Experimental Study of Thermochemical Treated Biomedical 3D Printed Titanium Alloy Implant

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Abstract. For medical and dental individual implants are made by additive technology. The patient-specific usable implant material is the Ti alloy (Grade 23). The used 3D printer do LMF (Laser Metal Fusion) process and melts the metal particle by the laser layer by layer. Surface treatment of implants affects mechanical strength, aesthetic and osseointegration properties [1]. Of these, our study investigates the mechanical strength properties of plasma nitride surface treatment. The plasma nitrided 3D printed biomedical Ti alloy (Ti6Al4V, Grade 23) mechanical properties. The influence of the nitrided layer on tribological behaviour of plasma nitrided film was studied using microhardness tester. The microhardness results pointed out that the surface treatment increased the surface hardness and reduced the plastic deformation of the alloy.

1. Introduction

In the medical field, custom-made implants are used for individual cases. These implants are manufactured with additive technologies thanks to 21st-century innovations in manufacturing technology. In this study, custom-made patient-specific subperiosteal dental implants were investigated. These are called cortically supported implants in current practice. They have substantially changed in recent years considering the framework, perforation and fixation of their supporting base and the detachable joint of the denture. Fixing method to the cortical ridge, surgical insertion strategy, implant material and postoperative care have all transformed significantly. In the case of the medical implant required the corrosion resistance, the suitable mechanical properties and the biocompatibility and high corrosion resistance.

1.1. 3D printing of patient-specific dental implants

Nowadays, the development of 3D printing technologies has made ever-increasing demands on perfect and precise products. During product processing, the design is carried out in a virtual environment, the product is printed out additively, its geometric sizes are then checked, and the processed blank implant part inspected after burr-drilling. Metal additive manufacturing technology provides a more homogeneous material structure for the manufactured part in comparison with the previously used casting procedure. Manufacturing productivity is also higher, and it is easier to control the final product quality.

In current practice, implants, which fit patients’ bone anatomy, are designed in a virtual environment based on CBCT images. Afterwards, an STL file is created from DICOM format. Manufacturing is carried out with a metal 3D printer. Our 3D printer uses the energy of laser photons.
to fuse metal particles layer-by-layer with LMF (Laser Metal Fusion) technology [2-4]. The material of patient-specific implants is Grade 23 titanium alloy.

1.2. Surface treatment by nitridation
It was treated the 3D printed test samples by nitridation. The nitriding efficiency depends on the chemical composition of the treated sample, it needs to contain some high nitrogen affinity elements. By the way of diffusion, the nitrogen establishes in the surface layer some nitride compound and increase the surface hardness [5]. The formed compound volume depends on the nitridation treatment temperature and time, and also the media nitrogen concentration and the test samples chemical composition. The used alloy base metal is the titanium, which has a big affinity to join by nitrogen to form TiN or TiN2 compounds in the surface layer.

Figure 1. The nitrided test samples.

The nitrided microstructure also consists of a region of nitrogen-stabilized α-titanium, that is, α-case, and a nitrogen diffusion zone (typically 15–25 µm deep) underneath the compound layer. The plasma-nitried microstructure is strongly correlated with the composition of titanium substrate and the nitriding process parameters such as duration, temperature, pressure, and composition of the nitriding medium, among which temperature has the most significant influence [6, 7]. The nitrided test samples are shown in Figure 1.

2. Used material and heat-treating processes
2.1. 3D printed test samples
The test samples made by additive technology (3D printing). LMF process was performed by using a Sisma Mysint 100 3D printer. The parameters for manufacturing Ti6Al4V was next: laser power 125 W, scanning speed 1000m/s, layer thickness 20 µm, laser beam spot size 50 µm. Argon atmosphere was used to shield the melted pool during the additive process.

Table 1. Chemical composition (content in wt. %) of Ti alloy, Grade 23 remain is Ti.

| V   | Al   | C    | Fe   | N    | H    |
|-----|------|------|------|------|------|
| 3.5-4.5 | 5.5-6.5 | Max. 0.08 | Max. 0.25 | Max. 0.03t | Max. 0.0125 |
Chemical composition of the test samples showed in Table 1. The Grade 23 alloy is a special high purity version of the Ti 6Al 4V alloy. This kind of titanium alloys suitable for biomedical applications [6]. It has high corrosion resistance, it is lightweight and biocompatible also the mechanical properties are suitable for several applications [7, 8]. Density is 4,43 g/cm³, the melting point is between 1604-1660°C. Mechanical properties are the next: tensile strength is 860 MPa, yield strength 790 MPa, hardness 341 HV, elastic modulus 113,8 GPa.

2.2. Annealing of samples
The test samples were annealed after the printing process. The heat-treating is useful for homogenise the printed microstructure and decrease the heat affected stress conditions [9-11]. The heat-treating process parameters shown in Table 2. The heat-treating T-t diagram shown in Figure 2.

Table 2. Heat treating of the samples.

| Treatments       | Parameters |
|------------------|------------|
| Annealing        | 600 °C     |
| Cooling media    | Water and air |

Figure 2. Annealing T-t diagram of the 3D printed samples.

2.3. Surface thermochemical treating processes
The plasma nitridation carried out at 525 °C for 24 hours in a nitrogen-containing medium. The other group of the test samples was nitrided by gas nitridation carried out at 570 °C for 2 hours and other ones for 12 hours. All samples surface was prepared by polishing (Ra=0,01 µm) before the nitridation.

Table 3. Nitridation parameters.

| Number of the tested samples | Thermochemical treating parameters | Nitridation Temperature | Nitridation time (h) |
|------------------------------|-----------------------------------|-------------------------|----------------------|
| 1                             | Gas nitridation                   | 570 °C                  | 2 h                  |
| 2                             | Gas nitridation                   | 570 °C                  | 12 h                 |
| 3                             | Plazma nitridation                | 525 °C                  | 24 h                 |

The nitridation process parameters summarized in the Table 3. The used temperature much lower than the typical nitridation temperature (700-1100 °C) in the case of the same Grade 23 Ti alloys, but the high temperature can involve a microstructural changing (grain growing, overaging, embrittlement, unwanted phase precipitations, etc.), what we wanted to avoid [12]. The surface treating little bit modified the surface roughness (after nitridation Ra=0,05 µm). The average surface roughness measured by GD120 MarSurf surface roughness tester. The surface roughness did not change
significantly after the nitridation process. The suitable surface roughness is important about the wear and corrosion resistance [12, 13].

3. Results and conclusions

3.1. Results

The original hardness of the test samples was 341 HV. The nitridation aimed to increase surface hardness and wear resistance. The hardness tests made by microhardness tester (CSM Instruments MHT), using the diamond Vickers indenter, the maximum load was 50 g.

Table 4. The hardness of the tested samples.

| Number of the tested samples | Hardness HV<sub>0.05</sub> |
|-----------------------------|--------------------------|
| 1.                          | 386 HV<sub>0.05</sub>    |
| 2.                          | 412 HV<sub>0.05</sub>    |
| 3.                          | 423 HV<sub>0.05</sub>    |

Figure 3. The nitrided surface layer hardness as a function of the nitridation time.

The hardness of the nitrided sample shown in Table 4 and the relationship between the nitriding time and the earn hardness shown in Figure 3.

4. Conclusion

The nitridation significantly modified the hardness of the tested Grade 23 titanium alloys surface. The increasing of the surface hardness shows a strong relationship with the nitridation time. The used nitridation temperature was different than the typical nitridation temperature to avoid the unsuitable microstructural changing. The high temperature can increase the grain growth of the titanium grains and establish precipitation.

It can conclude, that even that the used nitridation temperature was much lower than the typical temperature, as a function of the nitridation time the surface thermochemical process was successful. It needs some microscopy test to compare the high temperature (700-1100°C) and the used (525-570°C) temperature effect for the surface microstructure and the nitridation affected differences in the grain size and mechanical properties. The used surface nitridation process not affected significant modification of the surface roughness.
It can conclude that the used nitridation parameters are suitable to increase the Grade 23 titan alloy surface hardness.

5. References
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