SURFACE PROPERTIES OF FUNCTIONALLY GRADED BIOMATERIALS PRODUCED BY RAPID MANUFACTURING

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Abstract

Rapid Manufacturing became important in the field of medical engineering recently. Newly developed methods increase the demand on overall properties and the new approaches are needed. In the multi-material functionally graded implants the mechanical, physical and chemical properties change from one side of the product to the other. Thus, the disadvantage of joint requirements in bioimplants can be eliminated and the risk of screw connections or corrosion of welding avoided. This study is focused on properties which are important from the biocompatibility point of view, namely contact angle, hardness, roughness and surface porosity.

1 INTRODUCTION

Material Printing Process (MPP) is a novel Rapid Prototyping and Manufacturing technology that aims to produce bio-implants, customized to the needs of individual patients [1]. The bio-implant is manufactured from a powder material which is sintered layer-by-layer, without need of final tooling. Moreover, MPP enables production of multi-material functionally graded structures, so that the material, mechanical properties and structure (especially porosity) is changing from one side of the implant to the other. This enables the final properties of the implant to match with the bone.

In general, a material or combination of materials for hard tissue replacement should have the following properties: 'biocompatible' chemical resistance, excellent corrosion resistance, acceptable strength, low Young's modulus to avoid implant-bone stress shielding and high wear resistance. Furthermore, implant's surface properties such as surface chemistry, surface energy, topography and roughness influence the initial cell response at the cell-material interface, ultimately affecting the rate and quality of new tissue formation [2]. Especially, controlled surface roughness and porosity are a key to excellent osseointegration [3]. These requirements on a bio-implant can be technically met when the MPP technology is utilized. A biomaterial which has a low Young's modulus and controlled porosity gradient can achieve excellent osseointegration on one side of the implant while on the other side a biomaterial with improved tribological properties is used. This arrangement is promising for various bio-applications. For example, the disadvantage of joint requirements in bioimplants can thus be eliminated and the risk of screw connections or corrosion of weldings avoided [3].
Fundamental materials which are recommended especially for joint and bone implants are pure Ti, Ti-6Al-4V alloy and Co-28Cr-5Mo alloy. Especially titanium and its alloys currently constitute the most favored implant materials for joint replacement and osteosynthesis. In comparison to other metallic implant materials, titanium is characterized by a high biocompatibility, a good workability and corrosion resistance with suitable mechanical properties (low Young’s modulus – high strength) [4]. Among all implant materials, Co-Cr-Mo alloys demonstrate the most useful balance in strength, fatigue and wear along with resistance to corrosion. The cast alloy containing 28 wt%Cr and 6 wt%Mo (balance Co) has been used for many years to produce medical implants such as hips, knees, ankles and bone plates. The wrought Co-Cr-Mo alloys exhibit superior mechanical and chemical properties compared with the cast alloys due to a finer grain size and more homogenous microstructure. Although fabrication of surgical implants by conventional methods are common, powder metallurgy (P/M) route offers additional advantages [5]. These materials can also be used in metal powder production. Development of biomaterials for powder metallurgy has recently received much attention. New compositions and sintering process parameters are widely investigated in order to produce optimal microstructures [3]. It is known that during co-sintering of composite layers, the two components must have the same or similar sintering behaviour in order to reduce mismatch stresses during the heating and cooling cycles [5].

Implant surface roughness influences osteoblast proliferation, differentiation, and local factor production. The success or failure of an implant is largely dependent on the degree to which it integrates into the bone. The physical, chemical, and biological events at the bone–implant interface play a major role in the ability of an implant to osseointegrate into the bone and are dependent on the chemical composition, surface energy, topography, and roughness of the implant. The interactions of different type of cells with various solid substrates depend mainly on surface characteristics such as wettability, chemistry, charge and roughness. The effect of wettability on the cellular adhesion is more difficult to evaluate. Surface roughness affects wettability in different ways depending on the topographical features, and wettability is one of the most important parameters when biomaterials for implant devices are designed [6]. There is accumulating evidence that surface roughness is a particularly important variable in this regard. In vivo studies have shown that implants with rough surfaces achieve better osseointegration than those with smooth surfaces, as evidenced by greater pull-out strength and increased bone–implant contact.

In this study MPP Ti6Al4V and CoCr alloy multi-material graded samples were investigated. The MPP samples were produced at various sintering temperatures to find optimal processing conditions. The surface structure and properties were analyzed in order to provide information basis for interpretation of bio-compatibility results.

2 MATERIALS AND METHODS

2.1 Materials

Ti6Al4V and CoCr alloys were supplied in a powder form by Arcam AB. The powder was produced by a gas atomization process and particle sizes laid within a size range from 10 to 70 µm. Multi-material functionally graded samples of CoCr alloy and Ti6Al4V alloy were manufactured by the MPP. They consisted of one part of CoCr and one part of Ti6Al4V, see Fig. 1. These were built in the shape of disks.
(30mm diameter, 3mm thickness) by the successive application of 10 to 11 pattern layers of CoCr and Ti6Al4V on a foundation of pure Ti6Al4V powder, consolidated at various temperatures as derived in Fig. 1. For comparison, one sample of pure CoCr alloy and one of pure Ti6Al4V alloy where also manufactured by a similar procedure. The consolidation took place in a protective atmosphere of 95% Ar and 5% H, while the compaction pressure during consolidation was set to 170 MPa.

![Fig.1. Layout of testing samples](image)

2.2 Contact angle measurement

Contact angle was measured by Surface Energy Evaluation System which is a computer-based instrument for contact angle measurement and surface energy calculation (Advex Instruments s.r.o). The samples were ultrasonic cleaned in ethanol bath and dried with agitated air. The sessile drop technique was used to measure the water contact angle. In this technique a small drop of distilled water was placed on the surface of a sample using a micropipette and the contact angle was measured using the See System software. The contact angle was measured three times on each specimen.

2.3 Hardness measurement

Hardness was measured with the help of Brinell tester, where the hardened steel ball-shape indenter was used. The diameter of indenter was 2.5mm and the applied load was 612.9N for 10 seconds. Specimens were measured at Ti6Al4V part and CoCr part three times to determine an average value.

2.4 Roughness measurement

Roughness measurement was carried out using Hommel Tester T 1000. The important roughness features for the measurement of porous samples were profile depth Pt (total height of P-profile, which is the sum of the largest profile peak height and the largest profile valley depth of the P-profile within the evaluation length), waviness height Wt (total height of W-profile, which is the sum of the largest profile peak height and the largest profile valley depth of the W-profile within the evaluation length), maximum peak-to-valley height Rt (which gives vertical distance between the highest peak and the deepest valley).

2.5 Porosity investigation

Surface porosity was evaluated using the confocal microscope Olympus LEXT OLS 3000. 3D-view images were taken to show the most realistic information about the surface topography of the samples. The Scanning Electron Microscopy images of surface were taken as well.
3 RESULTS AND DISCUSSION

3.1 Contact angle measurement

The contact angle results are given in Fig. 2. The contact angle of graded materials lay above those of pure Ti alloy and CoCr alloy. Furthermore, it can be seen that the contact angle value decreases with increasing sintering temperature. This can mean that at the higher sintering temperatures of 1020°C and 1040°C the graded samples are more compacted, which leads to a better surface wettability (lower contact angles). So far, it seems that the highest wettability is reached at pure CoCr sample. All MPP samples soaked the testing liquid in after a time period of about 5 seconds, which also evidences open porosity in the material. With regard to cell seeding, it can be assumed, that the moderate hydrophilic behaviour (e.g. of sample No. 4) will result in higher possibility of fluids’ access to the implant surface and thus in greater osseointegration.

![Fig.2. Results of contact angle measurement](image)

3.2 Hardness measurement

The Brinell hardness increases with sintering temperature, as shown in Fig. 3. The fact that Ti parts gave higher hardness values can be explained by a lower open porosity of Ti part than of CoCr part. This was changed at higher temperatures when CoCr part was partially melted.

![Fig.3. Results of hardness measurement](image)
3.3 Roughness measurement

The roughness parameters of MPP samples are given in Fig. 4, where the average value for Ti6Al4V part and for CoCr part is presented. It can be seen, that roughness characteristics of CoCr differ quite significantly from Ti alloy even though the powder size distribution was of the same interval 10-70µm. The profile depth Pt is close to the upper value of the powder size interval. This means that the top layer surface is formed by particles that are locally placed one on each other creating high peaks and deep valleys or that the top layer was locally incomplete. The typical wavelength RSm was about 140µm for Ti6Al4V alloy and about 190µm for CoCr alloy and the vertical distance between the highest peak and deepest valley Rt reached to 25 µm for Ti6Al4V alloy and about 40µm for CoCr alloy.

![Fig. 4. Results of surface roughness measurement](image)

3.4 Porosity investigation

3D topography images were acquired with the help of confocal microscope (Fig. 5) using a reflected light, a contrast between the highlighted powder peaks and darkened valleys can give some suggestion of surface porosity and surface structure. Samples’ surfaces were observed using electron microscopy (Fig.6). It is apparent that the top sintered layers were lacking large areas of powder particles. The surface porosity was not determined numerically since it was not possible to define an exact top reference layer and to exclude open pores from the measurement. The presence of open pores was also evidenced during contact angle measurement.

![Fig. 5. Topography results – confocal microscope](image)
4 CONCLUSION

Different characteristics were investigated within the MPP samples. The contact angle decreased at higher sintering temperatures, thus improving wettability of the samples. This fact is quite positive for the material-cell interaction. The Brinell hardness increased with sintering temperature and reached the highest value when CoCr part was partially melted, probably when pores in the material were less frequent. Higher hardness promises better wear properties and thus lower possibility of toxicity due to the worn debris of material. The roughness of CoCr part of MPP graded samples was higher than roughness of Ti parts, which might in some cases encourage the cell proliferation. Observed open pore structure would enable cells to grow easily on the surface. Samples prepared by this innovative method proved their ability to be used as bioimplants from their surface characteristics point of view. Nevertheless, further investigation in terms of biocompatibility has to be done to obtain detailed behaviour of these materials in presence of human body cells.

REFERENCES