IN-SITU ALLOYING PROCESS OF TI6AL4V-xCU STRUCTURES BY DIRECT METAL LASER SINTERING

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ABSTRACT

In this paper the fabrication of in-situ Ti6Al4V-xCu alloy structures by DMLS are investigated. Ti6Al4V is a commonly used biomedical alloy because of it suitable mechanical and biocompatible properties. Copper is a proven anti-bacterial agent and in small amounts is not toxic to the human body. Ti6Al4V-xCu implants can be constructed to have a biocompatible structure with copper additions to reduce the risk of bacterial infection and implant failure. Infection at the bone–implant interface is the most probable reason for implant failure directly after implantation. Ti6Al4V powder was mixed with Cu powder to form a master alloy. Optimal process parameters need to be established for in-situ alloying of Ti6Al4V-xCu to form dense parts with suitable surface quality. The effect of laser scanning speeds and hatch distance on surface characteristics was investigated. The surface roughness, chemical composition and distribution of Cu near the surface and within the synthesized layer, as well as micro hardness were considered. A rescanning strategy was employed and showed improved alloy homogeneity and surface quality.

Keywords: Direct Metal Laser Sintering, Ti6Al4V, advanced implants.

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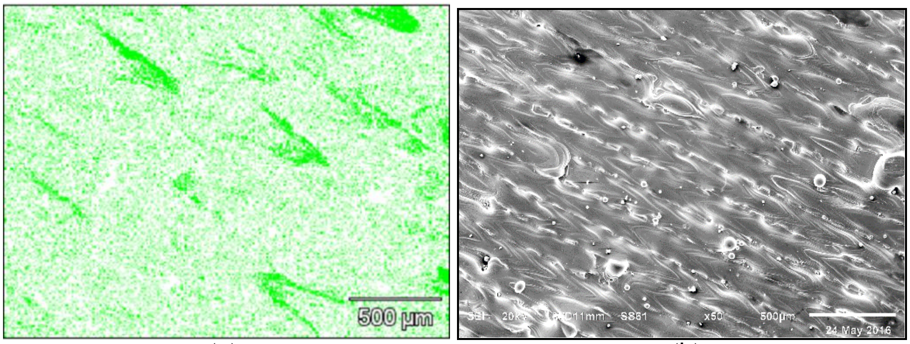
1. INTRODUCTION

The medical industry has successfully utilized the layer by layer nature of Direct Metal Laser Sintering (DMLS) to manufacture complex shapes from biocompatible materials to produce implants using CAD geometry based on Computer Tomography scan data. Ti6Al4V Extra Low Interstitials (ELI) is a commonly used biomaterial because of it suitable mechanical and biocompatible properties [1]. Infection at the bone–implant interface is the most probable reason for implant failure directly after implantation [2]. Coating the interface with materials that have antibacterial properties is a promising approach to infection prevention. Material such as silver, zinc and copper have shown such antibacterial properties. Though medication helps to cure infection, antibacterial materials are more efficient as they act locally and continuously at the site of infection. Copper is a proven antibacterial agent and in small amounts is not toxic to the human body [3]. Implants can be constructed to have a biocompatible Ti6Al4V structure with Cu additions at the bone–implant interface to reduce the risk of bacterial infection and implant failure.

Jung *et al.* [4] electrochemically deposited small amounts of Cu onto Ti discs to show the effect of Cu as an antibacterial agent. After 10 days of exposure to the Cu, bacteria such as *Escherichia coli (E. coli)* and *Staphylococcus aureus (S. aureus)* experienced a dramatic decrease in growth. Demonstrating that antibacterial functionalization of Ti implants by Cu also was suggested by Shirai *et al.* [5] which used of a Ti-Cu alloy as an anti-bacterial implant interface. It was indicated that 1% Cu addition retained the samples biocompatibility and inhibited the growth of bacterial microbes.

In a pilot study by Kinnear *et al.* [6] was compared in-situ alloyed Ti6Al4V-1at.%Cu surface and a surface that had Cu areas on a Ti6Al4V substrate so that the surface contains 1% Cu by means of surface area. The alloyed layers were produced at 170 W laser power and 1.2 m/s scanning speed. Results showed that the in-situ alloyed Ti6Al4V-1at.%Cu surface was more efficient at inhibiting the growth of *E. coli* and *S. aureus*. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscope (EDS) analysis showed that the in-situ alloyed Ti6Al4V-1%Cu surface had inhomogeneous surface composition (Fig. 1a) and high surface roughness of 54.4±3.94 μm (Fig. 1b). The work done in this paper aims to optimize the layer formation of in-situ alloyed Ti6Al4V-1at.%Cu.

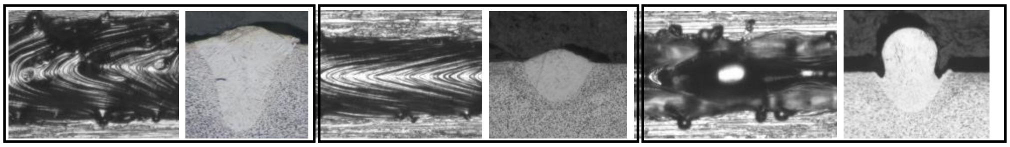


(a) (b)

Figure 1. In-situ alloyed Ti6Al4V-1at.%Cu: (a) EDS mapping of Cu and (b) SEM of top view.

Fundamentally, the DMLS process is a laser beam scanning over the surface of a thin powder layer. The laser beam melts material along a row of powder particles, forming a molten pool and finally single track. Single tracks or the continuous formation of the molten pool is the most basic building block in the DMLS process. The previously melted layer is the platform for applying a new layer of powder and the process repeats. Layers are produced by applying multiple single tracks next to one another or also known as track-by-track

formation. DMLS objects are formed by placing multiple single tracks layer by layer upon one another. Thus the optimization of formation of the molten pool and single track plays a major role in the quality and mechanical properties of the manufactured 3D object.
The geometric characteristics of the DMLS tracks are mainly determined by material properties, energy input (laser power, spot size and scanning speed) and the thickness of the deposited powder layer. The depth of penetration into the substrate is determined primarily by the power of laser beam, and the layer thickness causes the powder volume involved in melting process [7]. Process of single track formation is directly influenced by the process parameters. At optimal process-parameters, DMLS single tracks are continuous and have stable geometrical characteristics (Fig. 2b) At high laser power density, excessive energy input can lead to keyhole mode resulting in deep re-melting of the substrate and pores inside the molten pool [8] (Fig. 2a). Also if the scanning speed decreases, it results in a higher energy input, since time of irradiation increased, and irregular tracks formation, because the heat affected zone becomes larger involving more powder material [9]. Tracks tend to have satellites or dislodged sections that form during solidification. High scanning speed leads to insufficient remelting depth and long molten pool. Drops formation (balling effect) occurs when surface tension breaks the continuous molten pool into individual droplets (Fig. 2c). At low laser power density the molten pool experiences lower temperatures, so the surface tension coefficient, as well as melt viscosity, increases and can lead to drop formation [9].



(a) (b) (c)

Figure 2. Ti6Al4V (ELI) DMLS single tracks (top view and cross-sections) at different process-parameters (Yadroitsava et al., 2015).

While laser power and scanning speed have a major influence on single track geometry, hatch distance directly affects surface quality (hatch distance refers to the distance between centres of two neighbouring single tracks). Due to the denudation effect, the first track is wider than the next one [9]. The zone of powder consolidation does not have sufficient powder to form track with the same geometry Optimal hatch distances are also essential for reducing process time and thermal cycling.

In-situ alloying allows for the manipulation of microstructures, producing material with superior properties and facilitating easier processing of certain materials by adding alloying elements. In situ DMLS alloying from elemental powders is a cost and time effective means to produce a wide range of alloy compositions. Vrancken et al. [10] highlighted the capabilities of DMLS to in-situ processing of powder mixtures Ti6Al4V-ELI and 10 wt.% Mo powders. Krakhmalev & Yadroitsev [11] showed that an increase in laser power or a re-melting strategy are effective methods of improving homogeneity of Ti and SiC alloying. Fischer et al. [12] produced Ti–26Nb alloy by DMLS of elemental titanium and niobium mixed powders, noting that energy input has a significant effect on porosity and homogeneity of the produced part. Dadbakhsh & Hao [13] formed an Al/5 wt.%Fe2O3 alloy by in-situ DMLS, noting that the layer thickness had a strong influence on the microstructural outcome.

2. MATERIALS AND METHODS

To produce the Ti6Al4V-1 at.`%Cu (1.38 wt%) powder alloy 1.36 g of Cu powder is mixed with 98.64 g of Ti6Al4V(ELI) (Extra Low Interstitials) powder and mixed for 1 hour. Ti6Al4V (ELI) argon-atomized powder containing 89.26 wt% of Ti, 6.31 wt% of Al, 4.09 wt% of V, 0.12% of O was used for this study. A chemical composition of copper powder showed 99.9 %

of Cu. The 10th, 50th and 90th percentiles of equivalent diameter (weighted by volume) were respectively 12.6 μm, 22.9 μm, 37 μm for Ti6Al4V (ELI) powder and 9.45 μm, 21.9 μm and 37.5 μm for Cu powder. Both powders particles were highly spherical in shape. Before processing, the powders were dried at 80°C for 2 hours without protective atmosphere, to increase powder flowability.

To determine the effect of hatch distance and scanning speed on surface quality and homogeneity of the alloy, sintered single layers (4.5 mm x 12 mm) were manufactured by EOSINT M280 machine. Laser power was kept constant at 170 W and spot size was about 80 μm. Three intervals of scanning speed (0.7 m/s, 1.0 m/s and 1.3 m/s) and four interval of hatch distance (70 μm, 80 μm, 90 μm and 100 μm) were applied.

The powder layer thickness is a combination of the distance moved by the build platform in the Z-direction, the roughness and shrinkage of the previously processed layer. The average surface roughness of Ti6Al4V samples at standard EOS process-parameters for 30 μm Z-movement of build platform, was found to be Rz=30.2±5.52 μm and Ra=6.9±1.37 μm (perpendicular to the scanning direction). Thus, 60 μm powder layer thickness was utilized for the experiment with single layers.

3. RESULTS AND DISCUSSION

To investigate DMLS single layers manufactured at different hatch distance, images from SEM and cross-sections of the layers were analysed. Defects such as porosity, delamination of layer and solidification cracks have not been found in DMLS single layers before and after rescanning. At chosen process-parameters, laser power density which is ratio of laser power to the laser beam spot area was the constant. For 60 μm layer thickness and chosen process-parameters, total average remelted depth was about 60 μm for single layers sintered at different hatch distances (Fig. 4a). Roughness of the surfaces is shown in Table 1.

The surface roughness increased with an increase in hatch distance and scanning speed. Surfaces at higher scanning speeds and hatch distances produced more satellites on the surface, dramatically decreased the surface quality. Rescanning removed the satellites from the surfaces. Rescanning showed some improvement of the surface quality; however this was expected due to the fact that the single tracks where rescanned on the same position as the previous tracks (Fig. 3). Further rescanning strategies need to be investigated to further improve the surface quality of in-situ DMLS alloying.

Table 1. Roughness of DMLS surfaces

Hatch distance	70 μm		80 μm		90 μm		100 μm	
	R_a	R_z	R_a	R_z	R_a	R_z	R_a	R_z
Scanning speed	Single scan							
0.7 m/s	4.6±0.66	24.9±2.43	5.1±0.05	33.5±4.44	6.6±0.7	37.5±1.8	7.4±0.39	46.2±1.53
1.0 m/s	6.4±0.63	38.7±0.57	7.1±0.63	41.5±2.7	7.99±0.98	43.9±1.94	8.6±0.24	51.1±3.2
1.3 m/s	6.9±0.81	38.2±0.64	7.4±0.68	44.7±4.38	8.3±0.55	51.2±1.83	9.4±0.33	54.4±3.94
Rescanning								
0.7 m/s	4.4±0.1	24.8±1.12	5.4±0.7	26.5±2.74	6.4±0.31	36.1±1.29	7.3±1.24	40.3±4.4
1.0 m/s	5.9±0.86	35.6±2.22	6.3±0.92	35.7±0.59	7.3±1.39	40.3±2.18	7.5±0.48	50.5±1.39
1.3 m/s	6.8±0.3	37±1.05	7.4±0.46	37.4±1.83	9.4±0.45	50.4±4.8	9.3±1.04	51. 3±5.1

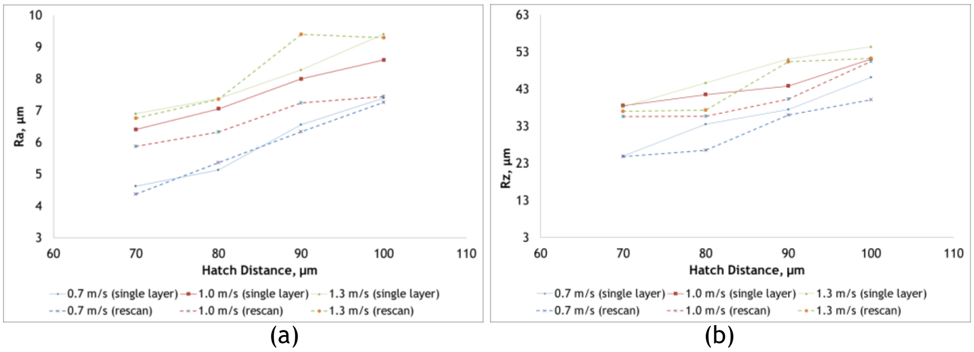


Figure 3. Surface roughness of in-situ alloyed Ti6Al4V-1 at.%Cu at laser power 170 W, scanning speed 0.7-1.3 m/s and 70-100 μm hatch distances for a single layer and rescanning: (a) Ra, (b) Rz.

Bergström et al. [14] showed that because of the onset of multiple scattering events, for normally incident light, the absorptance of the surface increases with roughness after a certain roughness threshold has been exceeded. The absorptance increased with roughness significantly in metals which have a low absorptivity in the flat, smooth state, such as Cu. It should be noted, that after single scanning of the mixture Ti6Al4V and Cu powders, copper particles melted and created islands repeated solidification lines of the material (Figs. 3a and 4a). High surface roughness after single scan of powder layer can increase absorption of the material that leads to higher temperature also more prominent flows in molten pool [15], which in turn, also can influence on the size of molten pool. After rescanning, the total remelting depth increased to approximately 110 μm (Fig. 4b).

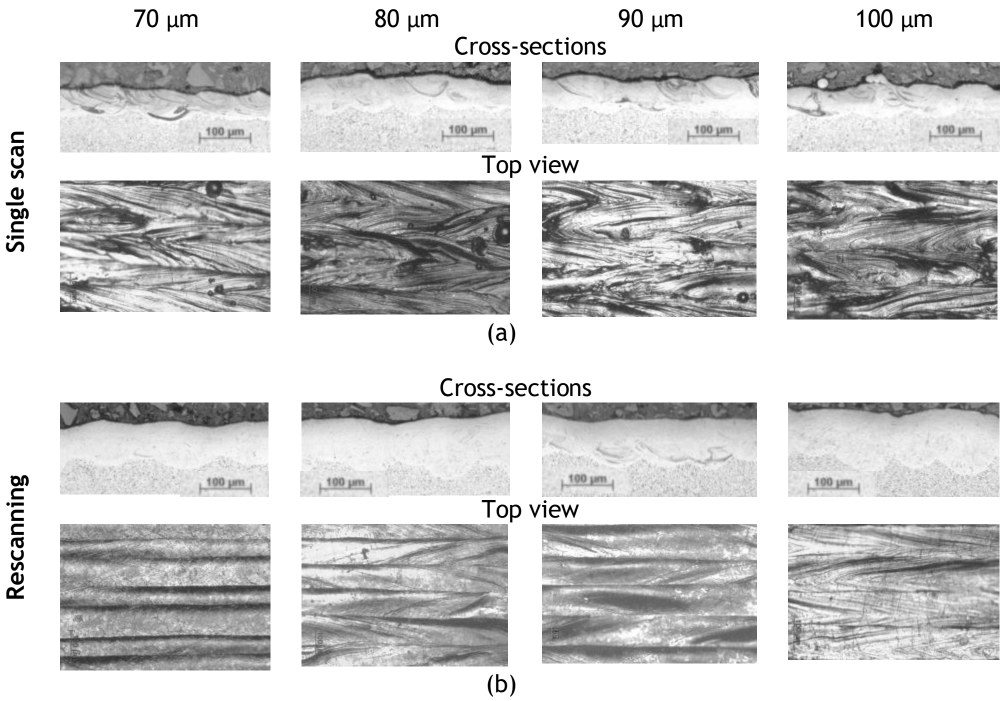


Figure 4. Cross-sections and top view of DMLS surfaces from mixture Ti6Al4V (ELI) and 1 at.% Cu at laser power 170 W, scanning speed 1.0 m/s and 70-100 μm hatch distances: (a) single scan, (b) after rescanning.

Investigation of homogeneity distribution of Cu in Ti6Al4V near the surface with situ alloying at various scanning speed (0.7-1.3 m/s) and hatch distances (70-100 μm) was performed by analysis of an EDS elemental maps. For a single exposure at 0.7 m/s scanning speed and 70 μm hatch distance, the surface composition was homogeneous. An increase in scanning speed and hatch distance resulted in a decrease in surface homogeneity. Rescanning had a profound effect on the surface homogeneity (Fig. 5). The rescanning strategy removed the concentrations of copper that formed at the peripheries of the single tracks. Similarly to single exposure, at rescanning the Cu inhomogeneity increased with scanning speed and hatch distance. An increase in input energy has a positive effect on surface homogeneity. A rescanning strategy provides an effective means to improving the surface homogeneity, by re-melting the surface and causing a stirring effect.

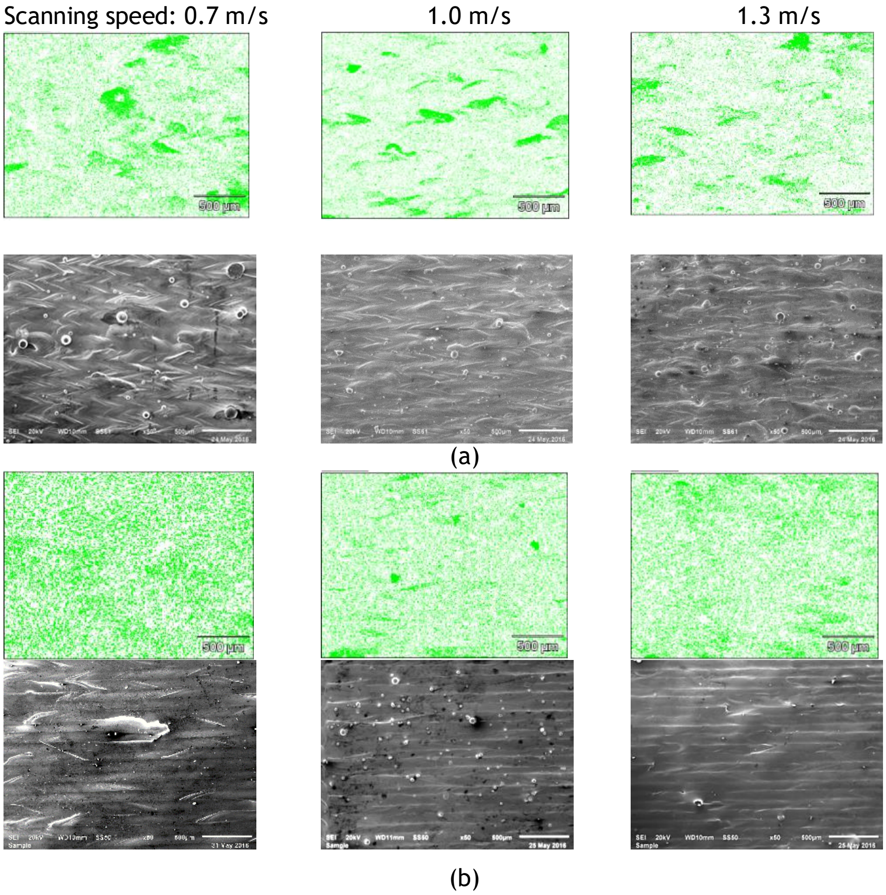


Figure 5. Cu distribution map by XRD spectra and top view photos in SE mode of DMLS surfaces from mixture Ti6Al4V (ELI) and 1 at.% Cu at laser power 170 W, scanning speeds 0.7-1.3 m/s and 90 μm hatch distances: (a) single scan, (b) after rescanning

In figure. 6 the surface composition of Cu (%wt) for in-situ Ti6Al4V-Cu alloyed layers is seen. The expected percentage Cu by weight percentage is 1.38% because 1% at. of Cu powder was mixed with the Ti6Al4V powder. For a single exposure at 0.7 m/s scanning speed and 70 μm hatch distance the surface composition was 1.05% Cu, and 2.31% for at scanning speed and hatch distance of 1.3 m/s and 100 μm, respectively. With an increase in scanning speed and hatch distance, the surface composition of Cu increased.

Rescanning improved the surface Cu composition of the in-situ alloyed layer. This deviation of surface compositions is the result to the vast difference in the material properties of Ti6Al4V and Cu. Ti6Al4V and Cu have a specific heat capacity 560 J/kg·K and 387 J/kg·K, thermal conductivity; 7.2 W/m·K and 401 W/m·K, density; 4430 kg/m^3 and 8940 kg/m^3, melting temperature of 1649°C and 1083°C respectively and viscosity in liquid state 5 mPa·s and 4.75 mPa·s. When the powders is exposed by the laser beam, the powder mixture melts, but since Cu has higher thermal conductivity, lower heat capacity and viscosity than Ti6Al4V alloy, copper transfer heat to surrounding titanium alloy and fluid flows pushed heavy copper to the peripheries of molten bath. The molten pool rapidly solidifies before the Cu can be completely mixed and alloyed with the Ti6Al4V.

Better results of surface homogeneity and surface composition are noted at higher energy inputs because the Cu has more time to alloy with the Ti6Al4V before the molten pool solidifies. Rescanning dramatically improves the surface homogeneity and surface composition because the molten pool is completely re-melted. At 0.7 m/s scanning speed and 70 μm hatch distance there is sufficent input energy and overlapping of single tracks to exhitbit similair surface homogeneity and surface composition as rescanning.

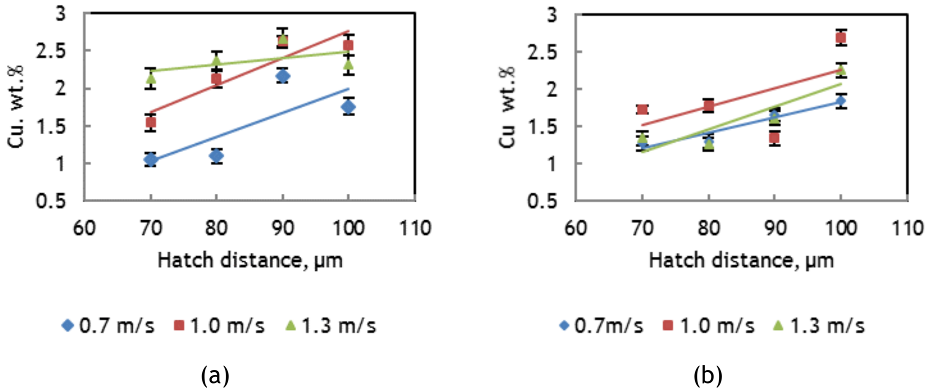


Figure 6. Average wt.% of Cu near the DMLS surface of Ti6Al4V+1at%Cu powder at different scanning speeds and hatch distances: single scan (a) and rescanning (b).

4. CONCLUSIONS

In-situ alloying of Ti6Al4V (ELI) and 1at.% Cu powder was successfully performed utilizing DMLS. Produced single layers exhibited no signs of porosity, delamination, or solidification cracks. The surface quality of the produced layers was improved with a decrease in scanning speed and hatch distance. The applied rescanning strategy had minimal effect on surface roughness but did remove surface satellite particles, improving the surface quality. Surface homogeneity and surface composition improved with an increase in input energy. Rescanning had a profound improvement on surface homogeneity and surface composition; this is attributed to the complete re-melting of the molten pool. It can be concluded that the surface quality and homogeneity of in-situ alloyed Ti6Al4V-1at.%Cu can be improved by decreasing the scanning speed and hatch distance, within the optimal process parameters, or applying a rescanning strategy.

5. ACKNOWLEDGEMENTS

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