Title	Comparison between shot peening and abrasive blasting processes as deposition methods for hydroxyapatite coatings onto a titanium alloy
Authors(s)	Byrne, Greg, O'Neill, Liam, Twomey, Barry, Dowling, Denis P.
Publication date	2013-02-15
Publication information	Byrne, Greg, Liam O'Neill, Barry Twomey, and Denis P. Dowling. "Comparison between Shot Peening and Abrasive Blasting Processes as Deposition Methods for Hydroxyapatite Coatings onto a Titanium Alloy" 216 (February 15, 2013).
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/5248
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 (Volume 216, 15 February 2013, Pages 224–231) DOI:10.1016/j.surfcoat.2012.11.048 Elsevier B.V.
Publisher's version (DOI)	10.1016/j.surfcoat.2012.11.048

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

Comparison between shot peen and abrasive blasting processes as deposition methods for hydroxyapatite coatings on Titanium alloy materials

Greg D. Byrne¹, Liam O'Neill², Barry Twomey² & Denis P. Dowling^{1*}

1. School of Mechanical and Materials Engineering, University College Dublin, Belfield, Dublin 4, Ireland
2. EnBio Ltd., NOVA UCD, Belfield Innovation Park, Dublin 4, Ireland

* Corresponding Author

Tel: + 353 1 716 1747

Fax: + 353 1 283 0534

Email: denis.dowling@ucd.ie

Highlights

- Comparison of two low temperature deposition methods for HA
- Combining silica shot with a flow of HA powder worked effectively
- Replacing the silica with alumina abrasive produced a more adherent coating
- Chemistry and crystallinity of the deposited HA coatings were comparable to the feedstock powder
- Results show favourable coating properties for CoBlast in comparison to the Shot Peen process in the deposition of HA

Abstract

Recent studies have shown that combining a compressed air jet with entrained hydroxyapatite (HA) particles with a jet of abrasive particles can be used to deposit a well adhered crystalline HA coatings onto titanium substrates. A similar particle bombardment process utilising a flow of shot peen particles and a flow of suitable powder particles has been used to deposit a range of coatings, though the deposition of bioceramic powders have not yet been reported by this method. In this study a direct comparison between the shot peen and abrasive bombardment processes has been undertaken to determine which technique yields coatings exhibiting higher levels of adhesion on titanium alloy substrates. Both processes were shown to effectively deposit a layer of crystalline apatite onto the titanium substrates over a range of pressures and jet to substrate heights. It was observed that for both processes that an increase in particle kinetic energy producing corresponding enhancements in both deposition rate and surface roughness. The shot peen process however produced a smooth layer of laminar apatite, which was readily removed from the surface using a scratch adhesion test technique. In contrast the combination of a jet of HA and abrasive powders resulted in an increase in surface abrasion and increased mechanical interlocking of the HA into the metal surface was observed. The mechano-chemical affect achieved resulted in a better adhered HA layer. The surface morphology obtained using the two treatments was significantly different with an increase in the average roughness (R_a) of ≈ 70 and 80% for samples treated with abrasive particles over shot peen. This difference in surface treatment is further highlighted by the removal of the HA using an acid etch. The roughness (R_a) of the underlying titanium layer after this removal is, on average, $>175\%$ higher for the surface treated with the abrasive particles during HA deposition.

Keywords: Hydroxyapatite, shot peen, grit blast, abrasive, crystalline, bioceramic

1. Introduction

Hydroxyapatite (HA) coatings are routinely applied to metallic implant devices to improve biocompatibility and enhance osteointegration of the implant into the bone [1, 2]. The most widely used technique for the application of HA coatings is plasma spray [1]. There are concerns however related to the stability and reproducibility of HA coatings at the high deposition temperatures (approx. 5700°C) [1]. During processing at these temperatures the crystalline HA can undergo partial transformation to amorphous HA as well as forming trace amounts of tri-calcium phosphate (α and β -TCP) [3]. These phases have a quicker resorption rate than crystalline HA and are associated with woven bone formation as well as issues at the coating-implant interface [3, 4]. Furthermore, the orthopaedics industry is moving towards carefully constructed surfaces with biologically optimised three dimensional metallic structures [5, 6]. The commonly applied plasma spray coatings are relatively thick (typically 20 - 100 μ m), which may blanket the carefully controlled surface structures and alter the pore sizes [7]. As such, numerous alternative techniques are being investigated for depositing HA onto metallic implants [7-9].

There have been a number of different reports on the use of particle bombardment techniques for the deposition of HA coatings. Ishikawa et al produced a coating by simply blasting HA at a metal implant, but this did not gain market favour, possibly due to low adhesion [10, 11]. Gbureck et al modified this process to include a hard alumina core to the HA particles [12]. Upon impacting the metal surface, the outer HA layer was found to fragment and deposit a HA layer without alumina incorporation. The presence of the alumina was found to enhance the HA adhesion through tribo-chemical bonding, however there have been no recent reports on the further development of this method.

Recent research has shown that by combining a simultaneous flow of abrasive (alumina) and a flow of HA onto a surface it is possible to impregnate apatite into a metal surface to form a coating with no detectable uptake of the abrasive. This technique which is called CoBlastTM has been shown to successfully deposit coatings which offer promising biological responses both *in-vitro* and *in-vivo* [11, 13, 14].

Shot peening is an alternative method that can be used to modify a metallic surface and numerous studies have shown that combining a flow of shot peening particles and a separate flow of coating powder can effectively be used to coat substrates [15-17]. Shot peening is differentiated from abrasive blasting in that the shot peening process works via the plastic deformation of the substrate material surface rather than abrasion of the surface. To the authors knowledge there have been no records of shot peening being used to deposit bioceramics. The objective of this study is therefore is to investigate if shot peening could produce a HA coating with similar properties to that obtained using the CoBlast technique. Titanium alloy substrates were treated using the two techniques over a range of jet pressures and blast heights and the modified surfaces were examined to compare the properties of the deposited HA coatings.

2. Experimental

2.1. Materials

Titanium (Grade 5, Ti-6Al-4V) coupons (15mm x 15mm x 1 mm), were obtained from Lisnabrin Engineering, Ireland. Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ powder with a particle size of 20-65 μm was sourced from S.A.I., France. Alumina abrasive (100 μm) and silica shot peen media (100 μm) were sourced from Comco Inc. (CA, USA). Figure 1 shows optical micrographs of the respective powders. The difference in shape between the abrasive

particles and the shot peen media is clearly evident with the former exhibiting a jagged structure and the latter, a spherical structure.

2.2 Sample preparation

Prior to surface modification, the coupons were ultrasonically cleaned in 1M HCL and then in isopropanol (Sigma-Aldrich) to remove any contaminants. All surface blasting was carried out using a Comco Standard Lathe as described previously [11, 13, 14]. The processing utilised twin nozzles, one for the HA stream and a separate nozzle for the abrasive/shot peen flow (Figure 2). The powders were blasted onto the titanium coupons using a gauge pressure of between 40 and 90 psig (0.28-0.62 MPa) and a working distance of 15 or 41 mm. All surface modifications were carried out at an applicator speed of 13 mm/sec. After the surface treatment step, each sample was ultrasonically washed in de-ionised water for 5 minutes to remove any loose powder from the treated surface.

2.3 Surface characterisation

The surface morphologies of the samples were examined using a bench-top Hitachi TM-1000 SEM equipped with an Oxford Swift-TM EDS system. Optical microscopy examination was conducted using an Olympus inverted microscope (GX51) with image capture and analysis software. The SEM and elemental analysis of the scratches was conducted using a FEI Quanta 3D FEG Dual Beam scanning electron microscope incorporating focused ion beam capabilities and equipped with an EDAX APOLLO XV Silicon Drift Detector EDX system. Surface roughness measurements were taken using a Wyko NT 1100 optical profilometer operating in vertical scanning interferometry (VSI) mode with a 50x magnification and 1.0 objective. The x-ray diffraction was conducted on a Siemens D500 glancing angle diffractometer with rotating stage and beam mono chromator. Scratch testing was carried out

to determining the adhesion of the HA coating to the titanium substrate using Teer Coatings Scratch Testing machine. This test involves dragging a Rockwell diamond indenter across the surface of the coating, similar to the operating principal detailed in BS EN 1071-3. The load applied to the indenter is increase as the indenter moves. Typically the loading starts at 5 N and is increased linearly to a maximum of 50 N.

3. Results

While the CoBlast process has been reported to operate at gauge pressures of 90 psig (0.62 MPa) and at a jet height of 20 mm from the surface [11, 13, 14]. The corresponding shot preening process typically runs at lower gauge pressures of 40 – 60 psig (0.28-0.41 MPa) and at nozzle orifice to substrate heights of up to 200 mm [15, 16]. Therefore a range of pressures and heights were investigated to determine how blast parameters influenced deposited coating properties from each process. Due to equipment limitations, the maximum height was limited to 41mm. The full range of conditions investigated is outlined in Table 1.

Coating chemistry and topography

Following HA deposition, the surface topography and chemical composition of the coatings were investigated using SEM-EDX. Both processes appear to show higher coverage when the nozzles are closer to the substrate surface. As shown in Figure 3 in back scatter mode the darker regions represent lighter element, thus indicate HA coverage. From these SEM images it was concluded that the CoBlast process yielded marginally better coverage compared with the Shot Peen processes. The images indicate increasing coverage with increased airline pressure for both systems. EDX analysis was used to provide a semi-quantitative measure of the Ca, P and Ti elemental composition on the coated surfaces. This elemental analysis confirmed the increased HA coverage with increased airline pressure. Significantly higher

levels of Ca and P being detected on samples prepared at low blast heights or with higher pressure, as shown in Figure 4. At the higher 41 mm nozzle height there is a clear trend of increasing HA deposition with increasing airline pressure. These results indicate that increased particle kinetic energy is a key factor controlling the chemistry of the deposited coatings. Lowering the nozzle height would also be expected to increase the particle kinetic energy and the quantities of HA detected at 15 mm height were found to increase significantly for lower airline pressures of when compared to coatings deposited at 41 mm nozzle height. However, at the lower 15 mm nozzle height there is no clear trend between the EDX results and airline pressure. For the CoBlast samples, this may be due to increased coating removal due to the higher kinetic energy of the abrasive particles at low heights resulting in a complex deposition-abrasion interaction. For the shot peen samples, the reason for the variation may be related to similar effects, with increased kinetic energy resulting in fracture and delamination of the deposited coating.

Glancing angle XRD analysis was undertaken in order to investigate the crystallinity of the deposited coatings and the results were consistent with the deposition of a crystalline HA material onto the titanium surface. The graphs in Figure 5 are representative of a large range of XRD results obtained [18]. While the equipment used was not sensitive enough to examine the full range of peaks in the HA range the XRD data demonstrated that the most significant HA peaks in the spectra of the deposited coatings were identical to those of the powder material for both processes (JCPDF: XXXX). The thin nature of the coatings produced meant that the XRD spectra were dominated by the titanium alloy substrates. However, since no additional peaks were detected, this suggests that there was no significant incorporation of the abrasive (alumina) or shot peen media (silica) in the HA coatings. Furthermore, the XRD

peaks remained narrow and well resolved with no indication of additional peaks associated with alternate calcium phosphate phases being formed.

Optical profilometry was used to measure the average roughness (R_a) of the Shot Peen and CoBlast deposited coatings. Figure 6 demonstrates that the average roughness increases as the blast pressure increases and the distance of the jet to the substrate decreases. Furthermore, it was found that all of the CoBlast surfaces possessed a higher degree of surface roughness than the corresponding Shot Peen samples. All but the 41mm and 40 psig Shot Peen processed samples represented an increase in surface roughness when compared to the untreated titanium ($R_a - 0.45\mu\text{m}$)

In order to obtain a more detailed evaluation of the effect of the CoBlast and shot peen treatments on the titanium alloy substrate the HA coatings were removed by dissolving them in dilute HCl. The acid treated surfaces were inspected using SEM-EDX to determine that all the HA had been removed and the samples were re-analysed to determine if the roughness was due to the structure of the HA or if the structure of the underlying titanium metal substrate had been disrupted. When comparing the results in Figure 6 and Figure 7, the roughness of the CoBlast samples is largely unchanged by the removal of the HA layer. In contrast, the surface roughness of the Shot Peen samples was found to significantly decrease. This suggests that the roughness of the Shot Peen coated samples was largely due to the structure of the HA coating and that the underlying metal is not significantly altered by the deposition process. In contrast the roughness of the CoBlast deposited HA coatings appear to be mainly due to the roughening effect of the impinging abrasive particles on the metal substrate during the coating deposition. This was confirmed by SEM examination of the metal surfaces after dissolving off the HA. As shown in Figure 8, the Shot Peen treated alloy

surface appears to be relatively homogeneous and smooth, while the CoBlast surface reveals a series of deep gouges, cracks and other features derived from the impact of the abrasive particles on the surface. This abrasion is associated with the removal of the outer titanium oxide layer and its replacement with a HA mechano-chemically bonded coating [11].

Microscopic investigations of cross-sectioned samples obtained from the two deposition techniques were used to evaluate the effect of the impinging particles on the alloy surface. As shown in Figure 9, the CoBlast samples show a wide variety of surface features at all gauge pressures from 40 – 90 psig (0.28-0.62 MPa), which indicate a complex interaction between the impinging particles and the substrate, which results in significant disruption of the base metal. The Shot Peen samples show few features, mainly shallow crater type indents typical of the surface dimpling effect associated with this process, but nothing to indicate significant working of the substrate surface region.

To further probe the surfaces, trenches were milled into the coatings using the FIB technique followed by SEM examination. As shown in Figure 10, both the CoBlast and Shot Peen samples were found to deposit a HA layer on the alloy surface to a depth of less than 10 μm , which is in agreement with previous CoBlast studies [11, 13]. There is a marked contrast however between the structures of the two treated surfaces, with the CoBlast surface clearly showing folding of the HA into the distorted metal surface, to form an intricate mechano-chemical surface structure in which both layers are blended together. The HA on the outer surface is also shown to maintain significant structure, which is in good agreement with the roughness values of the coated and etch titanium surfaces. The corresponding Shot Peen surfaces exhibit a laminar structure in which the HA sits on top of a smooth metal interface

and in contrast with the CoBlast deposited coatings there is little interpenetration of the HA into the alloy substrate.

Scratch testing

A scratch testing technique was carried out to assess the adhesion of the HA layer to the titanium substrates. While the scratch test has been developed to assess the adhesion of PVD deposited coatings by means of brittle failure, the test is also used to determine the adhesion of ceramic coatings (DD ENV 1071-3:1994). The resulting scratch was examined using SEM and SEM-EDX methods to determine the levels of HA present along the length of the scratch. Three different samples for each test condition were subjected to the scratch test to account for variation between samples. The scratched surfaces were then examined using optical microscopy and by SEM-EDX. The graphs given in Figure 11 demonstrate the average atomic % of calcium detected along the length of the scratches for samples prepared at 90 psi. These results are presented as surfaces prepared at this pressure have a thicker, more uniform HA layer and make it easier to determine a difference in HA coating performance.

For the Shot Peen modified surfaces, the calcium content detected within the scratches rapidly decreases to leave only trace levels and effectively all of the HA has been removed below loads of 25 N. For the CoBlast samples, significant levels of calcium are detected up to loads of >40 N. The calcium atomic % for CoBlast samples deposited at 65 and 90 psig at loads 50 N are greater than almost all Shot Peen scratch surfaces at any load, indicating that complete removal of the HA was not achieved even at loads of 50 N at these pressures. Similar trends were seen in the phosphorous levels detected within these scratches. The effect was more significant for the surfaces modified at a height of 41mm, where the Ca and P levels detected within the scratches were significantly lower in the case of the Shot Peen samples. The increased coating adhesion exhibited by CoBlast samples is most likely due to

the increased mechanical keying of the coating and the substrate due to the abrasive nature of the process. The evidence of oxide removal during this process [11] may also provide a route towards a chemical bond at the interface, similar to diffusion bonded/enamelled bioceramics [19, 20].

4. Discussion

This deposition study demonstrated the ability of both the CoBlast and shot peening techniques to deposit HA coatings onto titanium alloy substrates. In both cases, the HA layers were several microns thick and the crystallinity of the HA powder is retained in the coatings. As expected, the increase in the kinetic energy of the particle streams (higher air pressure or lower blast height) led to an increase in the surface roughness, deposition rate and adhesion of the deposited materials. Although both techniques utilise a flow of HA and a separate flow of abrasive particles to attach the HA, the processes produced coatings with notably different morphologies. The shot peening process effectively compresses the apatite onto the surface of the metal as a laminar layer with what appears to be minimal interaction between the HA and the substrate. In contrast, the cutting capability of the abrasive stream utilised in the CoBlast process significantly disrupts the surface of the metal and effectively combines the HA and substrate into a highly disordered surface structure. This produces mechanical interlocking of the HA into the metal substrate with the formation of mechano-chemical bonds [11]. This enhanced substrate-HA interaction significantly enhances the adhesive strength of the CoBlast deposited coating relative to that of the shot peened samples and has been shown to yield a more durable coating than plasma sprayed HA after repeated impaction [21].

It is worth noting that the impaction of the shot peen pellets on to the surface of the deposited HA appears to compress the surface and have little effect on the R_a value of the titanium, as observed after removal of the HA in Figure 7. However, the CoBlast surface provides a combination of roughened substrate structure with topographical HA surface features to provide a high degree of surface roughness. The smoother Shot Peen surface is less likely to provide contact guidance of osteoblasts while the rougher, CoBlast surface is more likely to enhance osteoblast attachment and bone-implant apposition resulting in improved implant fixation *in vivo* [3].

5. Conclusions

Combining a shot peening flow with a flow of hydroxyapatite powder was found to effectively deposit a layer of HA on to the surface of a titanium alloy. Although the coating exhibited the same chemical structure and crystallinity as for the HA powder precursor, the laminar nature of the coating limited the adhesion of the coating and the smoothening effect of the impacting shot peen particles also lowered the roughness of the outer surface. Surface roughness is a very important parameter with respect to cell adhesion and a reduction in this surface roughness is likely to reduce osteoblast cell attachment and proliferation *in vivo*. The laminar coating structure and relatively low surface roughness may thus potentially reduce the applicability of the shot peen technique for the application of HA coatings on hard tissue implants. Replacing the flow of peening particles with a flow of abrasive particles produced a hydroxyapatite surface with significantly higher levels of adhesion. The higher adhesion is most likely due to a mechano-chemical bond associated with increased mechanical interlocking of the HA and titanium substrate as well as possible chemical interaction based on previous studies. As well as achieving a higher surface roughness and better coating adhesion, the HA coating retains the chemistry and crystallinity of the HA powder. These

combinations of effects suggest that the inclusion of an abrasive into the coating process yields a superior HA coating for use with metallic implant devices.

Acknowledgements

This work is part supported by Science Foundation Ireland Grant 08/SRCI1411

References

- [1] R.B. Heimann, Surf. Coat. Technol.201 (2006) 2012–2019.
- [2] Y.C.Tsui, C. Doyle, T.W. Clyne, Biomaterials 19 (1998) 2015-2029.
- [3] T. Kokubo, *Bioceramics and their clinical applications*. (2008) CRC Woodhead Pub Cambridge
- [4] S.R. Sousa and M.A. Barbosa, Biomaterials, 17 (1996) 397-404
- [5] K. Hayashi, T. Inadome, H. Tsumura, Y. Nakashima and Y. Sugioka, Biomaterials 15 (1994) 1187-1191.
- [6] J.J. Ramsden, D.M. Allen, D.J. Stephenson, J.R. Alcock, G.N. Peggs, G. Fuller, G. Goch, Annals of the CIRP 56(2) (2007) 687 – 711.
- [7] P. Li, J Biomed Mater Res 66A (2003) 79–85.
- [8] Y.W. Gu, K.A. Khor, P. Cheang, Biomaterials 25 (2004) 4127–4134.
- [9] A.S. Turner, D.G. Eckhoff, R.D. Dewell, A.R. Villanueva, H.M. Aberman, Trans 44th Ann Meet Orthop Res Soc 23 (1998) 4.
- [10] K. Ishikawa, Y. Miyamoto, Y.Nagayama, K.Asaoka, J Biomed Mater Res 38 (1997) 129–34.
- [11] P. O'Hare, B.J. Meenan, G. A. Burke, G. Byrne, D. Dowling, J.A. Hunt, Biomaterials 31 (2010) 515-522.
- [12] U. Gbureck, A. Masten, J.Probst, R.Thull, Mater Sci Eng C 23 (2003) 461–5.
- [13] L. O'Neill, C. O'Sullivan, P. O'Hare, L. Sexton, F. Keady, J. O'Donoghue, Surf. Coat. Technol. 204 (2009) 484-488.
- [14] C. O'Sullivan, P. O'Hare, N. D. O'Leary, A. M. Crean, K. Ryan, A.D.W. Dobson, L. O'Neill, J Biomed Mater Res Part B: Appl. Biomater. 95B (2010) 141–149.
- [15] A.J. Babecki, C.L. Haehner, US Patent 3,754,976, published August 28, 1973.
- [16] H-P Chu, C.L. Staugaitis, US Patent 4,552,784, published November 12, 1985.

- [17] R.L. Spears, US Patent 4,753,094, published June 28, 1988.
- [18] C. O'Sullivan, P. O'Hare, G. Byrne, L. O'Neill, K. B. Ryan and A. M. Crean, Coatings 1 (2011) 53-71
- [19] K. Stanton, K. O'Flynn, S. Nakahara, J.-F. Vanhumbecq, J. M. Delucca and B. Hooghan, J Mater Sci: Mater Med. 20 (2009) 851-857
- [20] K. Stanton, K. O'Flynn, S. Newcombe, Key Eng. Mater. 361-363 (2007) 269-272
- [21] F. Tan, M. Naciri, D. P. Dowling and M. Al-Rubeai, Biotechnol Adv (2011) doi:10.1016/j.biotechadv.2011.07.008

Table 1: CoBlast and Shot peen deposition conditions

Process	Gauge Pressure (psi)	Gauge Pressure (MPa)	Nozzle Height (mm)
CoBlast	40	0.28	15
CoBlast	65	0.45	15
CoBlast	90	0.62	15
Shot peen	40	0.28	15
Shot peen	65	0.45	15
Shot peen	90	0.62	15
CoBlast	40	0.28	41
CoBlast	65	0.45	41
CoBlast	90	0.62	41
Shot peen	40	0.28	41
Shot peen	65	0.45	41
Shot peen	90	0.62	41

List of Figures:

Figure 1: Optical micrographs showing HA powder, Alumina abrasive and Silica Shot (10x magnification)

Figure 2: Schematic of the CoBlast process showing nozzle height and incident angles

Figure 3: SEM imaging of treated surface at a magnification of x200. The darker areas are indicative of enhanced HA coating coverage

Figure 4: EDX analysis of HA modified surfaces

Figure 5: Glancing angle XRD data collected from shot peen and CoBlast HA modified Ti surfaces produced at a height of 41 mm (-- HA peaks and – Titanium substrate)

Figure 6: Surface roughness (R_a) of HA treated surfaces as determined by optical Profilometry

Figure 7: Surface roughness of the treated titanium after undergoing an HCl immersion to remove the HA layer

Figure 8: SEM images at 2500x magnification showing a topographical comparison of CoBlast (left) and Shot Peen (right) surfaces after HA removal. Both samples were subjected to treatments at 15 mm height and 65 psi pressure

Figure 9: Optical images of cross sectioned CoBlast (left) and Shot Peen (right) surfaces treated at a height of 15mm and at pressures of 40 (top), 65 (middle) and 90 psi (lower). All images recorded at 50x magnification

Figure 10: SEM image of FIB milled CoBlast surface (left) and Shot Peen surface (right)

Figure 11: Typical scratch obtained at increasing loads, 5 – 50 N (top) and the corresponding calcium atomic % detected at various loads along the scratches (bottom). Results are given for shot peen and CoBlast samples were produced at 90 psi at 15 (-) and 41mm (--) treatment heights

Figures

Figure 1: Optical micrographs showing HA powder, Alumina abrasive and Silica Shot (10x magnification)

Figure 2: Schematic of the CoBlast process showing nozzle height and incident angles

Figure 3: SEM imaging of treated surface at a magnification of x200. The darker areas are indicative of enhanced HA coating coverage.

Figure 4: EDX analysis of HA modified surfaces

Figure 5: Glancing angle XRD data collected from shot peen and CoBlast HA modified Ti surfaces produced at a height of 41 mm (-- HA peaks and – Titanium substrate)

Figure 6: Surface roughness (R_a) of HA treated surfaces as determined by optical Profilometry

Figure 7: Surface roughness of the treated titanium after undergoing an HCl immersion to remove the HA layer

Figure 8: SEM images at 2500x magnification showing a topographical comparison of CoBlast (left) and Shot Peen (right) surfaces after HA removal. Both samples were subjected to treatments at 15 mm height and 65 psi pressure

Figure 9: Optical images of cross sectioned CoBlast (left) and Shot Peen (right) surfaces treated at a height of 15mm and at pressures of 40 (top), 65 (middle) and 90 psi (lower). All images recorded at 50x magnification

Figure 10: SEM image of FIB milled CoBlast surface (left) and Shot Peen surface (right)

Figure 11: Typical scratch obtained at increasing loads, 5 – 50 N (top) and the corresponding calcium atomic % detected at various loads along the scratches (bottom). Results are given for shot peen and CoBlast samples were produced at 90 psi at 15 (-) and 41mm (--) treatment heights