Shear strength of a three-dimensional capillary-porous titanium coating for biomedical applications

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Abstract. The effect of pretreatment and plasma preheating of Ti-substrate on shear strength of three-dimensional capillary porous Ti-coating was studied. After sandblasting the shear strength of the plasma sprayed coating was 200 ± 2 MPa, and after additional matting it was 68 ± 4 MPa. The use of plasma preheating of the substrates for 9 seconds decreased difference between values of the shear strength to 249 ± 17 MPa and 229 ± 16 MPa, respectively. After plasma spraying the microhardness of the surface layer of the substrate was 4.34 ± 0.35 GPa, the microhardness of the boundary between the coating and the substrate was 8.08 ± 0.45 GPa, and the microhardness of the coating was 3.48 ± 0.25 GPa. High shear strength of the coating was attributed to the activation of the substrate by means of plasma preheating and hardening of the boundary between the coating and the substrate by oxides and nitrides.

1. Introduction
This work considers a complex system "implant – bone tissue". The implant surface must simultaneously satisfy many requirements in the field of mechanics, plasma spraying, and medicine [1,2]. Over the last 40 years many works have been published on the topic, which is reflected in reviews [1,2].

The authors of this study developed three-dimensional capillary porous (3DCP) Ti-coating for endosteal implants with a thickness of 1 mm or more [3]. Such coatings consist of ridges and valleys. Coating valleys form the basic volume of pore space, up to 50%, in which new bone tissue can grow freely and operate. Ridges of the 3DCP Ti-coating transmit the main mechanical load between the implants and bone tissue. Owing to this effect, the strength of the formed ridges is comparable with that of monolithic materials. Bioactive properties of the coating are provided with additional surface layers, which are formed, for example, by micro-plasma oxidation or plasma spraying [4, 5].

The purpose of this study is to estimate the effect of the plasma preheating of the substrates to achieve the maximum shear strength of the 3DCP Ti-coatings with high porosity.

2. Materials and methods
VT1-00 (chemical composition of ≤ 0.15 wt% Fe, ≤ 0.04 wt% N, ≤ 0.1 wt% O, Ti constituted the balance) was used to manufacture cylindrical substrates with diameter of 9 mm. The wire for plasma spraying was made of VT1-00, too.
Before spraying, the cylindrical substrates were divided into two groups. The surface of the substrates in the first group was roughened by grit blasting with Al2O3 powder (average grit size 700 μm). The surface of the substrates in the second group was roughened by grit blasting with Al2O3 powder (average grit size 700 μm) and then it was additionally processed by means of matting using glass beads (average grit size 120 μm).

Plasma spray equipment was the plasma spray system UPU-3D (JSCo "Electromechanica", Rzhev, Russia) with the plasma spray gun PP-25. Optimization of the plasma sprayed modes (plasma gas Ar, arc voltage 30 V, arc current 300 A) was performed in work [3]. The angle between the axis of rotation of the substrate and the spray cone was 45°.

The surface of the substrate was preheated using plasma before plasma spraying. In this experiment the preheating time was changed from 0 to 15 s.

MultiFast plastic material (Struers, Denmark) with average shear strength of 96.1 MPa was used for modeling of bone tissue. The plastic was used to press-fit on the 3DCP Ti-coatings in accordance with method of the shear test [3].

The original procedure for determining the adhesion of the coating to the substrate was used [3]. Test specimens for shear test were performed on the universal testing machine Instron 5882.

The microstructure of the substrate, the coating, and the boundary between them were examined by means of the optical microscope (Carl Zeiss Jenavert Interphako).

The samples were etched in the bath 5% HF + 25% HNO3 + 70% H2O for metallography. The etching time was 5-10 s. The time of deep etching was 180 s.

The coating microhardness was determined in cross-section using the Vickers indenter (PMT-3) at loads of 0.098 and 1.96 N (10 and 200 gf) for 15 s. Minimum 15 indentations were applied to each sample.

The nitrogen and oxygen contents were measured with Leco TC-436 and Leco TC-600 analyzers, respectively.

3. Results

For the specimens from the first batch the average thickness of the 3DCP Ti-coating was 1.47 ±0.15 mm, and for the specimens from the second batch the average thickness was 1.24 ±0.15 mm.

Qualitative differences in the shear deformation curves of the Ti-bulk material and of the 3DCP Ti-coating on the Ti-bulk surface were not detected (Figure 1). The shear strength of the Ti-bulk material, which was used to manufacture the substrate, was 432 ± 29 MPa.

![Figure 1](image1.png)

**Figure 1.** Diagram of shear testing: (a) the specimen from the second group with preheating for 9 s; (b) the bulk specimen.
The highest value of the shear strength was determined for the specimens from the first batch after the sandblasting process (Figure 2). The maximum shear strength was 249±17 MPa. This value was obtained for the specimens with the preheating for 9 s.

For the specimens from the second batch, the maximum value of the shear strength was 229 ±16 MPa after the plasma preheating for 9 s, and the minimum value was 68± 4 MPa without preheating.

Figure 2. The shear strength of the specimens depending on the time of their preheating by the plasma jet. 1 – the specimens from the first batch, 2 – the specimens from the second batch.

Adhesive fracture of the boundary between the coating and the substrate was determined for the specimens from the second batch without the additional plasma preheating and after the additional preheating for 3 s. For all other specimens the fracture was originated in the coating.

The boundary between the coating and the substrate in the cross-section without etching was not determined by means of optical microscopy. A bright stripe with width of 10 to 20 µm appeared along the border after the etching up to 10 s (Figure 3). The chain of voids appeared on the boundary with increase of the etching time, the relative length of this chain increased with the increasing of the etching time. Near the boundary, the increase of Ti-grain size was identified both in the substrate and in the coating. In certain areas, the Ti-particles grew from the substrate into the coating (the so-called epitaxy).

Table 1 represents the content of oxygen and nitrogen in the Ti-wire and the plasma sprayed coating. The oxygen content in the coating increased 2.8 times, and the nitrogen content increased 15 times in comparison with the content in the Ti-wire.

Increase of the contents of oxygen and nitrogen enhanced the microhardness of the substrate to 4.34 ± 0.35 GPa, the microhardness of the coating to 3.48± 0.25 GPa, and the boundary between them to 8.08± 0.45 GPa, which confirmed the increase of the shear strength (initial microhardness was 1.86± 0.25 GPa) (Figure 4).

4. Discussion
The positive effect of sandblasting can be explained by the activation of the inert surface by removing the part of the coating material from the surface. The depth of the removed layer is about 4 µm, it was previously defined [4].

Moreover, the sandblasting increases the surface roughness, which increases the contact area of the sprayed particles and the substrate.
Additional matting with use of the glass beads decreases the roughness parameters of the surface [7]. For this reason, the specific surface area of the substrate is reduced, consequently, the value of the shear strength is reduced, too. This is confirmed experimentally.

![Image](image_url)

**Figure 3.** The boundary between the substrate and the coating in the cross-section of the specimen from the first batch, which was preheated for 12 s. Indentation of the diamond pyramid was obtained at the load of 10 gf.

| Sample            | Content of elements in % by weight | Ratio O/N |
|-------------------|------------------------------------|-----------|
| Ti-wire           | O 0.089 | N 0.001 | 89        |
| 3DCP Ti-coating   | O 0.249 | N 0.015 | 16.6      |
Figure 4. Distribution of values of microhardness (load 10 g) in the thickness of the shear sample: on the left Ti substrate, on the right TCP Ti coating.

The plasma preheating of the substrate for 3 s does not increase the shear strength, for this reason, adhesive fracture is determined between the coating and the surface of the substrate. That is, the surface morphology of the substrate does not provide enough mechanical adhesion with the coating and the low temperature does not allow achieving chemical interactions. There is no wetting of the surface of the substrate by the sprayed particles, which is necessary for solid connection.

Cohesive failure is determined for the coatings on the substrates after the sandblasting. The destruction occurs on the surface of a larger diameter than the diameter of the substrate, and capture valleys of the 3DCP Ti-coating, which are filled with plastic. An immediate challenge is to enhance the bond strength of the plasma sprayed porous coating with the substrate.

The influence of the substrate pretreatment on getting a strong connection with the coating is not fully studied. In our experiments the roughness factor determines the strength of the connection of the sprayed material with the substrate at relatively low substrate temperature (without additional plasma preheating). In this case, at the stage of cooling the sprayed particles can partially detach from the surface under the influence of residual stresses (thus some part of the pore volume is formed).

At temperatures of the substrate higher than 300 °C, the substrate surface becomes more active. The wetting of the substrate by the sprayed particles increases [1]. Preheating of the substrate reduces the difference between the temperature of the substrate and coating, for this reason, residual stresses reduce, and, consequently, the strength of the connection of the coating with the substrate increases.
The preheating of the substrate after sandblasting increases the shear strength of the 3DCP Ti-coatings by 30%. For the 3DCP Ti-coating with additional treatment of the substrate using matting the shear strength increases by 73%. We can assume that thermal activation is the dominant factor in relation to the factor of surface morphology.

High values of the microhardness at the surface of the coatings with the substrate can be explained by the influence of oxygen and nitrogen. Oxygen and nitrogen increase the strength and the hardness of the Ti [6].

5. Conclusion
1. The shear strength of the three-dimensional capillary porous Ti-coating without preheating of the Ti-substrate after the sandblasting was 200 ± 2 MPa, additional processing of the substrate by the glass beads reduced the shear strength to 68 ± 4 MPa.
2. After plasma preheating of the substrate for 9 s the value of the shear strength was 249 ± 17 MPa for the specimens with the substrate after the sandblasting and 229 ± 16 MPa for the specimens with additional treatment of the substrate by the glass beads. The plasma preheating decreased difference between values of the shear strength.
3. Increase of the contents of oxygen and nitrogen enhanced the microhardness of the substrate to 4.34 ± 0.35 GPa, the microhardness of the coating to 3.48 ± 0.25 GPa, and the boundary between them to 8.08 ± 0.45 GPa, which confirmed the increase of the shear strength (initial microhardness was 1.86 ± 0.25 GPa).

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References
[1] Berndt C, Hasan Md, Tietz U, and Schmitz K 2014 Advances in Calcium Phosphate Biomaterials (Berlin Heidelberg: Springer) pp267–329
[2] Dorozhklin S 2015 Mater. Sci. Eng. C 55 pp 272–326
[3] V.I. Kalita, et al., 2016 Mater. Sci. Eng. C 60 pp255–259
[4] Kalita V, Gnedovets A, Mamaev A, Mamaeva V, Malanin D and Pisarev V 2005 In Abstracts and Full-Papers CD of 17th Int. Symp. on Plasma Chemistry (Toronto: Univ. of Toronto Press) pp. 1105-1106
[5] Kalita V, Komlev D, Ivannikov A, Radyuk A, Komlev V, Mamonov V, Sevast’ianov M, Baikin A 2017 Inorganic Materials: Applied Research 8(2) pp 296–304
[6] Maltsev V 2013 Metallography of industrial non-ferrous metals and alloys (Moscow: Ripol Classic) p 367