Laser coating of zirconium + ZrO_2 composites on Ti6Al4V for biomedical applications.

Nkele Baloyi[1], Monname Tlotleng[2], Christopher Meacock[2], Sisa Pityana[1,2]and J. Dutta Majumdar[3]

[1]Tshwane University of Technology, Pretoria, 0001, South Africa
[2]Council for Scientific and Industrial Research, National Laser Center, Pretoria, 0001, South Africa
[3]Metallurgical and Materials Eng. Dept., I. I. T. Kharagpur, W. B. -721302, India

Abstract:

Laser coating is an advanced coating technology for improving the surface properties of various components. These coatings are extremely dense, crack-free and have non-porous microstructures. Coatings archived by laser based coating technology have uniform composition and coatings thickness which results in them displaying excellent metallurgical bonding properties with the base material. Laser coating of components can create a surface with high resistance against wear, corrosion and elevated temperatures. In this work Ti6Al4V base material was coated with Zirconium and Zirconia composite material to improve the corrosion and wear resistance of the base material. Zirconium powder mixed with binder (PVA and cold glue) was heated to produce a thin layer which was then bonded to the Ti6Al4V by irradiation with a fibre laser forming a Zirconium + Zirconia composite due to an in-situ reaction in the liquid state. Laser coating results show a gradual hardness increase of coated Ti6Al4V from top to bottom and was found that PVA produce better bonding as compared to Zr without binder and cold glue.

Keywords: Ti-6Al-4V, Zr; Laser cladding; microstructure; hardness bonding

1 INTRODUCTION

The use of Ti-6Al-4V in bio-applications following stainless steel and cobalt based alloys has been of tremendous attention. In the early development of bio-engineering stainless steel was regarded the best material; therefore the follow up by cobalt based alloy. It has been noticed that the use of stainless steel in biomaterial for hip implants results in the material fracturing the bones due to their high young's modulus while cobalt alloys have low fatigue strengths. The most requirements of biomaterial to be suitable for use for hip implants are that they must relate with the human anatomy without endangering it, be able to function as the anatomy and sustain the mechanical properties of the body.

In the recent years titanium and its alloys have received attention due to their excellent biocompatibility and corrosion resistance (Geethaet al, 2009). Titanium at an ambient temperature has a hexagonal closed packed (hcp) crystal structure referred to as alpha phase that can undergo an allotropic modification at around 883°C to a body centered cube (bcc) crystal structure known as beta phase. This phase may be retained at approximately 350 ^{o}c to makes it a duplex (α-β) alloy (Greger et al, 1987). In this regards it would seem acceptable that the manipulation of these crystallographic variations through alloying additions and thermo-mechanical processing will result in a wide range of alloys and properties (Jardini et al, 2011).

Titanium alloys have low hardness values, poor resistance to wear and oxidation at high temperature (Polmear, 1981 and Budinski, 1991). Poor tribological properties of these alloys have limited them for use in articulating components of the hip and knee prostheses (Geetha et al, 2009; Buchhanan et al, 1987). These problems can be overcome by changing the nature of the surface of titanium alloys using different surface engineering techniques. Many studies have been done on surface modification of titanium alloys in order to improve their surface properties, (Zhecheva et al, 2005, Liu et al, 2004 and Wang and Wang, 2004). Laser surface coating using additive manufacturing technology such as laser cladding is one of the advanced and effective methods which can be used to deposit a layer of a specific material without tempering with the functionality of the main material.

Ceramics that are considered for bioapplications are commonly termed bioceramics. These are usually polycrystalline inorganic silicates, oxides, and carbides, (Kurella and Dahotre, 2005). They are refractory in nature and possess high compressive strength. Bioceramics can be subclassified as bioinert, bioactive, and biodegradable materials (Park et al, 2003). Bioinert ceramics, like alumina and zirconia, maintain their physical and mechanical properties even in biological environments. Zirconia is highly wear resistant and tough; it undergoes stress-induced transformation toughening. The main application of zirconia ceramics is in total hip replacement (THR) ball heads (Piconi and Maccauro, 1999, Christel et al, 1988) and it will be used herein to coat duplex alloy Ti6Al4V.

This present study is concerned with the production of Zr + ZrO2 composite layer on the surface of Ti6Al4V alloys by laser metal deposition technique. Zirconium is selected as the main element for surface alloying because it is benefit to wear resistance and corrosion resistance of titanium alloys. Furthermore, Zr has α and β isomorphic properties to titanium and leads to solid solution hardening (Zhecheva et al, 2005; Kobayashi et al, 1998). The microstructure, chemical composition and hardness of the deposited layers were analysed to understand the mechanisms of laser coating and material bonding.

2 Experimental procedure

2.1 Materials and coating process

The duplex alloy used in the present study was Ti6Al4V in a thin plate specimen with dimensions of 30 x 30 x 8 mm as machined. The surfaces of the specimen was sandblasted and cleaned prior to laser cladding. The particle size distribution of the Zr powder which was deposited on the surface ranged from 20 to 150 microns therefore it was too fine to be fed through a conventional powder feeder system. The laser cladding process was performed with Zr powder loosely placed onto the surface of the substrate and with Zr powder mixed with an organic binder and pasted on substrate. The thickness of the paste was 1.0 mm. Two types of binders were also used; (i) polyvinyl alcohol PVA, $(C_2H_4O)_n$ and (ii) cold glue $(C_4H_6O_2)$ respectively. Three test samples were prepared as shown in **Table.1**

Table 1: Composition of powder beds

Test	Coating Composition	Coating Thickness (mm)
Sample 1	Zr	1.0
Sample 2	Zr + PVA	1.5
Sample 3	Zr + Wood glue	1.0

2.2 Laser cladding

The laser cladding was carried out using a Roffin Sinar DY044, CW Nd:YAG laser. A 600 µm optical fiber was used to guide the laser beam to an optical system focusing the beam at 1 mm on the surface. The cladding head is mounted on a controlled robot arm (KUKA). The laser head was set at a fixed distance of 12 mm above the powder bed. **Figure 1** shows a schematic diagram of the set-up. The process parameters are presented in **Table 2.** Single and multiple line scans of 25 mm in length and 0.08 mm overlap were cladded. The cladding experiments were conducted in an argon shielded environment, at a flow rate of 2 l/min.

Table 2: laser processing parameters

Power (w)	Scan speed (mm/s)	Beam Diameter (mm)	Layer overlapping (mm)	Shielding (l/min)
300	10	1	0.6	2
500	10	1	0.8	2
1000	10	1	0.8	2

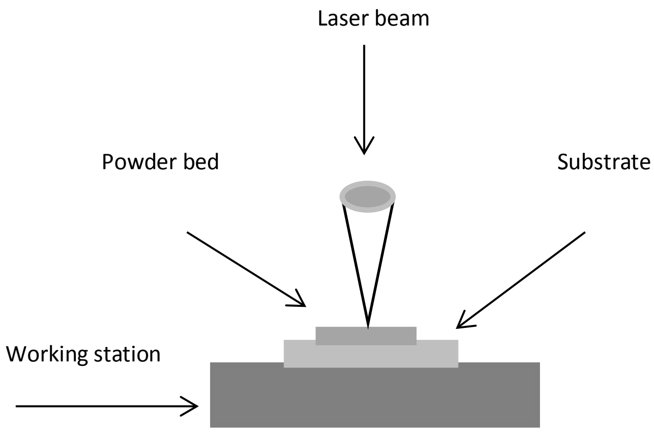


Figure 1: laser deposition system

2.3 Material Characterisation

Metallographic specimens were prepared by cutting the samples transversely across the clad layer. The mechanically polished surfaces were etched with Kellers's reagent (5 ml HNO_3, 1.5 ml HCl, 1.0 ml HF and 95 ml distilled H_20). The microstructures and elemental composition of the cladded Zr/Ti6Al4V were examined with an optical microscope and the Joel scanning electron microscopes (SEM) equipped with energy dispersive spectroscopy

(EDS), respectively. The hardness profiles of the laser cladded samples were obtained using a Matsuzawa hardness tester with a load of 50 g in an interval of 100 µm from the edge of the clad. Hardness profiles were constructed for each cladding process depicting hardness from the top of the clad down to the base material.

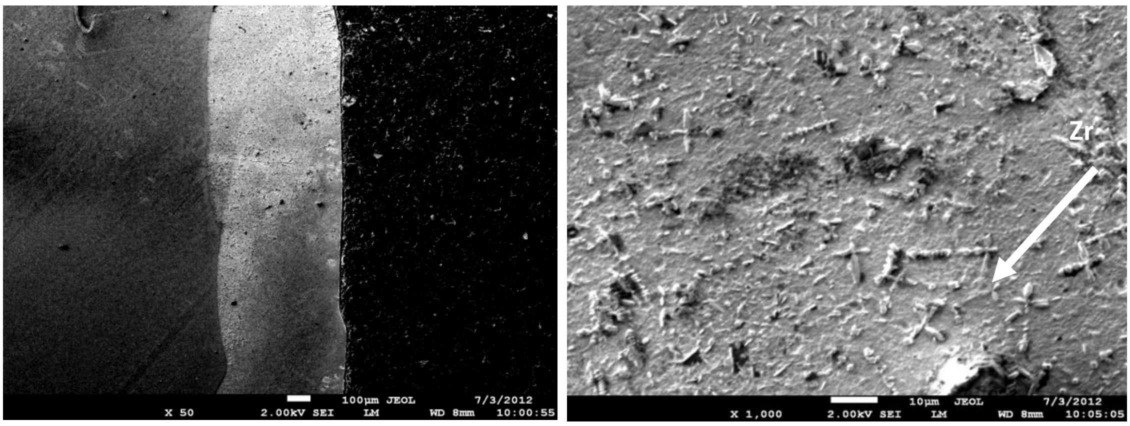
3 Results

3.1 Microstructure of the deposits

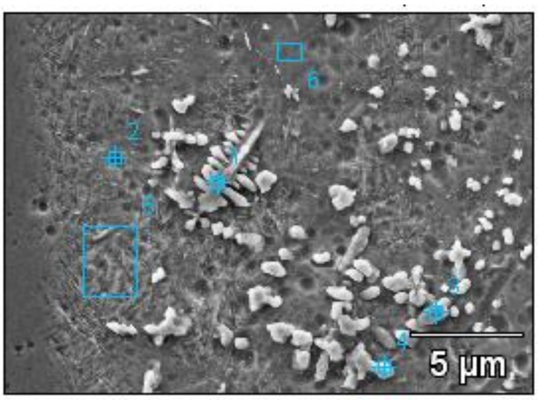
3.1.1 Zr powder on Titanium without a binder

Figure 2a shows a typical cross section of the laser melted Zr powder loosely preplaced on the titanium substrate (sample 1). The clad was obtained by irradiating the pre-placed powder bed (1 mm thick) using laser output power of 500 W, laser scan speed of 1 mm/s and beam spot size of 1 mm. The coating was bonded to the substrate. However, it can be observed to have some small pores and cracks. Similar deposits were obtained when the powder bed was increased to 1.5 mm thick using the same processing parameters and resulted in severe melting and no deposition was achieved.

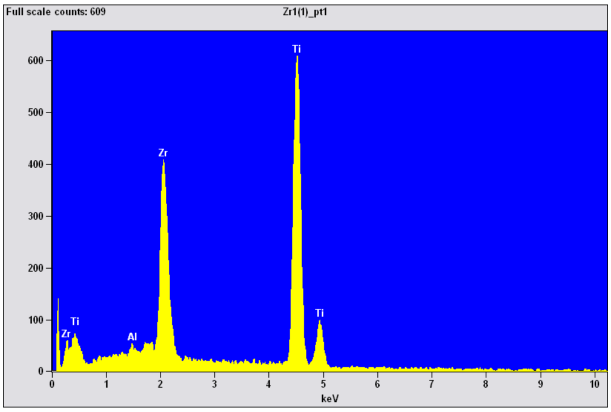
Fig. 2b shows detailed microstructure of the deposited layer. The microstructure consists of dendrites that are randomly distributed on the deposited layer. The dendrites arise from the rapid heating and cooling induced by the moving laser source. The quantitative EDS spot analysis of the dendrites, Fig. 2c is shown in Fig. 2d. The results indicate that the dendrites are Zr and O_2 rich. Fig. 2e shows the distribution of the Zr dendrite at the bottom of the coating also indicated as the transition zone. It can be observed that the volume fraction of resulting dendrites is high at the base of the coating.



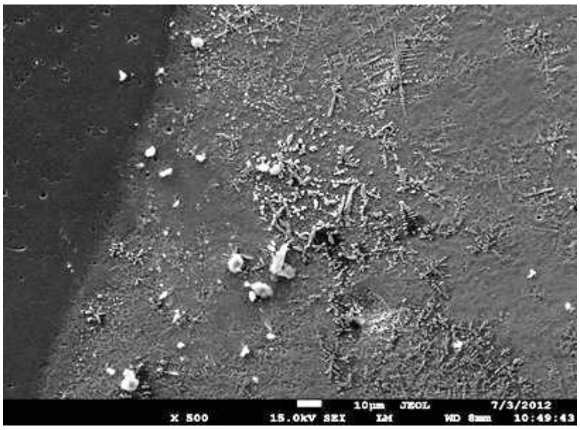
a) b)



c)



d)

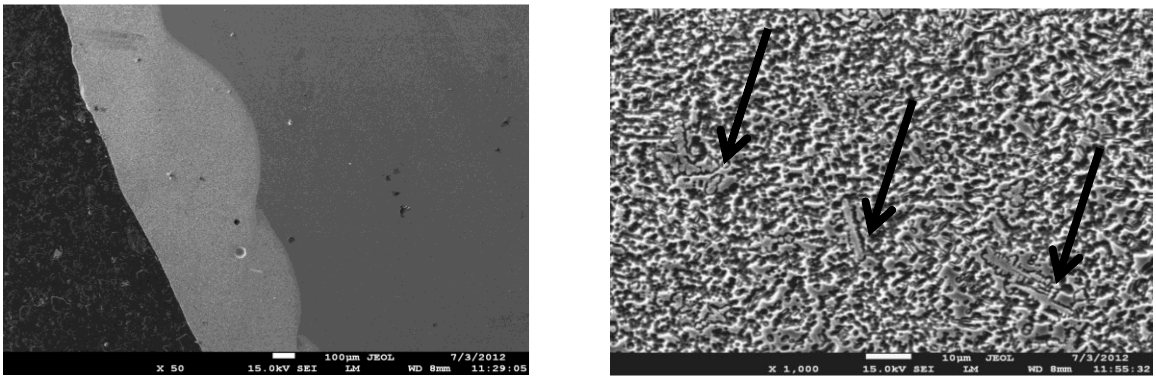


e)

Figure 2: Sample 1 analysis. (a) Representation of layer thickness, (b) microstructure analysis, (c) EDS analysis, (d) Spot analysis, (e) indication of dendrites close to the base material.

3.1.2 Zr powder on Ti64 with binders

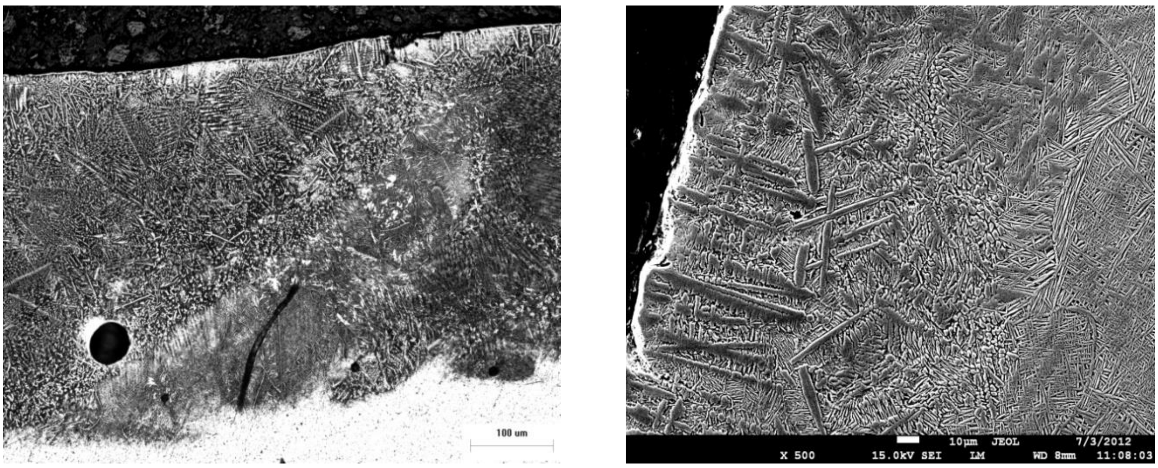
SEM micrographs of the cross sections for the clad obtained when the Zr powder was mixed with PVA $(C_2H_4O)_n$ as binder are shown in Fig. 3 (sample 2). The surface of the coating is smooth; there is good bonding between the coating and the substrate, Fig. 3a. There are no cracks observed. However, some micro-pores were observed. Some protrusion of the coating (dilution) into the substrate is also observed in some areas. The micro-structural features of the coatings taken at high magnification are shown Fig. 3b. Dendritic structures that formed in middle of the clad are clearly visible on the laser melted Zr coating. The microstructure also reveals some cellular like structure. The dendrites analysis by EDS shows these as ZrC and solidified Zr matrix.



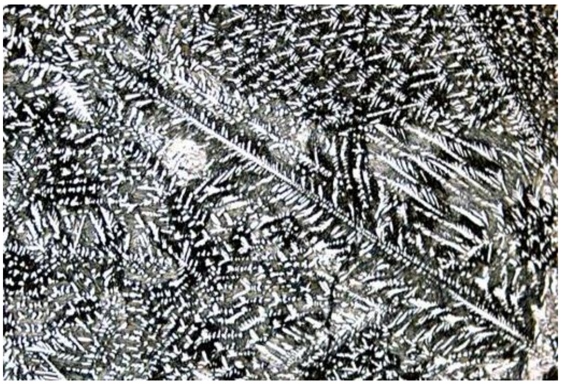
a) b)

Figure 3: SEM microstructures for sample 2. (a) Sectional view of the deposited layer, (b) presentation of the honey comb with the presence of dendrites

Fig. 4 represents the Optical and SEM micrographs obtained when the Zr powder was mixed with the cold glue ($C_4H_6O_2$) and pre-placed on the duplex alloy, recorded as sample 3. It indicates a minimal dilution of the deposited layer (Fig. 4a) to the duplex as well as the microstructural features of the deposits. The microstructures show complex types of matrices with the variation of regions. The coating contains coarse dendrites (Fig. 4a&b), long fine needle like dendrites (Fig. 4c&d) and a lath of martensitic matrix with a mixture of basket weave in the interior (Fig. 4e-f). The microstructure changes in morphology from the top of the coating to the bottom. At the centre there is a presence of grain boundaries separating the parallel plate structures mixed with basket-weave microstructure with matrix α-phase that are indicated in Fig. 4e&f.

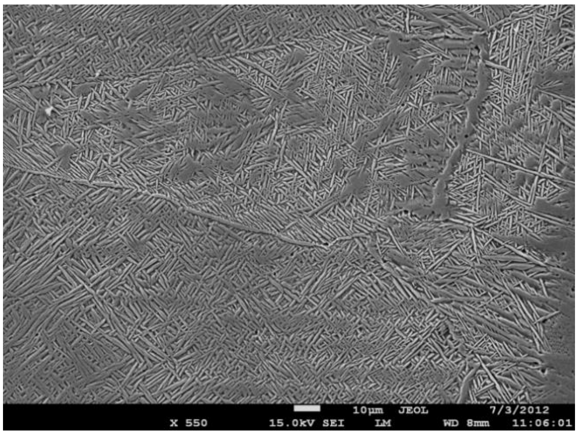


a) b)

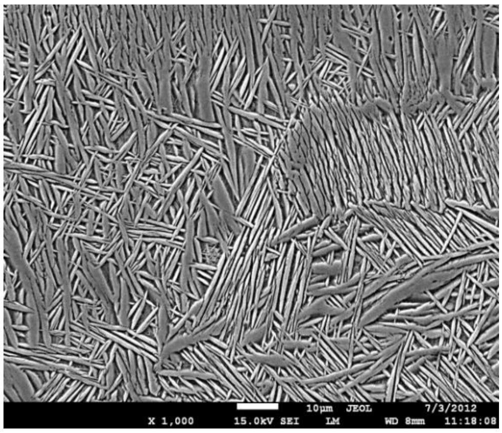


c)

d)



e)



f)

Figure 4: presentation of sample 3 microstructures. (a) indicates the thickness of the layer and the transition zone, (b) the edge of the deposited layer with the presence of dendrites, (c&D) the presence of long needle dendrites (taken from the interior of the clad), (e&f) indicates the presence of grain boundaries and basket weave matrix

3.1.3 Micro-hardness analysis

Fig. 5 shows the Vickers micro-hardness values of the coated layers for laser melted Zr powder. There is an increase in hardness values for all the laser clads, from ~ 300HV to ~ 900HV. Sample 1 represents the typical hardness variation of the deposited Zr and samples 2 and 3 are deposits obtained with the binders. The highest hardness was obtained for sample 3. The SEM analysis of this sample showed a large number of ZrC dendrites; therefore the increase in hardness is attributed to this. The microstructure for Sample 1 showed somewhat less occurrence of dendrites compared to sample 3.

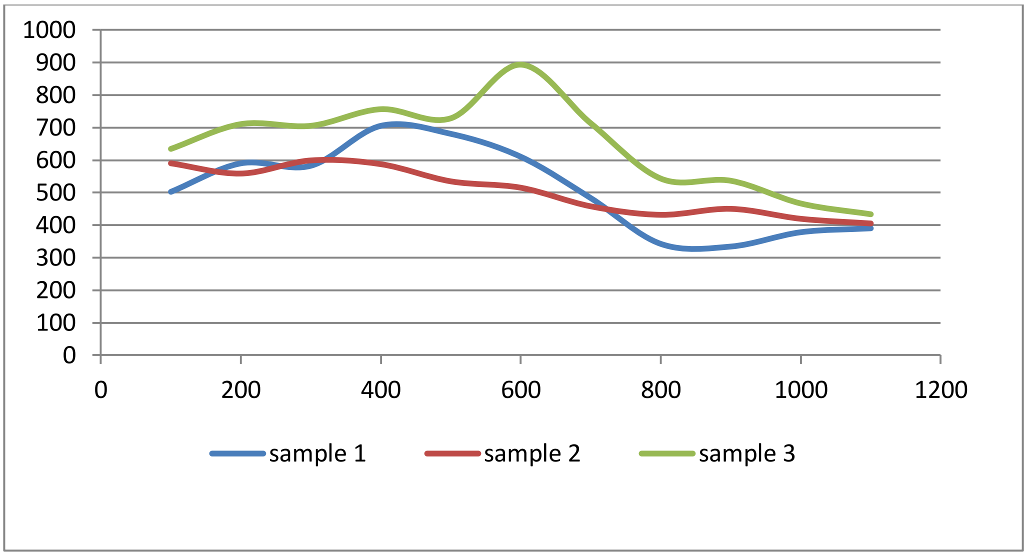


Figure 5: Vickers hardness measure, from the deposited layer to the substrate.

4 Discussion

Surface coatings of Zr + ZrO_2 were successfully deposited on the Ti6Al4V substrate using pre-placed powder laser cladding method. Microscopy was used to investigate the surface morphology and microstructures of the coatings. The coating was well adhered to the substrate. The hardness measurements showed an increase in the hardness of the coating. The increase in hardness was attributed to the presence of the ZrO_2 and ZrC phases along with grain refinement. There was very little surface cracking observed on the coatings.

The interaction of the high power laser/powder/metal causes melting of the powder and a thin layer of the substrate surface. The laser generated melt pool solidifies as soon as the laser beam moves along the laser track. The microstructures in the laser clad strongly depend on the cooling rate and any chemical species present in the melt-pool. The cooling rate of the melt pool depends on several factors such as, laser power, scan speed, and beam diameter. When the Zr powder was pre-placed on the substrate without any binder, ZrO_2 dendrites precipitates were formed in the clad. The formation of the $ZrO_2$was attributed to the reaction with oxygen from the atmosphere to the molten Zr, according to the following reaction:

$$Zr\ (l) + O_2\ (g) = ZrO_2\ (s) \qquad (1)$$

Although the experiment was carried out in an inert environment, some this oxidation in the coating was observed, oxygen was detected by the EDX analysis. The microstructure of the coating clearly shows the ZrO_2 dendrites were formed at solidification.

The laser melting of pre-placed powders mixed with the PVA resulted in the microstructure that comprised of an additional species of dendrites, identified by EDX as ZrC. The melting points of Zr, Ti64 and PVA are 1852.0 ^{o}C, 1615.2^{o}C and 240^{o}C respectively. The melting and dissociation of the PVA resulted in free C atoms that reacted with molten Zr to form ZrC. The laser energy induced very high temperatures to cause the melting of the Zr powder and a thin layer of the Ti64 substrate and nearly complete evaporation of the PVA such that there were C atoms available to form ZrC. This could explain the low volume fraction of ZrC dendrites and low hardness values of the coated layer when Zr was mixed with the PVA binder.

When the Zr powder was mixed with “cold glue” and irradiated with the laser, the coated layer consisted of high volume fraction of fine ZrC dendrites and lamella-like type microstructures from the top of the clad to centre of the clad as shown in Fig. 4 EDS analysis results showed that the dendrites phases were ZrC. The molten Zr reacted with free C atoms from the “cold glue” to the ZrC phase. The ZrC dendrites nucleated from the melt and grow into the bulk on the surface coating, Fig. 4(a&b). It can be seen in Fig. 4c&d that the dendrites can grow into different complicated morphologies. A transition zone viz. dendrites-lamella-like type microstructure was also observed. This type of microstructure is commonly known as Widmanstatten microstructure. The Widmanstten microstructure usually takes forms of the basket-weave or parallel plate structure. Fig. 4e shows the basket-weave structure and Fig. 4f shows a mixture of the two structures. The basket-weave appears as short intersecting plates with a parent grain. The parallel plate structure contains parallel plates growing from the grain boundary. The Widmanstatten structures in Zr alloys are associated with the availability of C atoms. Carbon has low solubility in Zr (Rudling and Adamson, 2000), and acts as nucleation site for the basket-weave structure. On solidification, the ZrC dendrites are formed, the excess carbon acts as nucleation sites for the basket-weave and parallel plate structures as observed by the SEM micrographs. The hardness measurement of the coating showed an improvement attributed to the ZrC dendrites.

5 Conclusion

As a first step toward laser coating of Ti6Al4 with zirconium and its composites for biological applications, preliminary experiments were conducted. The pre-placed powder bed laser cladding process was adopted. This method was necessitated by fine Zr powder particles used in the experiments. The powder was mixed with binders in order to firmly stick the fine powders onto the substrate before irradiating it with the laser beam. The findings in this work are summaries as follows:

1.) Laser clad coatings were achieved with Zr powder loosely placed on the Ti64 substrate. Adherent composite coating consisting of Zr and ZrO_2 phases was obtained. The hardness of the coating was also improved.
2.) When the pre-placed Zr powder was mixed with PVA as binder was used, crack-free coatings that were metallurgically bonded to the substrate were obtained. The microstructure of the coatings contained ZrC dendrites; consequently the same degree of hardness was obtained.
3.) The pre-placed powder mixed with “cold glue”, resulted in complex microstructures characterized by Zr dendrites of different morphologies. The microstructure contained basket-weave and plate like structures. The presence of ZrC phases resulted in significant improvement in the hardness of the coatings.

6 Acknowledgements:

The authors would like to thank Mr Lucas Mokwena for assisting with the operations of the laser system.

7 References

1. Budinski K.G., Wear 151 (1991) 203–217.
2. Buchanan R.A, Rigney E.D, Williams J.M, Wear-accelerated corrosion of Ti-6Al-4V and nitrogen-ion implanted Ti-6Al-4V – mechanisms and influence of fixed –stress magnitude. J.biomed, mater, Res., vol 21 (issue 3), 1987, p 367-377.
3. Chevalier, J.J., Deville, S., Mu¨nch, E., Jullian, R. and Lair, F. (2004). Critical Effect of Cubic Phase on Aging in 3 mol% Yttria-stabilized Zirconia Ceramics for Hip Replacement Prosthesis, Biomaterials, 25:5539–5545
4. Christel, P., Meunier, A. and Dorlot, J.-M. (1988). Biomechanical Compatibility and Design of Ceramic Implants for Orthopaedic Surgery, Ann. N.Y. Acad. Sci., 523: 234–256.
5. Geetha M., Singh A.K., Asokamani R., Gogia A.K.,Ti based biomaterials, the ultimate choice for orthopaedic implants – A review, Progress in Materials Science 54 (2009) 397–425
6. Jardini, A.L., Larosa, M.A., Bernardes, L.F Zavaglia, C.A.C., MacielFilho, R., Application of direct metal laser sintering in titanium alloy for cranioplasty, Brazilian conference on manufacturing engineering, 2011.
7. Kobayashi E., Doi H., Yoneyama T., Hamanaka H., Gibson I.R., Best S.M., Shelton J.C., Bonfield W., J. Mater. Sci.-Mater. Med. 9 (1998) 625–630.
8. Kurella Anil and Dahotre B. Narendra, Review paper: Surface Modification for Bioimplants: The Role of Laser Surface Engineering, Journal of Biomaterials applications, 2005
9. Liu X.Y., Chu P.K., Ding C.X., Mater. Sci. Eng. R 47 (2004) 49–121.
10. Mändl S., Surf. Coat. Technol. 201 (2007) 6833–6838.
11. Park, J.B., Bronzino, J.D. and Kim, Y.K. (2003). Metallic Biomaterials, Ceramic Biomaterials, Biomaterials Principles and Applications, pp. 1–45, CRC Press, Boca Raton, USA.
12. Piconi, C. and Maccauro, G. (1999). Zirconia as a Ceramic Biomaterial, Biomaterials, 20:125.
13. Polmear J.J., Titanium Alloys, in: Light Alloys, Edward Arnold Publications, London, 1981.
14. Rodling Peter and Adamson B. Ronald, Zirat special topical report on manufacturing, Advance Technology Nuclear Technology, 2000.
15. She Jia, Yongzhong, Li Chunliu, Novel in situ synthesized zirconium matrix composites reinforced with ZrC particles, Material science and Engineering A 527, 2010, 6454-6458
16. Wang Y., Wang H.M., Appl. Surf. Sci. 229 (2004) 81–86.
17. Wang Yanfang, Li Gang, Wang Cunshan, Xia Yuanliang, Sandip Bysakh, Dong Chuang, Microstucture and properties of laser clad Zr-Based alloy coatings on Ti substrates, Surface and coatings techonologies 176, 2004, 284-289.
18. Zhang Kai, Liu Weijun, Shang Xiaofeng, Research on the processing experiments of laser metal deposition shaping. Optics & Laser Technology vol 39, 2007, p 549-557
19. Zhecheva, W. Sha, S. Malinov, A. Long, Surf. Coat. Technol. 200 (2005), 2192–2207.
20. Bocanegra-Bernal M. H., Diaz de la Torre S. Review: Phase transition in Zirconium dioxide and related materials for high performamce engineering ceramics, Journal of materials science 37 (2002) 4947 – 4971