The Impact of Zn and Cu Reinforcements on Microstructural Enhancement and Performance of Laser Cladded Ti-Zn-Cu/Ti-6Al-4V Composite Coatings.

O.S. Fatoba 1*; S. A. Akinlabi 2, 3; E. T. Akinlabi 1, 3 and F. M. Mwema 1

1Department of Mechanical Engineering, University of Johannesburg, South Africa.
2Department of Mechanical and Industrial Engineering, University of Johannesburg, South Africa.
3Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria

Corresponding Author: drfatobasemeni@gmail.com; esther.akinlabi@covenantuniversity.edu.ng

Abstract: The effects of zinc and copper reinforcements on Titanium alloy via Direct Laser Metal Deposition (DLMD) process was investigated. Process parameters had great influence on the microstructure, metallurgical evolution, tensile and yield strengths performance. The process parameters had a significant influence on these factors considered, including the morphology of the surface, density, hardness, evolution of the microstructure, accuracy of the fabricated coatings dimensions and the mechanical performance of the Titanium alloy components processed by DLMD. The results of the investigation showed that the hardness had increased in proportion to the increase of the processing laser power coupled with the increase velocity of the laser scan. Moreover, for a laser power equivalent to and exceeding 1000 W, the hardness became less susceptible to the laser power. Morphological observations along the side of the surface showed the prominence of the adhesive powder, flow path of the melt pool and the areas which overlapped, attributed to the increase of the laser scanning speed. When the laser scanning speed was increased it attributed to the grain width reduction of the prior beta and a transformation in shape of the martensitic primary alpha into fine needle-like structures. In terms of the yield and tensile performance, the results revealed that increasing the scan velocity was favourable to the property, showing that the mechanical performance became better at higher scanning speeds. At the set laser intensity of 1000 W and a 1.0 m/min laser scanning speed, the fabricated coatings enhanced with 48.03 % hardness, 47.42 % tensile strength and 29.81% yield strength.

Keywords: Hardness; Microstructure; Hardness; Titanium alloy; Tensile strength; Zn-Cu-Ti coating; Yield strength.
1. Introduction

The base metal made of titanium alloy retains its characteristics while the surface is being improved. Despite the good properties exhibit by titanium alloy, drawbacks such as low hardness and poor wear property has necessitated improvement for better surface. Improvement of titanium surface can lead to enhanced properties and titanium alloys can be used in extended engineering applications [1-3]. Fatal accidents of engineering components in service can be avoided through surface modification. These can be achieved by fabricating hard-coatings that can withstand corrosion and friction [4, 5]. These can lead to excellent microstructures and enhanced mechanical properties without changing the properties of the base metal [6-8]. Different surface modifications techniques had been published by researchers worldwide but these techniques still have limitations such as adhesion of reinforcement and base metal, pores, cracks, long processing time and not cost effective [9-13].

However, direct laser metal deposition (DLMD) technique can take care of the limitations of the aforesaid conventional techniques. DLMD has been declared as 21st century surface modification technique with excellent characteristics such as good adhesion, near neat net shape, short processing time, small heat affected zone, minimal dilution, fast solidification and cooling, free of cracks and defects, minute porosity and concurrent melting and fusion [13-16]. Many researchers have coated titanium alloys with different combinations of reinforcements but reports on Ti-Zn-Cu reinforcements on titanium alloy is scarce in the literature. The characteristics of each reinforcement can be combined to form excellent coatings on titanium alloy with distinct microstructures and mechanical properties.

The present research is aimed at improving the microstructure, mechanical properties and innovative metal matrix composite of Ti-Zn-Cu/Ti-6Al-4V using DLMD technique for extensive engineering applications

2. Methodology

2.1. Materials Specifications and Sample Preparation Method

Dimensions 80 x 80 x 5 mm^3 was used for the rectangular substrate in this research. The composition of the titanium substrate in wt.% was 6.12 Al, 0.0039 N, 0.19 Fe, 0.0002 H, 3.76 V, 0.13 O, and Bal. 89.80 Ti. Preceding the contact of the base metal to laser treatment, the substrates were blasted with sand, washed in H_2O, eviscerated with acetone and desiccated at 25 degrees.
The process was necessary in order to avoid radiation reflection at the time of laser processing thereby allowing the substrate to absorb more laser irradiation. The reinforcement materials properties used in this research study is stated in Table 2. The reinforcement metallic powders were used as alloying powders mixed in Ti-15Zn-5Cu-0.8, Ti-15Zn-5Cu-1.0, Ti-20Zn-10Cu-0.8, Ti-20Zn-10Cu-1.0 fractions correspondingly. The in-depth mixing of the reinforcements was achieved in 16 hrs at a constant spinning velocity of 72 rpm in a Tube-shaped shaker mixer (T2F). The mixer has a 3-dimensional design that allows reinforcements of different particle sizes, weights and contents to be mixed unvaryingly. The mixture occurred in a bolted bottle that is air-tight.

Table 1: Reinforcement powders information

| Reinforcement | Ti       | Zn       | Cu       |
|---------------|----------|----------|----------|
| Particle size (μm) | 50-105   | 50-105   | 50-105   |
| Purity %      | 99.9     | 99.9     | 99.9     |
| Density (g/cm³) | 4.5      | 7.14     | 8.96     |

Characterizations were done on the coated samples using scanning electron microscopy and energy dispersive spectroscopy (EDS) analysis (SEM/EDS: VEGAS TESCAN). A 3-kW continuous wave (CW) Ytterbium Laser System (YLS) was used for the fabrication of the coatings. The distance between the substrate and the three co-axial nozzle was 2 mm. The mixed homogeneous reinforcements were delivered through powder feeders at 3.0 g/min and the argon inert gas protecting the powder was set at 3.0 L/min. Intersecting tracks were attained at 75% overlap. Design of experiment (DOE) was applied to obtain optimal process constraints. The best process parameters were used to fabricate the composite coatings at 950 and 1000 W and 0.8-1.0 m/min scan velocity.

3. Result and discussions

3.1. Ti-Zn-Cu/Ti-6Al-4V composite coating microstructure

Direct laser metal deposition (DLMD) has been a unique technique with exceptional characteristics over the years which allows powder mixing efficiency, laser process conditions synergy and coatings used in advanced engineering design. Titanium alloys have been beneficiary
of the DLMD technique especially in advanced engineering applications. Mechanical performance of composite materials is enhanced due to the second phase reinforcement in the titanium alloys. Properties of titanium alloys such as hardness, wear and corrosion resistance can be upgraded through reinforcement of copper and zinc in the titanium alloy matrix.

There are different phases in the morphology of Ti-Zn-Cu/Ti-6Al-4V coatings presented in Figure 3. The coatings, the Heat Affected Zone (HAZ), substrate. The HAZ is determined by the laser power and scan speed. The atomic constituents of the Zinc and copper were incorporated into the titanium alloy matrix grains. These caused the enhancement of the hardness. Titanium-zinc phases influence on the refinement of grain cannot be over-emphasised and this in-turn enhance the hardness and mechanical property [17, 18].

![Figure 1: SEM Images of Ti-Zn-Cu/Ti-6Al-4V composites at different wt.%](image)

Inducement of the degree of hardness is a function of the reinforcement added and this can also affect the other properties related. Figure 3 (b) indicated Zinc and copper reinforcement in the titanium alloy matrix. The degree of the influence in the matrix is linked with the wt.% in the matrix. Increase in scan speed from 0.8-1.0 m/min increased the hardness values both at 15 and 30 % Zn. It means the grain size reduced as the scan speed is increased. This is because finer grains are produced in the microstructure as scan speed increases due to rapid rate of cooling [19-24].
Mechanical and materials strengths increase had been reported in the literature as a result of refinement of grain via rapid solidification rate. This happens when the latent of solidification is less than the heat extraction rate [25-28]. The composite coatings had a maximum hardness value of 420 HV at 30 wt.% Zn and at scan speed of 1.0 m/min. From the cross-sectional view in Figure 4, it is apparent that the distribution of zinc and copper in the microstructure is dependent on the percentage increase of the reinforcements.

The speed in which the laser scanned on the surface of the substrate had influenced the morphology of the surface of the scanned tracks in such a way that the initial microstructure was ordered and visible but evolved into being non-uniform and unclear as the parameter was increased [20, 21]. Morphological observations along the side of the surface showed the prominence of the adhesive powder, flow path of the melt pool and the areas which overlapped, attributed to the increase of the laser scanning speed. When the laser scanning speed was increased it attributed to the grain width reduction of the prior beta and a transformation in shape of the martensitic primary alpha into fine needle-like structures. During the successive scanning of the laser beam on the material, small lamellae structures of alpha and beta were formed which were decomposed in-situ from the transformation of martensitic structures upon solidification in the zone which was identified being fully transformed.

Figure 2: SEM Images of Ti-Zn-Cu/Ti-6Al-4V composites at different wt.%
The utilization of independent processing parameters produced characteristics specific to the molten pool, but energy densities are in general proportional to the resulting characteristics of the molten pool. Observations showed that the size of the molten pool enlarged as successive tracks were scanned and this was consequent to the heat which was accumulated during the deposition of the multiple tracks. It was observed that the unsymmetrical shape of the molten pool after completion of the first deposited track had moved in the direction of the adjacent subsequent tracks deposited. As the adjacent tracks were deposited, the material was undergoing great cyclic heating and cooling [21]. The experiments produced results which revealed that the hardness of the clad was dependent highly on the laser scanning speed. Microstructural analysis on the substrate showed that the grain sizes were dominated by the laser processing intensity. The specimens produced had desirable tensile properties in attribution of the optimization of processing parameters which promoted a microstructure of fine dendrites. The microstructure of the specimens processed at 900 W laser intensity and 1.0 m/min laser scanning speed promoted the coarse microstructures to be transformed into fine structures and this attributed to the high rate of cooling.

![SEM Image of Ti-Zn-Cu/Ti-6Al-4V composites at different wt.%](image)

**Figure 3**: SEM Image of Ti-Zn-Cu/Ti-6Al-4V composites at different wt.%

### 3.4 Micro-hardness
Metallurgical analysis showed that the hardness of all the zones formed in the samples were harder than the initial hardness of the substrate. It is evident from Table 3 that as the Zinc content from the composition of the composite increases from 15-30%, the hardness value increases. Addition of titanium to copper increased the corrosion resistance of copper based composite as stated by Eze et al. [29]. At 15 and 30 wt. %, the least and peak micro-hardness are 352 HV, 362.56 HV 397.06 HV and 450 HV respectively at velocities of 0.8 and 1.0 m/min. The values shot up to 450 HV as the reinforcement varied from 15-30 wt.%. This was as a result of stable compound phases in the microstructure. The increase effect of zinc in the titanium matrix was noted as the tensile and yield strengths increased in values. Process factors also play a big role in determining the right proportions of zinc and copper that can go along with the optimized parameters.

Figure 4: Hardness performance of Ti-Zn-Cu/Ti-6Al-4V composites at different wt.%

Calculations of mechanical properties through the hardness were done as indicated by Cahoon et al. [30] and Palvina et al. [31] correspondingly as denoted by equations 1 and 2:
\[ \Gamma_S = \left( \frac{U}{2.9} \frac{k}{0.217} \right)^k \]  

(1)

\[ \Psi_S = \left( \frac{U}{3} \right)(0.1)^k \]  

(2)

U denotes vickers hardness, \( \Gamma_S \) denoted tensile strength, \( \Psi_S \) represents yield strength and \( k \) denotes coefficient of strain hardening taken as 0.15 [30]. Enhancement of the mechanical properties of the Ti-Zn-Cu/Ti-6Al-4V composite coatings could be seen in Table 2 as matched with the titanium alloy base metal. Table 2, Figure 5, and Figure 6 shows the various values obtained for yield and tensile strengths from the hardness values as stated in equations 1 and 2.

**Table 2: Mechanical properties of Ti-Zn-Cu/Ti-6Al-4V composite Coatings**

| Samples          | Laser Power (W) | Average Hardness (HV_{0.1}) | \( \Gamma_S \) (GPa) | \( \Psi_S \) (GPa) |
|------------------|-----------------|-----------------------------|----------------------|-------------------|
| Ti-6Al-4V alloy  | 304             | 0.97                        | 0.73                 |                   |
| Ti-15Zn-5Cu-0.8  | 900             | 352                         | 1.13                 | 0.82              |
| Ti-15Zn-5Cu-1.0  | 900             | 363                         | 1.16                 | 0.84              |
| Ti-20Zn-10Cu-0.8 | 1000            | 397                         | 1.27                 | 0.92              |
| Ti-20Zn-10Cu-1.0 | 1000            | 450                         | 1.43                 | 1.04              |
Figure 5: Yield Strength performance of Ti-Zn-Cu/Ti-6Al-4V composites at different wt. %
4. Conclusion

- Observations showed that the size of the molten pool enlarged as successive tracks were scanned and this was consequent to the heat which was accumulated during the deposition of the multiple tracks. It was observed that the unsymmetrical shape of the molten pool after completion of the first deposited track had moved in the direction of the adjacent subsequent tracks deposited.

- Titanium-zinc phases influence on the refinement of grain cannot be over-emphasized and this in-turn enhance the hardness and mechanical property. At 15 and 30 wt. %, the least and peak micro-hardness are 352 HV, 362.56 HV 397.06 HV and 450 HV respectively at velocities of 0.8 and 1.0 m/min. The values shot up to 450 HV as the reinforcement varied from 15-30 wt.%. This was as a result of stable compound phases in the microstructure.
The utilization of independent processing parameters produced characteristics specific to the molten pool, but energy densities are in general proportional to the resulting characteristics of the molten pool.

Acknowledgements

The authors wish to acknowledge the National Research Foundation (NRF) South Africa for their funding support and CSIR South Africa for the laser equipment.

References

[1] Veiga, C., Davim, J. & Loureiro, A. (2012). Properties and applications of titanium alloys: a brief review. Rev. Adv. Mater. Sci, 32(2):133-148.

[2] Fatoba O.S; Akinlabi, E.T., Makhatha, M.E. (2018). Effects of Cooling Rate and Silicon Content on Microstructure and Mechanical Properties of Laser Deposited Ti-6Al-4V Alloy. Materials Today: Proceedings. Vol. 5, issue 9, part 3. Pp. 18368-18375. https://doi.org/10.1016/j.matpr.2018.06.176.

[3] Bloyce, A., Qi, P.Y., Dong, H. & Bell, T. (1998). Surface modification of titanium alloys for combined improvements in corrosion and wear resistance. Surface and Coatings Technology, 107(2–3), 9/10/:125-132.

[4] Chikarakara, E., Naher, S. & Brabazon, D. (2012). High speed laser surface modification of Ti–6Al–4V. Surface and Coatings Technology, 206(14), 3/15/:3223-3229.

[5] Fatoba, O.S., Akinlabi, E.T. Akinlabi, S.A. (2018). Effects of Fe addition and Process Parameters on the Wear and Corrosion Properties of Laser Deposited Al-Cu-Fe Coatings Ti-6Al-4V Alloy. 2018 IEEE 9th International Conference on Mechanical and Intelligent Manufacturing Technologies (ICMIMT 2018), Cape town, South Africa, pp. 74-79. doi: 10.1109/ICMIMT.2018.8340424.

[6] Bansal, D.G., Eryilmaz, O.L. & Blau, P.J. (2011). Surface engineering to improve the durability and lubricity of Ti–6Al–4V alloy. Wear, 271(9–10), 7/29/:2006-2015.

[7] Dutta Majumdar, J. & Manna, I. (2015). Laser surface engineering of titanium and its alloys for improved wear, corrosion and high-temperature oxidation resistance. In: Waugh, J.L.G. (ed.). Laser Surface Engineering. Woodhead Publishing:483-521.

[8] Fatoba O.S., Akinlabi S.A., Gharehbaghi R., Akinlabi E.T (2018). Microstructural Analysis, Microhardness and Wear Resistance Properties of Quasicrystalline Al-Cu-Fe Coatings on Ti-6Al-4V Alloy. Materials Express Research. 5(6), 1-14. https://doi.org/10.1088/2053-1591/aaca70.

[9] Adesina, O., Popoola, P. & Fatoba, O. (2016). Laser Surface Modification: A Focus on the Wear Degradation of Titanium Alloy, Fiber Laser, Mukul Chandra Paul, IntechOpen, DOI: 10.5772/61737.
[10] Fatoba O.S., Adesina O.S. Popoola A.P.I. (2018). Evaluation of microstructure, microhardness, and electrochemical properties of laser-deposited Ti-Co coatings on Ti-6Al-4V Alloy. The International Journal of Advanced Manufacturing Technology. 97(5), 2341-2350. http://dx.doi.org/10.1007/s00170-018-2106-7.

[11] Gharehbaghi, R., Fatoba, O.S., Akinlabi, E.T. (2018). Experimental Investigation of Laser Metal Deposited Icosahedral Al-Cu-Fe Coatings on Grade Five Titanium Alloy. 2018 IEEE 9th International Conference on Mechanical and Intelligent Manufacturing Technologies (ICMIMT 2018), Cape town, South Africa, pp. 31-36. doi: 10.1109/ICMIMT.2018.8340416.

[12] Fu, Y., Zhang, X.C., Sui, J.F., Tu, S.T., Xuan, F.Z. & Wang, Z.-D. (2015). Microstructure and wear resistance of one-step in-situ synthesized TiN/Al composite coatings on Ti6Al4V alloy by a laser nitriding process. Optics & Laser Technology. 67(0), 78-85.

[13] Weng, F., Chen, C. & Yu, H. (2014a). Research status of laser cladding on titanium and its alloys: a review. Materials & Design, 58:412-425.

[14] Akinlabi E.T., Fatoba O.S., Akinlabi S.A. (2019) Numerical Modelling and Influence of Cu Addition on the Microstructure and Mechanical Properties of Additive Manufactured Ti–Al–Cu/Ti–6Al–4V Composite. In: Lambotte G., Lee J., Allanore A., Wagstaff S. (eds) Materials Processing Fundamentals 2019. The Minerals, Metals & Materials Series. Springer, Cham. Pp. 143-152. DOI: 10.1007/978-3-030-05728-2_13

[15] Li, H.C., Wang, D.G., Chen, C.Z. & Weng, F. (2015a). Effect of CeO2 and Y2O3 on microstructure, bioactivity and degradability of laser cladding CaO–SiO2 coating on titanium alloy. Colloids and Surfaces B: Biointerfaces, 127(0), 15-21.

[16] Fatoba O.S; Gharehbaghi, R., Akinlabi, S.A., Akinlabi, E.T. (2018). Effect of Rapid Solidification and Numerical Modelling of Laser Cladded Ti-Al-Cu Coatings on Ti-6Al-4V Alloy. Contributed Papers from the 14th Materials Science and Technology 2018 Conference (MS&T 2018), 14th-18th October 2018, Greater Columbus Convention Center, Columbus, Ohio, USA. Doi 10.7449/2018/MST_2018_230_239

[17] El-Faramawy, H.S., Ghali, S.N. & Eissa, M.M. (2012). Effect of Titanium Addition on Behaviour of Medium Carbon Steel. Journal of Minerals and Materials Characterization and Engineering, 11, 1108-1112.

[18] Fatoba, O.S; Popoola, A.P.I; Aigbodion, V.S (2016). Experimental study of Hardness values and Corrosion Behaviour of Laser Alloyed Zn-Sn-Ti Coatings of UNS G10150 Mild Steel, Journal of Alloys and Compounds, 658, 248-254.

[19] Gong, X., Lydon. J., Cooper, K. & Chou, K. (2014b). Beam Speed Effects on Ti-6Al-4V Microstructures in Electron Beam Additive Manufacturing, Journal of Materials Research, 29, 1951-1959.

[20] Gharehbaghi, R., Fatoba, O.S., Akinlabi, E.T. (2018). Influence of Scanning Speed on the Microstructure of Deposited Al-Cu-Fe Coatings on a Titanium Alloy Substrate by Laser Metal Deposition Process. 2018 IEEE 9th International Conference on Mechanical and Intelligent Manufacturing Technologies (ICMIMT 2018), Cape town, South Africa, pp. 44-49. doi: 10.1109/ICMIMT.2018.8340418.

[21] Makhatha, M.E., Fatoba, O.S. & Akinlabi, E.T. (2018). Effects of rapid solidification on the microstructure and surface analyses of laser-deposited Al-Sn coatings on AISI 1015
steel. Int J Adv Manuf Technol. 94 (1-4), 773-787.  https://doi.org/10.1007/s00170-017-0876-y.

[22] Fatoba, O.S; Popoola, A.P.I Aigbodion, V.S. (2018) Laser Alloying of Al-Sn Binary Alloy onto Mild Steel: InSitu Formation. Hardness and Anti-Corrosion Properties. Lasers in Engineering, 39(3-6), 292-312.

[23] Fatoba, O.S., Akinlabi, E.T., Akinlabi, S.A. (2018). Numerical Investigation of Laser Deposited Al-Based Coatings on Ti-6Al-4V Alloy. 2018 IEEE 9th International Conference on Mechanical and Intelligent Manufacturing Technologies (ICMIMT 2018), Cape town, South Africa, pp. 85-90. doi: 10.1109/ICMIMT.2018.8340426.

[24] O.S. Fatoba; A.P.I Popoola; V.S. Aigbodion (2018). Electrochemical Studies and Surface Analysis of Laser Deposited Zn-Al-Sn Coatings on AISI 1015 Steel. International Journal of Surface Science and Engineering. 12 (1), 40-59.

[25] Grosselle, F., Timelli, G., Bonollo, F., Tiziani, A. & Della Corte, E. (2009). Correlation between Microstructure and Mechanical Properties of Al-Si Cast Alloy. La Metallurgia Italiana, 6, 25-32.

[26] Dobrzanski, L.A., Maniara, R. & Sokolowski, J.H. (2006). The Effect of Cast Al-Si-Cu Alloy Solidification Rate on Alloy Thermal Characteristics. Journal of Achievements in Materials and Manufacturing Engineering, 17, 217-220.

[27] Popoola, A.P.I., Fatoba, O.S., Aigbodion, V.S. And Popoola, O.M. (2017). Tribological Evaluation of Mild Steel with Ternary Alloy of Zn-Al-Sn by Laser Deposition, International Journal of Advanced Manufacturing Technology, 89(5-8), 1443-1449. DOI 10.1007/s00170-016-9170-7.

[28] Fatoba O.S., Popoola A.P.I., Aigbodion V.S., Rambau T.G. (2017). The Influence of Laser Parameters on the Hardness Studies and Surface Analyses of Laser Alloyed Stellite-6 Coatings on AA 1200 Alloy: A response Surface Model Approach. International Journal of Microstructure and Materials Properties, 12(5-6), 319-331.

[29] Eze, A.A., Jamiru, T., Sadiku, E.R., Durowoju, M.O., Kupolati, W.K., Ibrahim, I.D., Obadele, B.A., Olubambi, P.A. and Diouf, S., (2018). Effect of titanium addition on the microstructure, electrical conductivity and mechanical properties of copper by using SPS for the preparation of Cu-Ti alloys. Journal of Alloys and Compounds, 736, pp.163-171.

[30] J. R. Cahoon, W. H. Broughton, and A. R. Kutzak (1971). The determination of yield strength from hardness measurements. Metallurgical Transactions, vol. 2, no. 7, pp. 1979–1983.

[31] E. J. Pavlina and C. J. Van Tyne (2008). Correlation of Yield strength and Tensile strength with hardness for steels. Journal of Materials Engineering and Performance, vol. 17, no. 6, pp. 888–893.