC grinding paper to provide a uniform surface roughness ($R_a = 8.5 \times 10^{-2} \mu\text{m}$). Prior to coating all coupons were immersed in isopropyl alcohol, placed in an ultrasonic bath for 10 min and then dried in air. The CoBlast™ coating technique was then used to modify the surface of coupons. A detailed description of the process involved is provided elsewhere [26,27]. Alumina (Al_2O_3 , 100 μm average particle size, Comco Inc.) was the abrasive used for all modifications. The powders selected for the coating study were Teflon ($\text{C}_n\text{F}_{2n+2}$, 12 μm average particle size, Zonyl MP 1300, DuPont®), ‘green’ silicon carbide (SiC, 20 μm average particle size, F400, Electro Abrasives Corp.) and boron carbide (B_4C , 18 μm average particle size, F500, Electro Abrasives Corp.). The process conditions chosen for surface modifications involved use of MB 1500-29 nozzles (1.2 mm diameter circular nozzle, Comco Inc.) with 90 psi line pressure for all particle streams. The abrasive nozzle was set at 79° to and 17 mm above substrate coupons, with the dopant nozzle fixed at 75° to and 23 mm above the same plane (as depicted in Figure 1). A stage velocity of 12 mm.s^{-1} was employed throughout. The ‘microblasting’ of selected coupons with Teflon was also performed for the purpose of comparison with the CoBlast™ process. This involved directing the air jet containing the coating precursor at the Ti alloy surface in the absence of the alumina abrasive jet stream.

2.2 Sample Characterisation

A tabletop Hitachi TM-1000 SEM was used to examine surface morphologies of both unmodified and modified coupons. The elemental compositions at coupon surfaces were established via an Oxford Instruments SwiftED-TM EDS system. Coefficient of friction

quantification was performed on a TEER Coatings POD-2 pin-on-disc tribometer using an indexable 3 mm WC ball. Surface roughness and wear track characteristics were examined using a Wyko NT 1100 optical profilometer (50X objective, 1.0X field-of-view lens) operating in phase shift interferometry (PSI) mode. Contact angle measurements were obtained via the sessile drop technique using an OCA 20 video capture apparatus from Dataphysics Instruments. 1.0 μl drops of deionised water, ethylene glycol and diiodomethane were used for surface energy measurements via the OWRK (Owens, Wendt, Rabel and Kaelble) method [28]. Hardness assessment was carried out by CSM Instruments (www.csm-instruments.com) using a Nano Indentation Tester (NHT) in conjunction with the Instrumented Indentation Technique (IIT) [29]. The NHT test equipment was particularly apt for characterisation of the μm -thick modified surfaces fabricated throughout this work as it allowed for control of load and quantification of penetration depth and, thus, minimised influence of bulk Ti6Al4V on measurements. Tests were performed in air at 296 °C and 40% humidity using a Berkovich indenter at an approach speed of 2 $\mu\text{m}.\text{min}^{-1}$. Surfaces were loaded linearly at a rate of 50 $\text{mN}.\text{min}^{-1}$ to a maximum of 25 mN. Unloading at a rate of 50 $\text{mN}.\text{min}^{-1}$ commenced 15 s after arrival at maximum load. All hardness and elastic modulus results were obtained using the Oliver and Pharr method and via a supposed Poisson's ratio of 0.3 for estimations of the latter [30].

3. Results and Discussion

3.1 Lubricant Coatings

A baseline pin-on-disc study was carried out on the Ti6Al4V alloy substrate using 1,000 and 9,000 pin cycles at loads of between 1 and 10 N and angular velocities of between 1 to 19 cm s⁻¹. Friction coefficients in the 0.35 – 0.65 range and track depths of 11 – 172 µm were recorded, indicating that Ti6Al4V offers poor wear resistance in the native state.

Ti6Al4V coupons were initially modified via Teflon microblasting (i.e. without concurrent abrasive flow). The resulting surfaces were examined via SEM and, as demonstrated in Figure 2(b), the Teflon layer was deposited as a non homogeneous coating on the alloy surface. EDS established the presence of fluorine (74 At.%) and contact angle (CA) measurements confirmed the expected hydrophobic nature of these Teflon surfaces with an average water droplet CA of 112° [31]. This compared with a CA of just 47° for the unmodified Ti6Al4V. Wear evaluation of Teflon microblasted samples was performed using a pin-on-disc test load of 1 N at an angular velocity of 5.2 cm s⁻¹, and resulted in a friction coefficient estimation of approximately 0.6. This value is high compared to the 0.35 – 0.65 range determined for unmodified Ti6Al4V, indicating that Teflon microblasting did not yield any significant reduction in friction as would be expected for this solid lubricant material. Inspection of the wear tracks formed on Teflon microblasted surfaces showed complete removal of the Teflon coating, which would indicate poor adhesion to the Ti6Al4V. It was concluded from this study that microblasting alone did not yield Teflon layers with sufficient adhesion to be use as a solid lubricant coating on the metal alloy.

A second set of trials combined flows of Al₂O₃ abrasive with Teflon powder using the CoBlast™ process. The SEM micrograph provided in Figure 2(c) shows the surface morphology of an Al₂O₃-Teflon CoBlast™ modified Ti6Al4V coupon. The white material was confirmed as Teflon as a consequence of both high fluorine content (79 At.% detected via EDS) and high average water droplet CA (128°). This CA is significantly higher than the

value of 112° recorded for Teflon microblasted Ti6Al4V and may suggest that additional surface roughening combined with the natural hydrophobic properties of Teflon to produce a surface with an increased degree of water repellency. Profilometry confirmed this effect by demonstrating that Teflon microblasting led to a slight reduction in surface roughness ($R_a = 1.7 \times 10^{-2} \mu\text{m}$) relative to the unmodified metal alloy ($R_a = 8.5 \times 10^{-2} \mu\text{m}$), whereas Al_2O_3 -Teflon modification via CoBlast resulted in a significant increase in roughness ($R_a = 2.1 \mu\text{m}$). No evidence of Al_2O_3 abrasive contamination of the deposited Teflon layer was detected either microscopically or via EDS for CoBlast modified samples, which is in accordance with previous reports on the deposition process [26, 27].

Wear testing of Al_2O_3 -Teflon modified Ti6Al4V using the same 1 N load and 5.2 cm s^{-1} angular velocity test conditions as were employed for Teflon microblasted surfaces established a friction coefficient of approximately 0.1. This shows a considerable reduction compared with the 0.35 – 0.65 range obtained for unmodified Ti6Al4V surfaces, and is in line with the value reported by Johnson et al. for low friction oxidative treatments [10]. The performance of Al_2O_3 -Teflon modified surfaces were then investigated with pin-on-disc loads and angular velocities of up to 20 N and 23.6 cm s^{-1} respectively. The friction coefficient remained at approximately 0.1 for all test conditions, even after periods of up to 6,000 pin cycles. The wear rate of both unmodified and Al_2O_3 -Teflon modified Ti6Al4V surfaces was determined using the pin-on-disc equipment under conditions of 10 N load at 19 cm s^{-1} angular velocity for 1800 s. The resulting wear tracks of 1393 and 448 μm in width (172 and 17 μm in depth) respectively demonstrated a significant reduction in wear rate with the latter coating.

It is reported in the literature that blasting of metals with particulate materials can lead to work hardening and thus this increase in hardness can give rise to enhanced surface wear resistance [32,33]. Figures 4(a) and 4(b) show the wear tracks which formed on Al_2O_3 microblasted and Al_2O_3 -Teflon modified Ti6Al4V respectively as a result of various pin-on-

disc tests. The two tracks on the Al_2O_3 microblasted surface and the two inner tracks on the Al_2O_3 -Teflon modified surface were generated using identical test conditions (1 N load at $0.67/1.0 \text{ cm s}^{-1}$ angular velocity for 1800 s). The contrast in the physical appearances of these tracks demonstrates that the degree of wear experienced by the Al_2O_3 microblasted surface was significantly greater than for the Al_2O_3 -Teflon modified surface. This suggests that, although Al_2O_3 microblasting may have increased Ti6Al4V surface hardness in accordance with reports in literature, this did not translate into a positive effect in terms of wear resistance.

These results indicate that CoBlast™ processed Al_2O_3 -Teflon coatings exhibit superior wear resistance to samples processed with either Al_2O_3 or Teflon in isolation. The authors postulate that this enhancement may be due to impregnation of Teflon within the metal alloy surface with the energetic alumina bombardment producing a tribochemical bond formation between the substrate and Teflon particles, as similar effects have been reported for deposition of bioceramic dopants via CoBlast™ (26,27). This could lead to enhanced bonding of the dopant to the metal alloy relative to a microblasted approach, and may explain the enhanced wear resistance demonstrated by Al_2O_3 -Teflon CoBlast™ modified Ti6Al4V.

3.2 Hard Coatings

Independent CoBlast™ deposition studies were carried out for both SiC and B_4C powders in order to investigate if these hard ceramics could enhance the wear resistance of Ti6Al4V. SEM examination of Al_2O_3 -SiC and Al_2O_3 - B_4C modified Ti6Al4V showed treated alloy surfaces both exhibiting an almost identical appearance to that of the Al_2O_3 microblasted metal alloy (Figure 2(d)). This indicated that, in contrast to the Teflon powder, there was limited adhesion of either SiC or B_4C onto the alloy surface. EDS analysis demonstrated the presence of elemental Si on the surface of the Ti alloy, but only in low concentrations (16.2 At.%), again suggesting poor adhesion of these harder ceramic powders. Pin-on-disc analysis

of both $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified surfaces led to the measurement of friction coefficients comparable to those which were recorded for the unmodified metal alloy under the same test conditions (1 N load at 1 cm s^{-1} angular velocity for 1800 s), indicating that neither of these modifications demonstrated appreciable enhancement in wear resistance performance over Ti6Al4V in its native state.

While there appeared to be some degree of incorporation of SiC and B_4C dopants into Ti6Al4V, it would appear that bonding was insufficient to generate a positive impact on wear properties. Thus, a heat-treatment step was carried out in the case of both these ceramic dopants as a means of enhancing adhesion of the weakly attached powder grains. $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ CoBlast™ modified coupons were heat-treated under vacuum within an Ar atmosphere at 673°C for 6 hrs. The coupons were heated to 673°C from room temperature using a ramp rate of 2°C min^{-1} and cooled to room temperature post-treatment using the same rate. The Vickers Hardness of heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ (546 HV) and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ (563 HV) modified surfaces was found to have increased considerably in comparison to the unmodified metal alloy (468 HV). However, despite this increased surface hardness, the widths (and thus depths) of wear tracks resulting from pin-on-disc tests of heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified surfaces were similar to those which formed on unmodified Ti6Al4V, indicating no noticeable increase in wear resistance (refer to Table (i)).

3.3 Hard and Lubricant Combination Coatings

Since heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ coatings were found to enhance Ti6Al4V surface hardness, while $\text{Al}_2\text{O}_3\text{-Teflon}$ coatings decreased friction coefficient and increased wear resistance performance, it was proposed that a surface modification comprising a combination of both hard and solid lubricant properties may further improve wear resistance. Such coatings were prepared via addition of a microblasted Teflon layer over heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ CoBlast™ modified surfaces.

The successful deposition of Teflon on heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified Ti6Al4V surfaces was confirmed by both EDS (89 and 73 At.% F contents respectively) and CA analysis (average water droplet CA's of 112 and 122° respectively). The detection of Si atoms (2.4 At.%) during EDS in the case of Teflon coated heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ surfaces suggested that deposition of the lubricant layer via microblasting did not lead to removal of the SiC layer.

Teflon microblasted heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified Ti6Al4V surfaces were subjected to pin-on-disc wear testing under 10 N load at 19 cm s^{-1} angular velocity for 1800 s and both surfaces demonstrated friction coefficients of approximately 0.1, corresponding to the same low friction levels as were associated with $\text{Al}_2\text{O}_3\text{-Teflon}$ CoBlast modified Ti6Al4V. The improvement in Ti6Al4V wear performance from modifications comprising hardened surfaces with low surface energies was further verified from inspection of the tracks formed as a result of these pin-on-disc tests. While unmodified metal alloy surfaces showed an average track width of 1393 μm and $\text{Al}_2\text{O}_3\text{-Teflon}$ modified surfaces an average of 448 μm , their Teflon microblasted heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified counterparts demonstrated tracks with average widths of just 288 and 267 μm (depths of 7 and 6 μm) respectively.

Thus, the hard and lubricant combination Ti6Al4V modifications undertaken using CoBlast represented the highest degree of wear resistance enhancement encountered during this study. In fact, both Teflon microblasted heat-treated $\text{Al}_2\text{O}_3\text{-SiC}$ and $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ modified surfaces exhibited resistance to the sliding wear and frictional effects induced via pin-on-disc analysis for up to 280 s when tested with loads of 30 N and angular velocities of 44 cm s^{-1} , at which time coating failure occurred in each case and friction coefficients increased back to within the 0.35 – 0.65 range associated with the underlying bulk unmodified Ti6Al4V.

4. Conclusions

It was found that use of the CoBlast™ process to impregnate Ti6Al4V with fluorocarbons produced significantly enhanced wear resistance. The Al₂O₃ abrasive used in this process was found not to be incorporated into surfaces, but was nonetheless essential to produce optimum bonding between substrate and dopant. Attempts to increase Ti6Al4V wear resistance using either of the hard ceramic dopants SiC or B₄C was found to have no impact on wear performance despite measurable increases in surface hardness. Al₂O₃-Teflon modified surfaces on the other hand did demonstrate superior wear resistance when compared to the unmodified metal alloy by reducing the friction coefficient from within the 0.35 – 0.65 range to approximately 0.1. However, most impressively, Teflon microblasted over either heat-treated Al₂O₃-SiC or heat-treated Al₂O₃-B₄C modified Ti6Al4V not only achieved this same degree of friction coefficient reduction, but also dramatically decreased the width (and thus depth) of the wear tracks formed as a consequence of pin-on-disc testing. In short, CoBlast™ is established as a successful technology for the enhancement of wear resistance properties of Ti6Al4V.

References:

- [1] M. Niinomi, Sci. Technol. Adv. Mater. 4 (2003) 445-454.
- [2] S. Fukumoto, H. Tsubakino, S. Inoue, L. Liu, M. Terasawa, T. Mitamura, Mater. Sci. Eng. A 263, (1999) 205-209.
- [3] A. Choubey, B. Basu, R. Balasubramaniam, Mater. Sci. Eng. A 379, (2004) 234-239.
- [4] M. Geetha, A. Singh, R. Asokamani, A. Gogia, Prog. Mater. Sci. (2009) 397-425.
- [5] Y. Zhou, M. Niinomi, T. Akahori, H. Fukui, H. Toda, Mater. Sci. Eng. A 398 (2005) 28-36.
- [6] K. Maehara, K. Doi, T. Matsushita, Y. Sasaki, Mater. Trans. 43 (2002) 2936-42.
- [7] C. Boehlert, M. Niinomi, M. Ikeda, Mater. Sci. Eng. C 25 (2005) 247-252.
- [8] R. Kirby, S. Heard, P. Miller, I. Eardley, S. Holmes, J. Valve, J. Urology 148, (1992) 1192-1195.
- [9] R. LeGeros, R. Craig, J. Bone Miner. Res. 8-Supp2 (1993) 583-596.
- [10] R. Johnson, J. Eberhardt, 'Thermal Oxidation: A Promising Surface Treatment for Titanium Engine Parts', Transportation Program Oak Ridge National Laboratory, 2006.
- [11] R. Boyer, G. Werhard, E. Collings, Material Properties Handbook; Titanium Alloys, ASM International, 1994, pp. 347-360.
- [12] R. Boyer, Mater. Sci. Eng. A 213 (1996) 103-114.
- [13] J. Donachie, Titanium: A Technical Guide, second ed., ASM International, 2000, pp. 143.
- [14] W. Head, D. Bauk, R. Emerson Jnr., Clin. Orthop. 311 (1995) 85-90.
- [15] R. Namba, J. Keyak, A. Kim, L. Vu, H. Skinner, Clin. Orthop. 347 (1998) 261-267.
- [16] J. Jacobs, J. Gilbert, R. Urban, J. Bone Joint Surg. 80-A (1998) 268-282.
- [17] J. Galante, J. Lemons, M. Spector, P. Wilson Jnr., T. Wright, J. Orthopaed. Res. 9 (1991) 760-775.
- [18] E. Marsh, A Technological and Market Study on the Future Prospects for Titanium to the Year 2000, European Commission Joint Research Centre, Institute for Prospective Technological Studies, 1996.
- [19] G. Crowley, How to Extract Low Cost Titanium: A New Process for Titanium Extraction and Production Promises to Cut Costs and Expand Applications, Adv. Mater. Process 161 (2003) 25-27.
- [20] K. Bundinski, Wear 151 (1991) 203-217.
- [21] M. Long, H. Rack, Biomaterials 19 (1998) 1621-1639.

- [22] American Academy of Orthopaedic Surgeons, in: Survey presented at the Orthopaedic Research Society Annual Meeting, Orlando, Florida; Feb. 1995.
- [23] C. Alves Jnr., C. Guerra Neto, G. Morais, C. da Silva, V. Hajek, Surf. Coat. Tech. 194 (2005) 196-202.
- [24] X. Liu, P. Chu, C. Ding, Mater. Sci. Eng. R 47 (2004) 49-121.
- [25] J. O'Donoghue, D. Haverty, Method of Doping Surfaces, PCT Application No.: WO2008/033867, March 2008.
- [26] L. O'Neill, C. O'Sullivan, P. O'Hare, L. Sexton, F. Keady, J. O'Donoghue, Surf. Coat. Tech. 204 (2009) 484-488.
- [27] P. O'Hare, B. Meenan, G. Burke, G. Byrne, D. Dowling, J. Hunt, Biomaterials, 31 (2010) 515-522.
- [28] D. Owens, R. Wendt, J. Appl. Polym. Sci. 13 (1969) 1741-1747.
- [29] http://www.csm-instruments.com/en/webfm_send/51 (last accessed 16-09-2010).
- [30] W. Oliver, G. Pharr, J. Mater. Res. 7 (1992) 1564-1583.
- [31] E. Burkarter, C. K. Saul, F. Thomazi, N. C. Cruz, L. S. Roman, W. H. Schreiner, Surf. Coat. Tech. 202 (2007) 194-198.
- [32] X. P. Jiang, X. Y. Wang, J. X. Li, D. Y. Li, C. S. Man, M. J. Shepard, T. Zhai, Mater. Sci. Eng. A 398 (2005) 28-36.
- [33] F. J. Gil, J. A. Planell, A Padrós, C Aparicio, Dent Mater 23 (2007) 486-491.

Table (i): Summary of pin-on-disc, surface energy and surface roughness measurements.

Ti-6Al-4V Surface	Friction Coefficient	Pin-On-Disc Wear Track Width, Depth (μm)	Surface Energy (mN m^{-1})	Average Surface Roughness (R_a, μm)
Smoothened unmodified	0.35 – 0.65	353, 11 ^a 1393, 172 ^b	48.7	$8.5 \times 10^{-2} \pm 0.8 \times 10^{-2}$
Teflon microblasted	0.6	380, 12 ^a	13.5	$1.7 \times 10^{-2} \pm 0.9 \times 10^{-2}$
Al ₂ O ₃ -Teflon CoBlast TM modified	0.1	448, 17 ^b	6.5	2.1 ± 0.2
Heat-treated Al ₂ O ₃ -SiC CoBlast TM modified	0.6	265, 6 ^a	48.0	1.8 ± 0.2
Heat-treated Al ₂ O ₃ -B ₄ C CoBlast TM modified	0.65	358, 11 ^a	41.6	2.0 ± 0.2
Teflon microblasted heat- treated Al ₂ O ₃ -SiC CoBlast TM modified	0.1	288, 7 ^b	13.4	1.6 ± 0.3
Teflon microblasted heat-treated Al ₂ O ₃ -B ₄ C CoBlast TM modified	0.1	267, 6 ^b	7.0	1.8 ± 0.2

a Test conditions: 1 N load at 1 cm s⁻¹ angular velocity for 1800 s.

b Test conditions: 10 N load at 19 cm s⁻¹ angular velocity for 1800 s.

Table (ii): Summary of EDS and contact angle (CA) measurements.

Ti-6Al-4V Surface	Elemental Composition (At.%)					Contact Angle (CA) with Water Droplets (°)
	Ti	Al	V	F	Si	
Smoothened unmodified	85.1	9.6	5.3	-	-	47 ± 5
Al ₂ O ₃ microblasted	94.6	1.1	3.7	-	0.6	70 ± 7
Teflon microblasted	22.6	1.4	2.1	73.9		112 ± 2
Al ₂ O ₃ -Teflon CoBlast TM modified	17.8	1.4	1.0	78.7	1.1	128 ± 3
Heat-treated Al ₂ O ₃ -SiC CoBlast TM modified	75.1	4.6	4.1	-	16.2	103 ± 7
Teflon microblasted heat-treated Al ₂ O ₃ -SiC CoBlast TM modified	6.5	1.6	0.4	89.1	2.4	112 ± 2
Teflon microblasted heat-treated Al ₂ O ₃ -B ₄ C CoBlast TM modified	24.4	1.6	1.3	72.7	-	122 ± 5

Figure 1: Schematic representation of CoBlast™ process depicting abrasive and dopant particle streams impacting surface to be modified.

Figure 2: SEM micrographs of surfaces of unmodified (a), Teflon microblasted (b), Al₂O₃-Teflon CoBlast™ (c), Al₂O₃ microblasted (d), Teflon microblasted on heat-treated Al₂O₃-SiC CoBlast™ (e) and Teflon microblasted on heat-treated Al₂O₃-B₄C CoBlast™ modified (f) Ti6Al4V.

Figure 3: Pin-on-disc wear tracks which formed on unmodified (a) and Al₂O₃-Teflon CoBlast™ modified (b) Ti6Al4V under test conditions of 10 N load at 19 cm s⁻¹ angular velocity for 1800 s.

Figure 4: Pin-on-disc wear tracks which formed on Al₂O₃ microblasted (a) and Al₂O₃-Teflon CoBlast™ modified (b) Ti6Al4V. Inner tracks on both surfaces resulted from tests under 1 N load at 0.67 cm s⁻¹ angular velocity for 1800 s, while tracks next furthest out formed from tests at 1 N load at 1.0 cm s⁻¹ angular velocity for 1800 s

Figure 1:

Figure 2:

Figure 3:

Figure 4: