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Adhesion of Dental Ceramic to Ti6Al4V Alloy, Fabricated by CAD/CAM Technologies

ABSTRACT

of PhD Thesis

SCIENTIFIC SPECIALTY

Prosthetic Dental Medicine

SCIENTIFIC ADVISORS:

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The PhD thesis has been approved and directed for defense at a meeting of the Department of Dental Materials Science and Prosthetic Dentistry at the Faculty of Dental Medicine of the Medical University "Prof. Dr. Paraskev Stoyanov" - Varna.

The dissertation contains 152 standard pages and is illustrated with 15 tables and 63 figures. The bibliography consists of 185 sources, 28 of which are in Cyrillic and 157 are in Latin.

The public defense of the dissertation will take place on 21.04.2023 at 1:30 p.m. in the Auditorium "Assoc. Dimitar Klisarov" of FDM, MU - Varna, and online through the Webex platform. The work of the candidate will be evaluated by a scientific jury composed of:

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The defense materials are available in the Scientific Department of the MU - Varna and are published on the website of the MU - Varna.

Note: In the abstract, the numbers of the formulas, tables and figures correspond to the numbers in the dissertation work.

CONTENT

DESIGNATIONS

E – energy density, J/mm^3

E – modulus of elasticity, GPa

F_{fail} – loading at which the coating fails, N

k – a coefficient that depends on the thickness and modulus of elasticity of the metal base

l_c – distance between melted traces in SLM, mm

m – sample mass, g

$m+m_1-m_2$ – mass of water displaced by the sample, g

N – laser power, W

Ra - arithmetic mean roughness deviation, μm

Rq – root mean square deviation of the profile, μm

Rz - maximum profile height, μm

t_c - thickness of the building layer in SLM, mm

V – scanning speed, cm/s

V – sample volume, cm^3

ρ and ρ_1 - density of the sample and water respectively, g/cm^3

$\sigma_X, \sigma_Y, \sigma_Z$ – normal stresses along X, Y, Z axes

σ_{eq} – von Mises equivalent stresses

$\tau_{xy}, \tau_{xz}, \tau_{yz}$ – tangential stresses

τ_b – adhesion strength of the coating, MPa

ABBREVIATIONS

ADC - amplitude distribution curve
AM – additive manufacturing
BAC - material-ratio profile curve
CAD/CAM - Computer Aided Design/Computer Aided Manufacturing
CTE – coefficient of thermal expansion
DMLS – direct metal laser sintering
FEA – finite elements analysis
FPD – fixed partial dentures
HTT – hard teeth tissues
ISB - ideal solid body
ISO – International Standard Organization
RDB - rigid deformable body
SDB – solid deformable body
SEBM - Selective Electron Beam Melting
SLM – selective laser melting
SLS – selective laser sintering

INTRODUCTION

Metal-ceramic crowns and bridges are the main fixed prosthetic restorations in daily clinical practice because they meet all prophylactic, functional and aesthetic requirements. A wide range of noble and base alloys are used for their manufacture. Until now, cobalt-chromium dental alloys have been most widely used due to their high mechanical properties, high corrosion resistance and biocompatibility, easy production technology by casting, high durability and relatively low cost.

In prosthetic dentistry, much attention has recently been paid to pure titanium and its alloys for the production of metal-ceramic frameworks. The increased interest is dictated by its specific properties: low relative mass - almost 2 times lower than that of Co-Cr alloys, relatively high mechanical properties and modulus of elasticity, closest to that of bone. The disadvantage is the high melting temperature and reactivity of titanium, which make it difficult to produce details by casting.

Modern CAD/CAM technologies of milling and selective laser melting (SLM) are a good alternative for manufacturing dental constructions from titanium and its alloys. They provide higher accuracy and guaranteed or even higher mechanical properties of the details compared to the conventionally cast ones. Each of these technologies determines a specific morphology and surface roughness that can influence the adhesion strength of the ceramic to the titanium infrastructure.

Since adhesion strength is essential for the durability of metal-ceramic prostheses, different methods are used to increase it - mechanical, chemical, physical and combined. These include from the standard sandblasting and oxidation of the metal skeleton to its surface treatment with a bonding agent, chemical etching with various reagents, application of various coatings, laser etching or combined treatments.

The application of titanium and its alloys in the manufacture of metal-ceramic fixed partial dentures (FPD) has only been discussed in recent years, thanks to the introduction of modern CAD/CAM technologies in dental laboratories. There is still insufficient data on the properties of titanium costructions produced by selective laser melting.

The influence of different types of surface treatments on the adhesion of ceramics to titanium and its alloys made by milling and SLM is not clear. Therefore, the aim of the present work is to investigate the properties and adhesion of dental ceramics to Ti6Al4V alloy produced by modern CAD/CAM technologies - milling and selective laser melting, and to propose laboratory protocols for the fabrication of metal-ceramic fixed partial dentures that provide high adhesion strength.

CHAPTER 1
LITERATURE REVIEW

A literature review of the treatment of defects of the dental crown and tooth row by means of FPD - artificial crowns and bridges was made. The classifications of FPD are discussed in detail. The features of metal-ceramic prosthetic restorations are reflected. The application of titanium and titanium alloys in prosthetic dentistry is reviewed. Technologies for the production of prosthetic restorations from titanium and its alloys, such as casting, CAD/CAM milling and additive technologies, were examined. Attention is paid to the dental ceramics used to make FPD. An analysis was made of the adhesion of ceramics to titanium and its alloys and the influence of different types of surface treatments.

AIM of PhD thesis:

To investigate the adhesion of dental ceramics to Ti6Al4V alloy produced by CAD/CAM technologies.

TASKS:

1. To investigate the properties of Ti6Al4V alloy made by milling and selective laser melting.
   1.1. To examine the geometric characteristics and density;
   1.2. To examine the morphology and roughness of the surface;
   1.3. To test the hardness and determine the modulus of elasticity.
2. To conduct an experimental study of the adhesion strength of dental ceramics to Ti6Al4V alloy made by milling and selective laser melting.
   2.1. To determine the adhesion strength in application of different surface treatments;
   2.2. To investigate the fracture mechanism of the coating;
3. To determine the adhesion strength of porcelain to Ti6Al4V alloy by finite element analysis.
4. To develop a laboratory protocol for manufacture of metal-ceramics from Ti6Al4V alloy, produced by CAD/CAM technologies.

CHAPTER 2
MATERIALS AND METHODS
2.1 Materials and technologies for samples manufacturing
2.1.1 Material and sizes of the samples

Ti6Al4V alloy is used in the present study. The type and dimensions of the samples are selected according to the EN ISO 9693:2019 standard. The samples are plate-shaped with a length of 25+/-1 mm, a width of 3+/-0.1 mm and a thickness of 0.5+/-0.05 mm. To make them, a virtual model was created using SolidWorks software (Fig. 2-2). Two groups of samples (28 pieces in each group) were made using two types of technologies: CAD/CAM milling and selective laser melting.

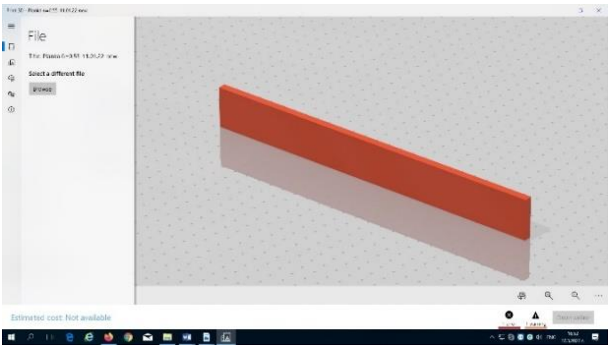


Fig. 2-2 Virtual model of the sample.

2.1.2 CAD/CAM milling

Specimens were fabricated from Starbond Ti5 Disc titanium alloy (Ti6Al4V Milling Grade 5 “ELI”) for ISO 22674 Type 4 dental restorations with the chemical composition given in Table 2-1.

Table 2-1.

Chemical composition of Ti6Al4V alloy (milling disc - 1 and powder for SLM - 2).

Chemical element, (%) → Alloy ↓		Al	C	H	Fe	N	O	Ti	V
1	Starbond Ti5 Disc	6.2	<0.4	<0.4	<0.4	<0.4	<0.4	89.4	4
2	CT PowderRange Ti64 F	5.50-6.50	0.08	0.012	0.25	0.05	0.13	Rest	4.50

The workpiece used is in the shape of a disk with a thickness of 10 mm and a diameter of 98.3 mm, Ref. 136510 of manufacturer: Scheftner Dental Alloys, S&S Scheftner GMBH, Mainz, Germany. The posiiton of the specimens during milling is shown in Fig. 2-3. The plates were milled on a CORITEC 650i Loader machine (Imes-Icore GmbH, Eiterfeld, Germany) in SOFIA PRINT and MILL EOOD, Sofia, Bulgaria.

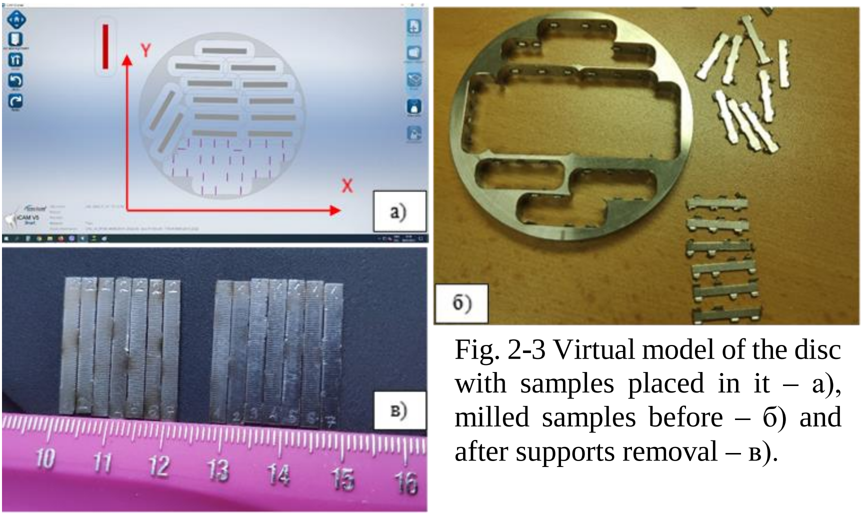


Fig. 2-3 Virtual model of the disc with samples placed in it – a), milled samples before – б) and after supports removal – в).

2.1.3 Selective laser melting

CT PowderRange Ti64 F (Ti6Al4V) alloy with chemical composition given in Table 2-1, from the manufacturer Carpenter Additive (Liverpool, UK) was used as the starting material for the samples made by SLM. The alloy is in powder form with an average particle size of 15-45 μm.

The samples were made by the 3D MEDICAL PRINT company (Pleven, Bulgaria) on a SYSMA MySint 100 machine (SYSMA S.p.A., Vicenza, Italy), equipped with a fiber laser. The following parameters of the SLM process were used: laser power 200W, laser beam spot diameter 55 μm, layer thickness 20 μm, scanning step -

0.020 mm, protective gas - argon. The placement of the specimens and supports during SLM is shown in Fig. 2-4.

After their fabrication, the samples are subjected to isothermal annealing to relieve internal stresses. It was carried out in a protective environment of argon and consists of heating and holding the samples at a temperature of 600 ^{o}C for 30 min, subsequent heating to 800 ^{o}C with holding for 1h 40 min and cooling with the furnace.

The SLM samples were produced with the help of Desislava Vlasakieva and Miroslav Simeonov and were provided free of charge for the purposes of this study.

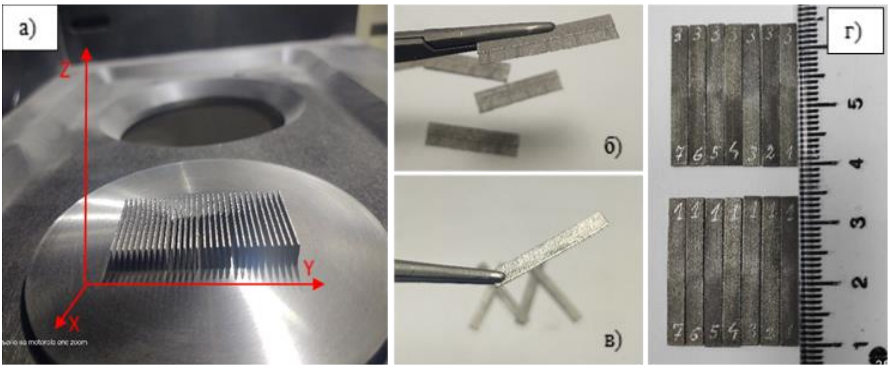


Fig. 2-4 Position of the samples on the table of the SLM machine – a); general view of a sample before – б) and after supports removal – в); ready to use samples – г).

2.1.4 Surface treatment

The samples from each group are divided into 4 subgroups of 7 pieces each depending on the treatment of their surfaces.

- The first subgroup of samples are without surface treatment and serve as a control group.
- The plates from the second subgroup are subjected to sandblasting on only one surface. Sandblasting was performed with Al_2O_3 (110 μm) under a pressure of 2 bar for a time of 10 s. The sample is located 10 mm from the

nozzle at an angle of 45°. After sandblasting, the samples were steam cleaned and air dried.

- On the surface of the samples from the third group, one layer of bonding agent VITA NP BOND PASTE (VITA Zahnfabrik H. Rauter GmbH & Co.KG, Bad Sackingen, Germany) was applied, which was fired at a temperature of 960 °C for 1 min in the oven for ceramics, according to the manufacturer's instructions.
- The surface of the samples of the fourth group underwent a combined treatment: first, they were sandblasted and then a bonding agent was applied according to the modes indicated above.

2.1.5 Porcelain coating

According to EN ISO 9693:2019, a coating of VITA LUMEX AC porcelain (VITA Zahnfabrik H. Rauter GmbH & Co.KG, Bad Sackingen, Germany) with a thickness of 1.1±0.1 mm and a length of 8±0.1 mm was applied in the middle of the treated surface along the entire width of the specimens. For this purpose, a silicone matrix was made in advance to ensure uniform dimensions of the coating. Four layers of ceramic were then sequentially applied and fired, according to the manufacturer's instructions (Table 2-3).

The metal-ceramic samples were made in "SMTL - Plamen Atanasov EOOD" headed by Plamen Atanasov.

Table 2.
Regime of porcelain firing.

Layer	Porcelain	Firing temperature, ^{o}C	Time, min
1	Opaque	800	1
2	Dentin	760	1
3	Enamel	755	1
4	Glaze	750	1

2.2 Samples characterization

2.2.1 Geometrical characteristics

The thickness and width of each plate were measured with a digital caliper "ABS Digimatic Caliper" (Mitutoyo, Japan) with an accuracy of 0.01 mm. Three measurements were made for each parameter, and the arithmetic mean value was taken for the statistical analysis.

2.2.2 Density

The density of the samples was determined using a pycnometer. First, the mass of the samples - m was measured on an analytical balance KERN ABJ-NM/ABS 220-4N (KERN&SOHN GmbH, Germany) with an accuracy of 0.0001g. Then the mass of the pycnometer filled with water - m_1 - was measured. The sample was placed in the pycnometer and the mass of the pycnometer with the water and the sample was measured - m_2. The density of the studied samples was calculated according to formula (3):

$$\rho = \frac{m}{\frac{m + m_1 - m_2}{\rho_1}} = \frac{m}{m + m_1 - m_2}\rho_1 \qquad (3)$$

Where: ρ – sample density, [g/cm^3]; m – sample mass, [g]; $m+m_1-m_2$ – mass of water displaced from the sample, [g]; ρ_1 - density of water [g/cm^3]. According to [ASTM B311-17, 2017; Metrological Handbook 145, 1990] at a temperature of 19 ^{o}C during the experiment, the density of water ρ_1 is 0.9984 g/cm^3.

The density of 5 randomly selected samples of each technology was determined and the arithmetic mean was taken.

2.2.3 Investigation of surface morphology

The surface morphology of the samples was examined using an Olympus SZ51 optical microscope equipped with a digital camera №TP6080000B.

2.2.4 Investigation of surface roughness

Roughness parameters were examined using a Surftest SJ-210 apparatus (Mitutoyo Corporation, Takatsu-ku, Japan). The roughness of each sample was measured on both surfaces 25 mm x 3 mm after fabrication and on one after sandblasting. Three measurements were made along the length of each surface.

The values of Ra - mean arithmetic deviation of the profile, Rq - mean square deviation of the profile and Rz - maximum height of the profile were studied. The plots of the BAC and ADC curves of the surface profile of the samples before and after sandblasting are shown. The BAC (material-ratio profile) curve shows the material-ratio of the profile in the evaluated length. ADC (amplitude distribution curve) is a profile amplitude distribution curve.

2.2.5 Microhardness measurements

The microhardness of milled and SLM samples before and after heat treatment, simulating porcelain firing, was investigated. The hardness measurement was carried out by the Vickers method on previously prepared microslices. Five measurements per sample were made with a ZHVμ-S microhardness tester (Zwick/Roell, Germany), applying a load of 25 g for 10 s. The arithmetic mean value was taken for the analysis.

2.2.6 Experimental investigation of adhesion strength of porcelain to Ti6Al4V alloy

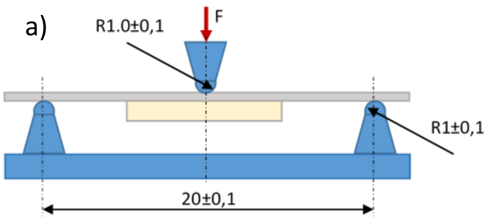
The experimental study of the adhesion strength of the porcelain coating to the titanium alloy was performed by a 3-point bending test, according to the EN ISO 9693:2019 standard. A special device was made for this purpose (Fig. 2-10). The tests were performed on a combined static and dynamic testing machine ZWICK Roell Vibrophore 100 (ZWICK Roell, Germany). A static bending test was implemented with a loading speed of 1.5 mm/min until a displacement of 0.2 mm was reached. The result of the conducted tests is a force/displacement diagram, on which a drop is registered at the moment of delaminating the ceramic layer.

The adhesion strength is calculated according to formula (4) [ISO 9693:2019]:

$$\tau_b = k * F_{fail} \qquad (4)$$

Where: τ_b is the adhesion strength of the coating (the stress at which a crack appears or the coating delaminates from the metal base); F_{fail} is the load at which the coating fails; k is a coefficient that depends on the thickness and modulus of elasticity of the metal base.

The microhardness measurement and the bending experiment were done with the help of Prof. Angel Anchev from TU-Gabrovo.



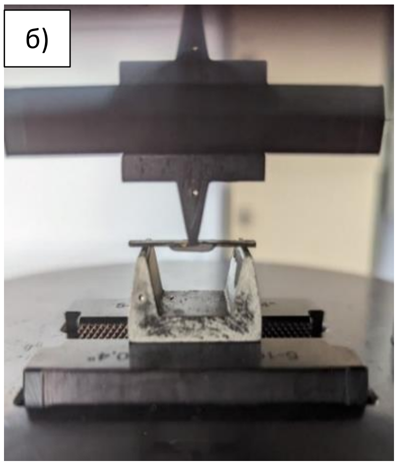


Fig. 2-10 Three-point bending test for investigation adhesion strength of porcelain to Ti alloy: scheme – a) and test device – б).

2.2.7 Determination of the modulus of elasticity

A combined approach, including three-point bending test and subsequent finite element (FE) analysis, is applied to define the Young's modulus. Physically, the experiment represents bending of a beam on two supports loaded with punch. The supports and punch are rounded with 1 mm radius. The beam is bent in the middle up to 0.3 mm, in order to preserve the linear relationship between force and displacement (Fig. 2-11), thus ensuring loading only in the elastic region. Three samples of the milled and SLM Ti6Al4V alloy are subjected to bending with a ZWICK Roell Vibrophore 100 machine (ZWICK Roell, Germany). The specimens are preliminary heat treated according to the modes from Table 2-3, imitating firing of the porcelain coating.

In order to minimize the computational time and due to the test symmetry, a FE model was used only for half of the calculation scheme (Fig. 2-12). The 3D FE stress analysis was carried out via ABAQUS software. The model consists of three bodies - beam, punch and support. The beam was modeled as a linearly deformable body with the absolute dimensions of the tested samples (the length of the beam is half of the real one). The punch and the support were modeled

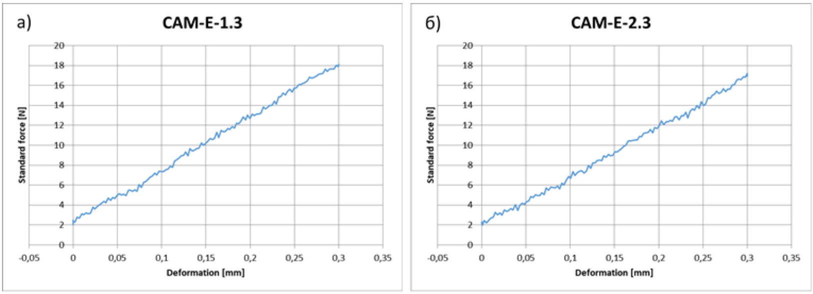


Fig. 2-11 Bending stress-strain plots of titanium alloy specimens used to determine modulus of elasticity. Milled alloy before - a) and after heat treatment - б).

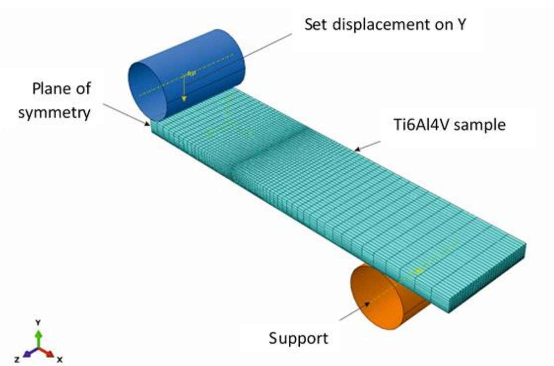


Fig. 2-12 FE model for determining the modulus of linear deformations of TiAl6V4 alloy.

as cylindrical analytical rigid bodies with a base radius of 1 mm. In order to read the force accurately for the entire load duration, the punch displacement and time period were adopted to be 0.3 mm and 0.3 s, respectively. The Poisson's ratio for the titanium alloy was assumed to be 0.33. For fitting of the Young's modulus, an iterative approach was developed, in which the magnitude of the modulus varied to match the force-displacement dependence obtained by the experiment (Fig. 2-11) with this in the FE model.

The determination of the modulus of elasticity and the adhesion strength by the finite element method were carried out with the help of Assoc. Prof. Vladimir Dunchev from TU-Gabrovo

2.2.8 Determination of the adhesion strength of porcelain to Ti6Al4V alloy using finite element analysis

2.2.8.1 3D finite elements model

With the help of ABAQUS.CAE software, a 3D finite element model of the studied system was developed (Fig. 2-13). The TiAl6V4 alloy plate and the ceramic plate are modeled as SDBs with geometry consistent with their actual dimensions in the experimental test. The support and punch are modeled as RDBs (rigid bodies). Their rounding radii correspond to those of the support and punch in the test. Following the physical nature of the experiment (three-point bending), half of the studied system was simulated with an axis of symmetry passing through the axis of the punch. FE model contains 31800 tridimensionally stressed (3D stress) linear finite elements of type C3D8R. A technique was applied to thicken both plates near the critical section coinciding with the end of the ceramic plate.

Since the system is loaded in the linear region, purely elastic isotropic behavior is assumed for both materials.

Poisson's ratios were adopted, respectively: 0.33 for TiAl6V4 and 0.2 for ceramics. For the titanium alloy, the modulus of elasticity determined according to the newly developed methodology in Chapter 3, item 3.4.3 was used: 180 GPa for the milled and 120 GPa for the SLS-made samples. A Young's modulus of 60 GPa was adopted for porcelain [Dikova T. et al., 2017]. There were no data on the characteristics of binding agents. The value of 75 GPa was assumed for the modulus of elasticity of bond, based on the following: 1) the bonding agents consist of different types of oxides, similar to ceramics; 2) they serve as elastic layers to compensate for the different coefficients of thermal expansion of dental alloys and porcelains.

Between the two plates, a normal rigid contact with the possibility of separation and a tangential contact with a friction coefficient of 0.1 is set. This contact is also set in terms of interactions between the punch and the titanium plate, as well as between the titanium plate and the abutment. The "master-slave" surface technique was used.

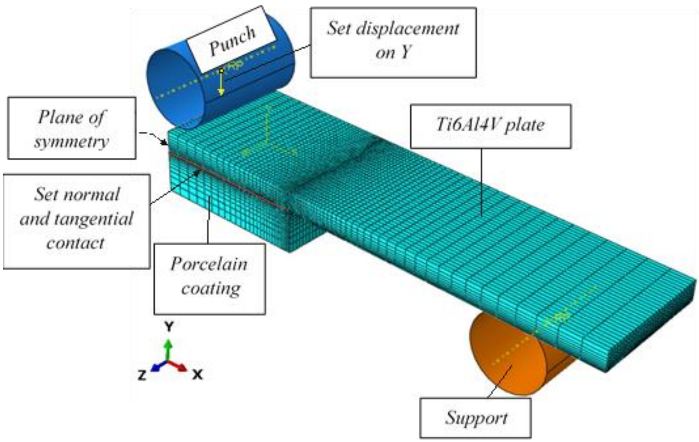


Fig. 2-13 3D Finite Element Model for Determining Bending Stresses in Porcelain Coated Titanium Alloy.

2.2.8.2 Boundary conditions

To simulate the load from the punch on the plates, a displacement of the so-called Reference Point (RP) of the punch in the direction of the Y-axis (Fig. 2-13) is set. The magnitude of the set displacement is equal to the displacement from the experimental test. For convenience in reporting the analysis results, the magnitude of the punch displacement is equal to the pseudo time specified for the static analysis.

The plane of symmetry is constrained to move in the X-axis direction. The longitudinal surfaces of the plates are constrained to move in the Z-axis direction. The support is stripped of all 6 degrees of freedom assigned to its respective Reference Point. Analogous to the punch, all degrees of freedom have been removed except for the Y-axis displacement.

The normal stresses in the X, Y and Z directions, the tangential stresses in the XY, YZ and ZX planes, as well as the minimum and maximum von Mises equivalent stresses are determined.

CHAPTER 3

PROPERTIES OF Ti6Al4V ALLOY, FABRICATED BY MILLING AND SELECTIVE LASER MELTING

The two technological processes – milling and selective laser melting, which are included in the machines from the CAM module, are fundamentally different in the production method. In the first case, the details are made by removing material from a blank with guaranteed properties, and in the second case, by melting successive layers of metal powder with a laser until the finished form is obtained. This leads to differences not only in the geometric and surface characteristics, but also in the physical and mechanical properties of the resulting parts. Therefore, in this chapter, the properties of Ti6Al4V alloy produced by milling and selective laser melting are investigated.

3.1 Geometric characteristics and density

It was found that the width of the milled plates is within the limits of tolerance, and their thickness is greater, while for the laser-built samples it is the opposite - their width is greater than the permissible, and the thickness is according to the requirements (Fig. 3-1). Sandblasting does not affect the thickness of the samples.

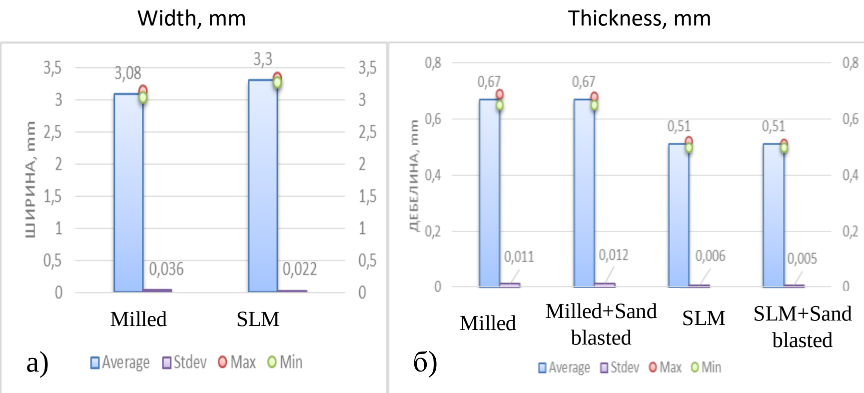


Fig. 3-1 Dimensions of the samples, made by milling and SLM: width – a) and thicness – б).

The density of the milled samples is comparable to that of the original blank (Fig. 3-3), but the relative density of the SLM parts is significantly lower - 87.45%-86.85%. Inspection of the alloy produced by SLM showed the presence of partially melted powder and voids on the surface (Fig. 3-5) and pores in the volume of the samples, which are the main reason for the lower density.

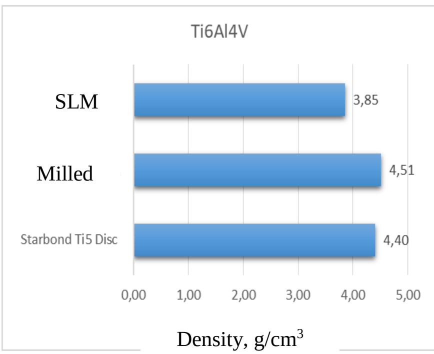


Fig. 3-3 Density of the samples, made by milling and SLM.

3.2. Surface morphology and roughness

The main factors that determine the surface topography in this study are the type of technological process and the position of the part. It was found that the surface morphology of the samples from the two groups is radically different and is typical for each production process (Fig. 3-5).

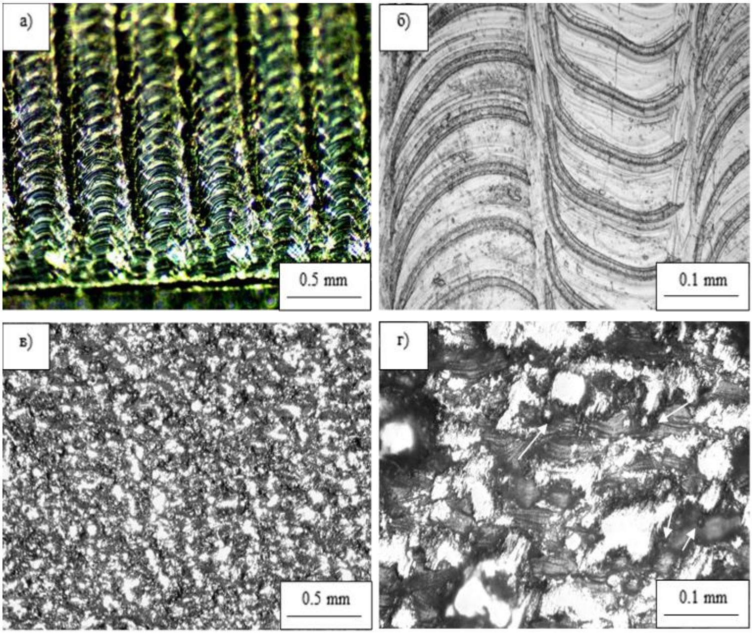


Fig. 3-5 Surface morphology of titanium alloy samples, produced by milling – а), б) and SLM - в) and г).

The surface of the milled plates is characterized by a periodically repeating profile with an almost uniform distribution of peaks and valleys and with a larger peak radius (Fig. 3-7).

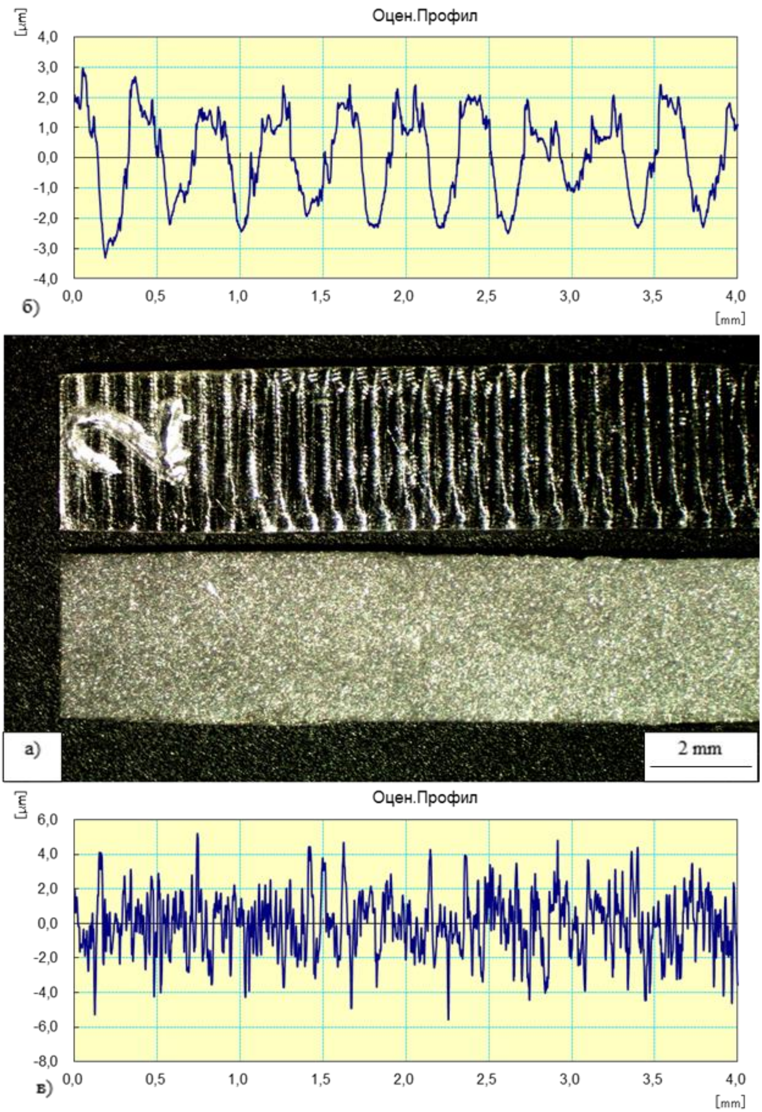


Fig. 3-7 Surface morphology of titanium alloy samples – a), produced by milling (2) and milling and sandblasting (down). Surface profiles of milled – б) and milled and sandblasted - в) samples.

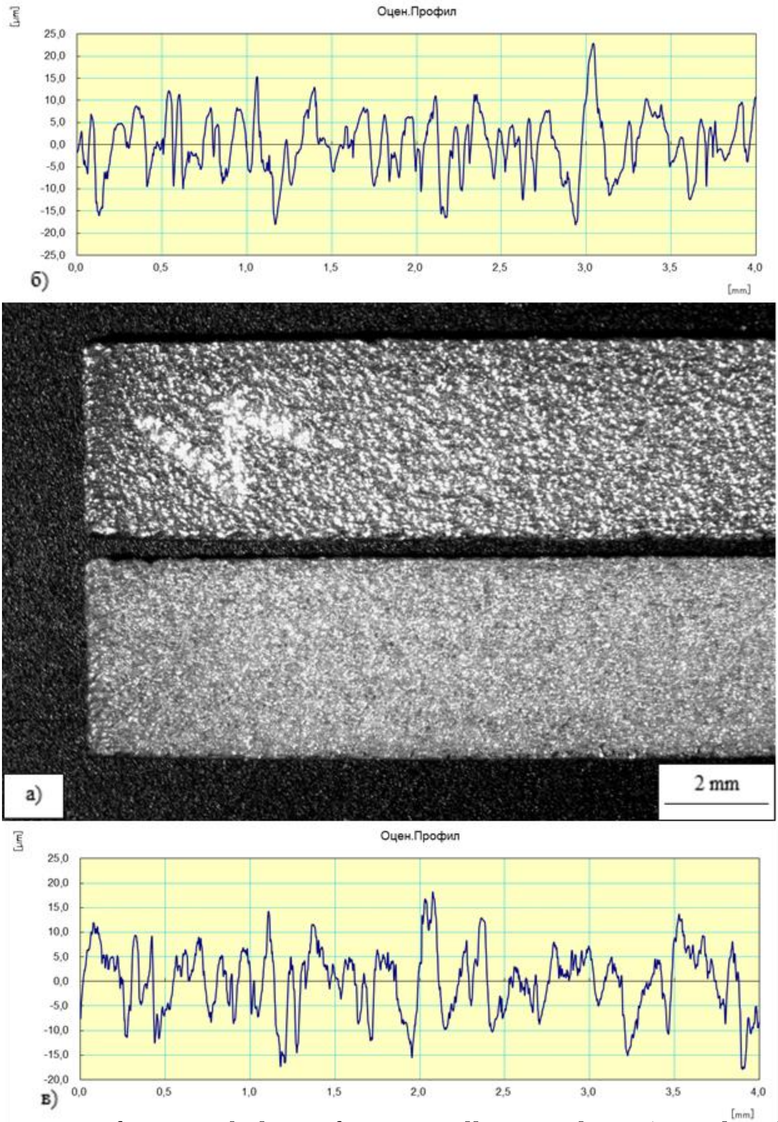


Fig. 3-9 Surface morphology of titanium alloy samples – a), produced SLM (4) and SLM and sandblasting (down). Surface profiles of SLM – б) and SLM and sandblasted - в) samples.

On the surface of the laser-built parts, individual melted layers and a large number of partially melted powder particles are noticeable (Fig. 3-5), which predetermines the topography to be mainly characterized by peaks with a larger radius of rounding (Fig. 3-9).

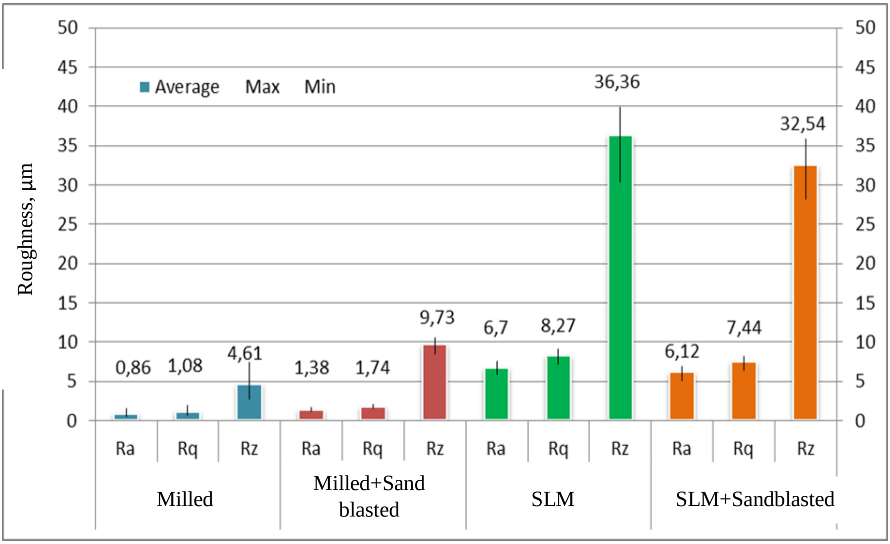


Fig. 3-11 Roughness of titanium alloy samples, produced by milling and SLM and subsequent sandblasting.

The roughness of the samples produced by SLM (Ra=6.7 µm and Rz=36.36 µm) is several times higher than the milled ones (Ra=0.86 µm and Rz=4.61 µm) (Fig. 3-11).

Sandblasting had a different effect on the roughness and topography of the samples from the two groups. It reduces the roughness of the laser-built parts by about 10%, but increases the roughness of the milled parts almost twice (Fig. 3-11). After sandblasting, the peaks on the surface of both groups of samples become sharper-edged, the surface profile of the milled plates is characterized by uniform amounts of peaks and valleys (Fig. 3-7), and that of the SLM samples changes and consists mainly of from slopes (Fig. 3-9).

3.3. Hardness and modulus of elasticity

The manufacturing method defining a specific microstructure of the Ti6Al4V alloy leads to differences in the microhardness and elastic modulus values of the milled and laser-built samples.

The measured microhardness of the Ti6Al4V alloy (Fig. 3-12) was higher for the laser-built samples (396 HV) compared to the milled (347 HV).

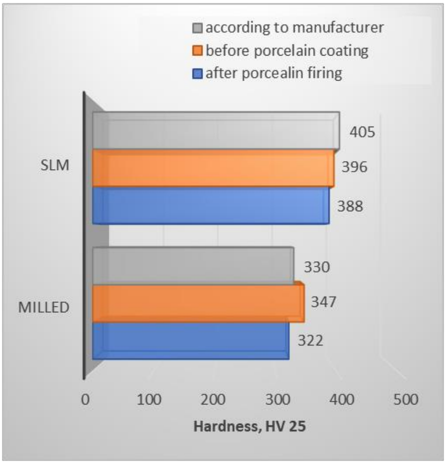


Fig. 3-12 Microhardness of Ti6Al4V alloy.

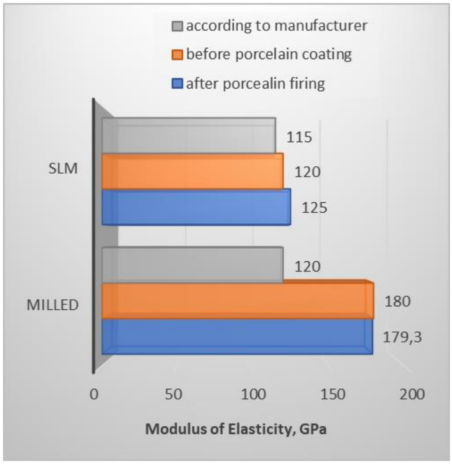


Fig. 3-13 Modulus of elasticity of Ti6Al4V alloy.

The values of the modulus of elasticity of Ti6Al4V alloy (Fig. 3-13), determined by the newly developed methodology, are 180 GPa for the milled and 120 GPa for the SLM fabricated samples. They are higher than the data given in the literature or by the manufacturers.

Subsequent heat treatment with porcelain firing modes slightly lowered the microhardness to 322 HV for the milled and 388 HV for the SLM produced and had almost no effect on the modulus of elasticity for both groups.

In order to determine the real reason for the lower density of parts produced by SLM, it is necessary to: 1) investigate the density with standardized samples and 2) investigate the microstructure and make a qualitative and quantitative assessment of the porosity. Appropriate recommendations for increasing density can then be made.

Further studies of the modulus of elasticity of the titanium alloy using the newly developed methodology are needed to determine the influence of the scale factor on the obtained results and to compare them with the results of standard tests.

CHAPTER 4

EXPERIMENTAL INVESTIGATION ADHESION STRENGTH OF DENTAL CERAMIC TO Ti6Al4V ALLOY, FABRICATED BY MILLING AND SELECTIVE LASER MELTING

The durability of a metal-ceramic dental prosthesis depends on the adhesion between the porcelain coating and the metal base. To increase the adhesion strength, various types of surface treatment of the alloy are applied - sandblasting, etching, laser treatment, preliminary heat treatment - oxidation and application of a layer of bonding agent. They are designed to affect both the mechanical and chemical components of adhesion. The latter occurs thanks to the presence of an oxide layer on the surface of the metal substructure. Although new CAD/CAM manufacturing technologies such as milling and SLM provide successful control of the thickness of titanium oxide on the surface of the metal substructure, the unsolved questions not only do not decrease, but also increase due to the constant development of new types of dental ceramics.

In the present chapter, an experimental study of the adhesion strength is performed and the failure mechanism of a dental ceramic coating to a Ti6Al4V alloy produced by milling and selective laser melting is analyzed.

4.1 Adhesion strength

It was found that the adhesion strength of the porcelain coating to the titanium alloy produced by both methods has close values: 17.63 – 30.89 MPa for the milled and 22.12 – 31.04 MPa for the laser-built alloy (Fig. 4-3). The milled samples treated with the given bond do not meet the requirements of the 25 MPa standard, and those made by SLM with combined surface treatment.

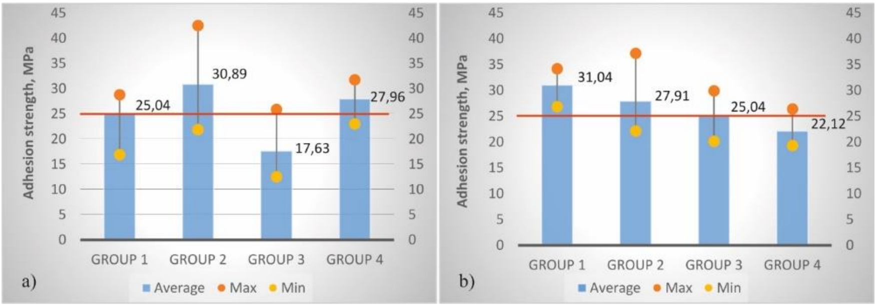


Fig. 4-3 Adhesion strength of porcelain coating on milled - a) and SLM - b) samples.

The surface treatments of the metal base have a different effect on the adhesion strength. Sandblasting and combined treatment increase the adhesion strength of porcelain to milled specimens, but decrease it in those made by SLM (Fig. 4-3). The use of the given bonding agent lowers the adhesion strength of the Ti6Al4V alloy produced by both technologies.

In the milled samples group, adhesion strength was highest after sandblasting the alloy surface, followed by the combined treatment, the control group, and the application of bond (Fig. 4-3). In the samples fabricated by SLM, the adhesion strength was highest in the control group, without surface treatment, followed by the application of sandblasting, bond and combined treatment.

4.2 Fracture mechanism of the porcelain coating

The type of surface treatment of the titanium alloy prior to the application of the porcelain affects the failure mechanism of the coating. This influence is stronger in the milled alloy.

Table 4-2

Surface of Ti6Al4V alloy after fracture of the porcelain coating.

Surface treatment		**Metal, %**	**Oxide layer, %**	**Bond, %**	**Porcelain, %**	**Fracture mode**
Milled alloy						
Control group 1		70	30	-	Traces	Adhesive-cohesive (cohesive through oxide layer)
Sandblasted group 2		10	80	-	10	Adhesive-cohesive (cohesive through oxide layer and porcelain)
Treated with bond group 3		5	70	25	Traces	Adhesive-cohesive (cohesive through oxide layer and bond)
Combined treatment, group 4	4 p.	-	-	-	100	Cohesive by porcelain cracking
	3 p.	Traces	20	70	10	Adhesive-cohesive (cohesive mainly through bond)
SLM alloy						
Control group 1		80	10	-	10	Adhesive-cohesive
Sandblasted group 2		70	10	-	20	
Treated with bond group 3		5	10	85	Traces	Adhesive-cohesive (cohesive mainly through bond)
Combined treatment, group 4		5	10	80	5	

It was found that the failure of the ceramics in all samples occurred by a mixed adhesion-cohesion mechanism (Table 4-2, Fig. 4-5a and Fig. 4-6a). A difference is found in the layer in which the adhesive or cohesive failure occurs. These differences are greater for the milled alloy compared to the one made by SLM.

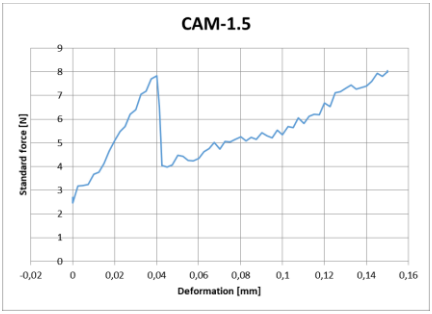


Fig. 4-5a Stress-strain graph in delamination of porcelain coating from milled Ti6Al4V alloy without surface treatment.

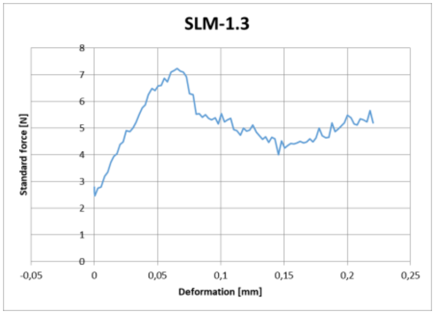


Fig. 4-6a Stress-strain graphs in delamination of a porcelain coating from SLM Ti6Al4V alloy without surface treatment.

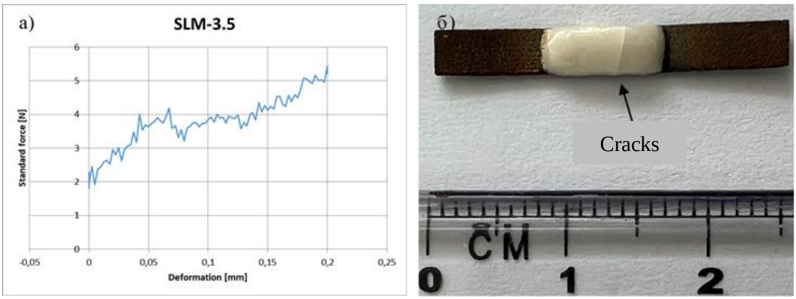


Fig. 4-8 Destruction by cracking and delamination of a porcelain coating of Ti6Al4V alloy, made by SLM, the surface of which was treated with a bond (stress-strain graph – a) and picture of a sample with a fractured coating – b).

In the milled titanium alloy, adhesive failure occurs between the metal and the oxide layer and cohesively through the oxide layer (Fig. 4-10). After sandblasting, both adhesion and cohesion fractures were observed between the oxide layer and the porcelain (Fig. 4-11).

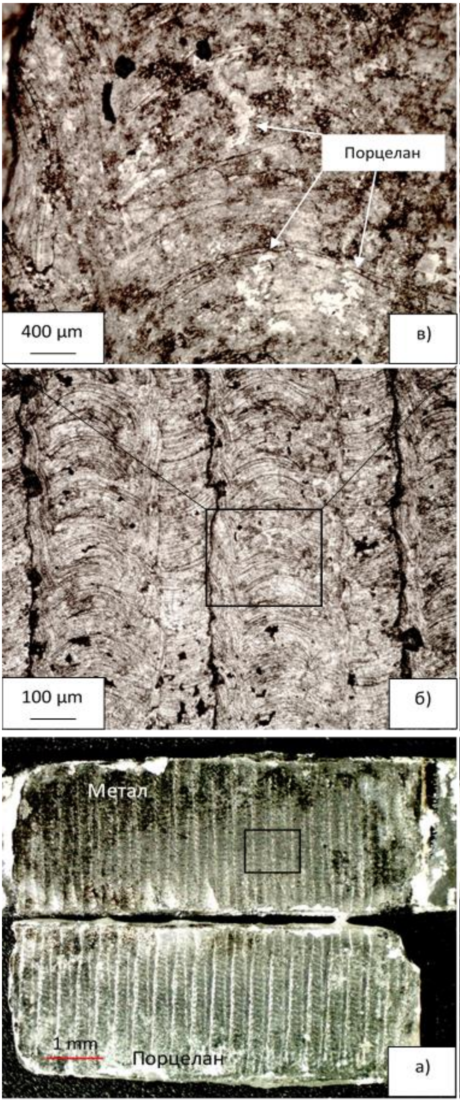


Fig. 4-10 Surface of milled sample (1.6) of Ti6Al4V alloy after failure of the porcelain coating.

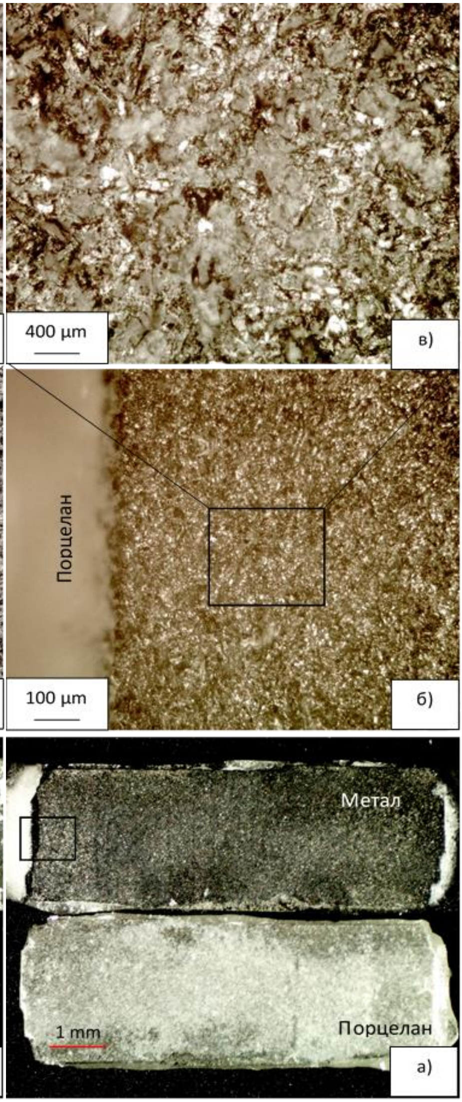


Fig. 4-11 Surface of milled and sandblasted sample (2.6) after failure of the porcelain coating.

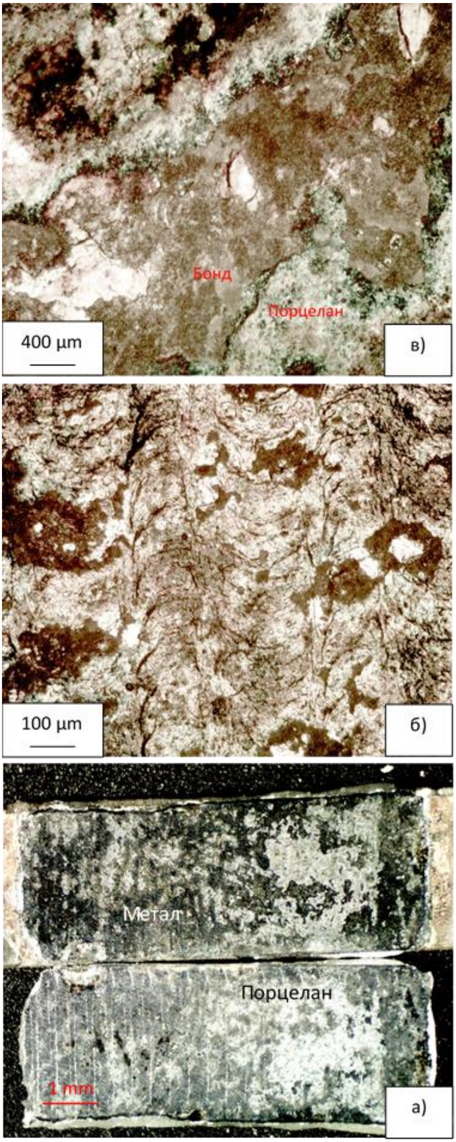


Fig. 4-12 Surface of milled and treated with bond sample (3.2) of Ti6Al4V alloy after failure of the porcelain coating.

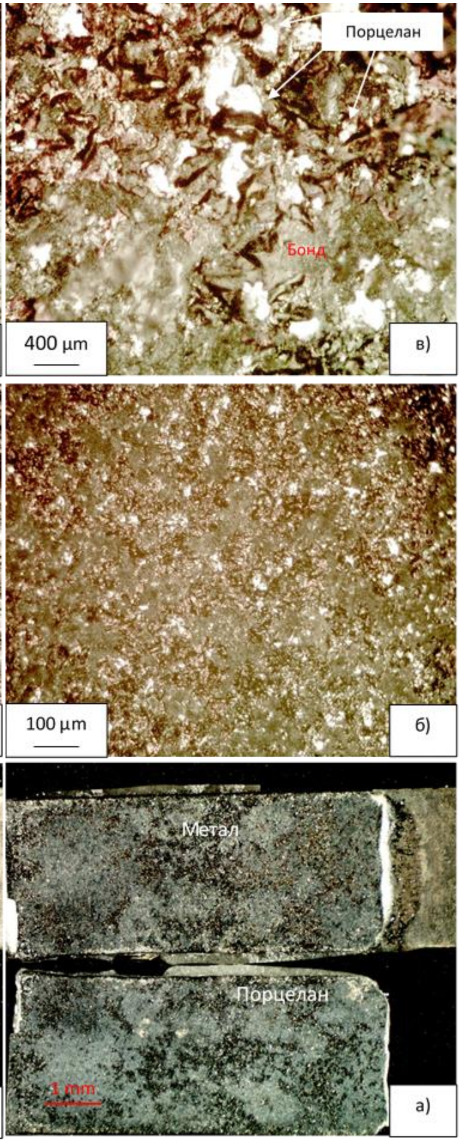


Fig. 4-13 Surface of milled sample with combined treatment (4.5) after failure of the porcelain coating.

In the samples treated with the given bond, adhesive and cohesive failures occur mainly between the oxide layer and the bond (Fig. 4-12).

Most of the specimens with combined treatment (sandblasting and application of bond layer) failed cohesively by cracking the ceramic coating (Fig. 4-8 and Fig. 4-13).

Since cohesive fracture is more favorable in clinical practice, it is necessary to conduct additional studies on the adhesion strength of porcelain to sandblasted and bond-treated milled Ti6Al4V alloy specimens.

In the Ti6Al4V alloy group made by SLM, there are no such large differences.

In the control and sandblasted subgroups (Fig. 4-14 and Fig. 4-15), the porcelain coating is destroyed in an adhesive-cohesive manner: adhesive, between the alloy and the oxide layer, and cohesive - through the porcelain.

Ceramic fracture in the subgroups, treated with bond and combined by sandblasting and application of bond, occurs adhesively, between the bond and porcelain, and cohesively, also through the bond and porcelain (Fig. 4-16 and Fig. 4-17).

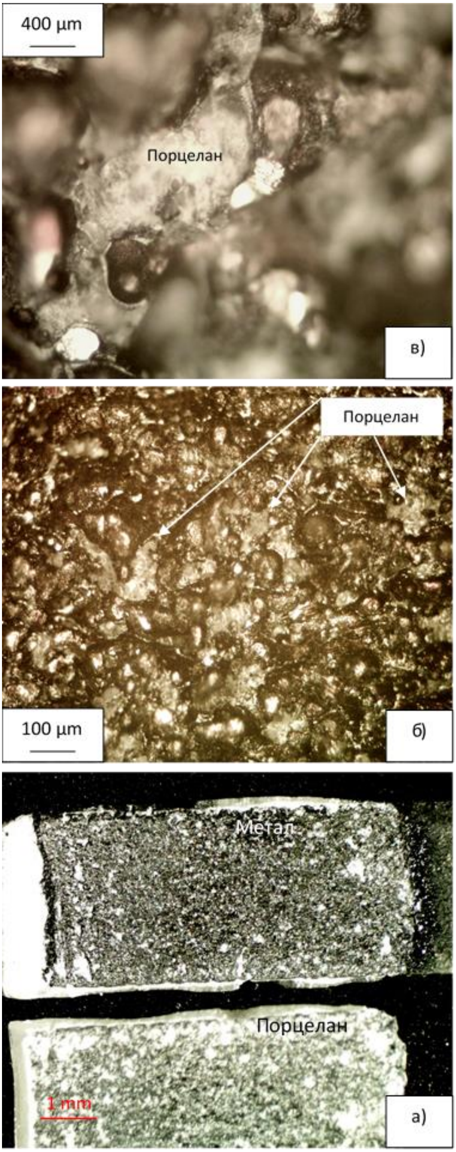


Fig. 4-14 Surface of SLM sample (1.7) of Ti6Al4V alloy after porcelain coating failure.

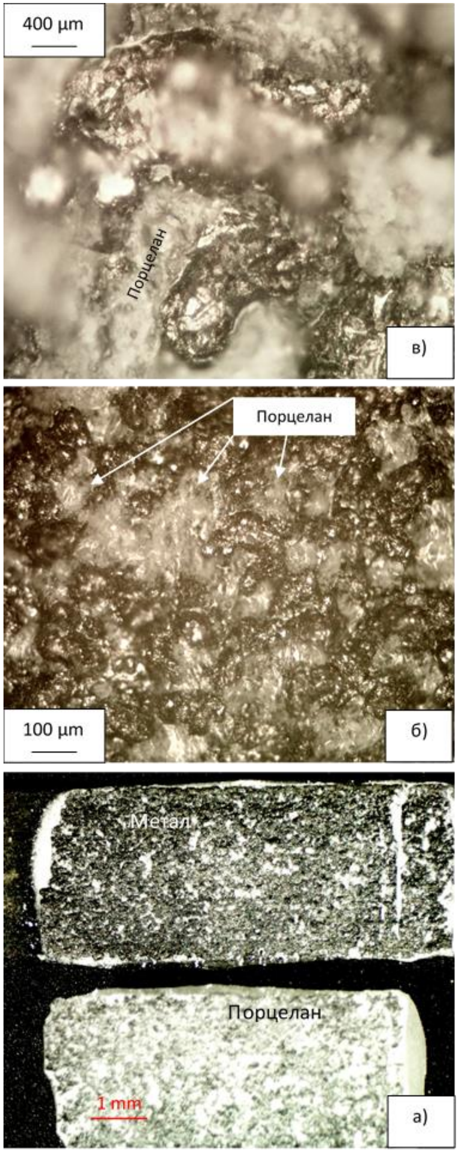


Fig. 4-15 Surface of sandblasted SLM sample (2.5) of Ti6Al4V alloy after porcelain coating failure.

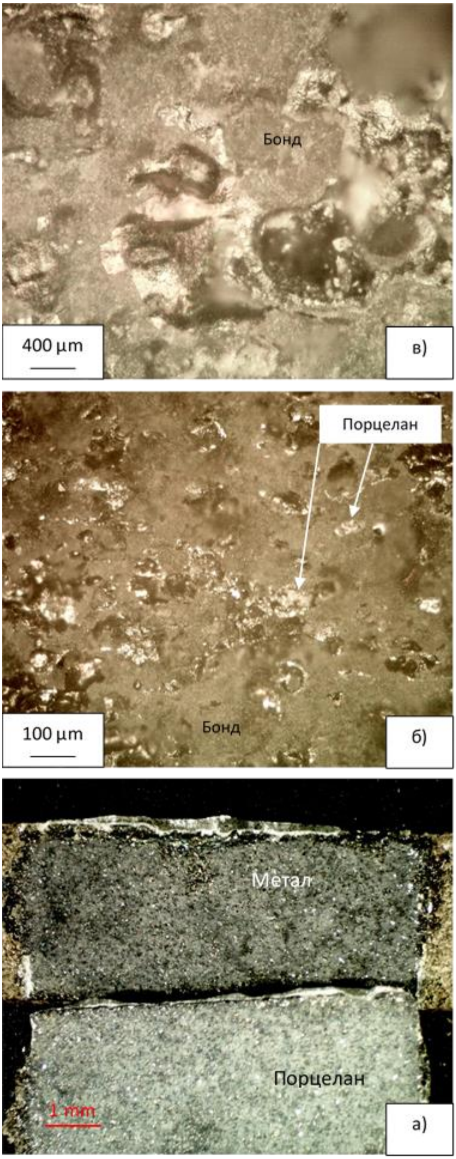
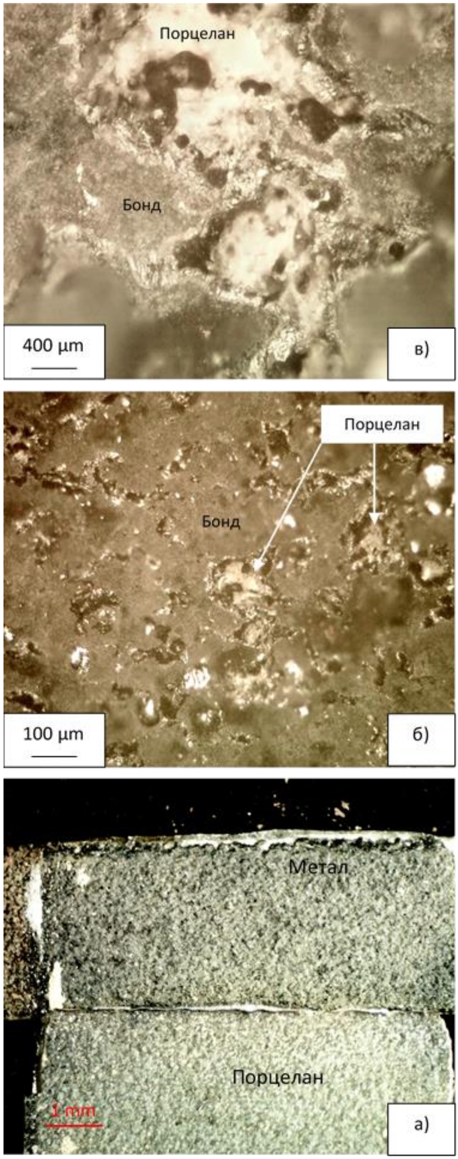


Fig. 4-16 Surface of treated with bond SLM sample (3.3) of Ti6Al4V alloy after porcelain coating failure.



Фиг. 4-17 Surface of SLM sample with combined treatment (4.2) after porcelain coating failure.

CHAPTER 5
INVESTIGATION ADHESION STRENGTH OF DENTAL CERAMIC TO Ti6Al4V ALLOY BY FINITE ELEMENTS ANALYSIS

In this chapter, the normal stresses σ in the X, Y and Z directions, the tangential stresses τ in the XY, YZ and ZX planes, as well as the minimum and maximum von Mises equivalent stresses σ_{eq}, which occur in bending of titanium alloy with porcelain coating, are determined using the FEA method. A simulation was made of one sample with real dimensions - a typical representative from each subgroup. The simulation of the bending process continues until a complete match is obtained between the stress-strain plots from the experiment and from the FEA. Two different FEA models were generated. The first consists of two parts - a metal plate with a porcelain coating, and the second - of three: a metal plate, a bond sublayer and a porcelain coating. On this basis, the samples are divided into two groups. The first includes 2 pieces of milled and 2 pieces of SLM samples of titanium alloy with identical surface treatments - control and sandblasted. In the second - also 2 pieces of both types of alloys with and without sandblasted surfaces, but with an underlayer of bonding agent.

The normal, tangential, as well as the minimum and maximum equivalent von Mises stresses at a point at the end edge of the porcelain coating and the bonding agent sublayer were determined for all groups of specimens studied.

5.1 Stresses in samples with no bonding layer

An uneven distribution of the equivalent stresses along the edge of the porcelain on the interface with the metal was found (Fig. 5-1). They are low at both ends and reach a maximum value in the central part (see the graph).

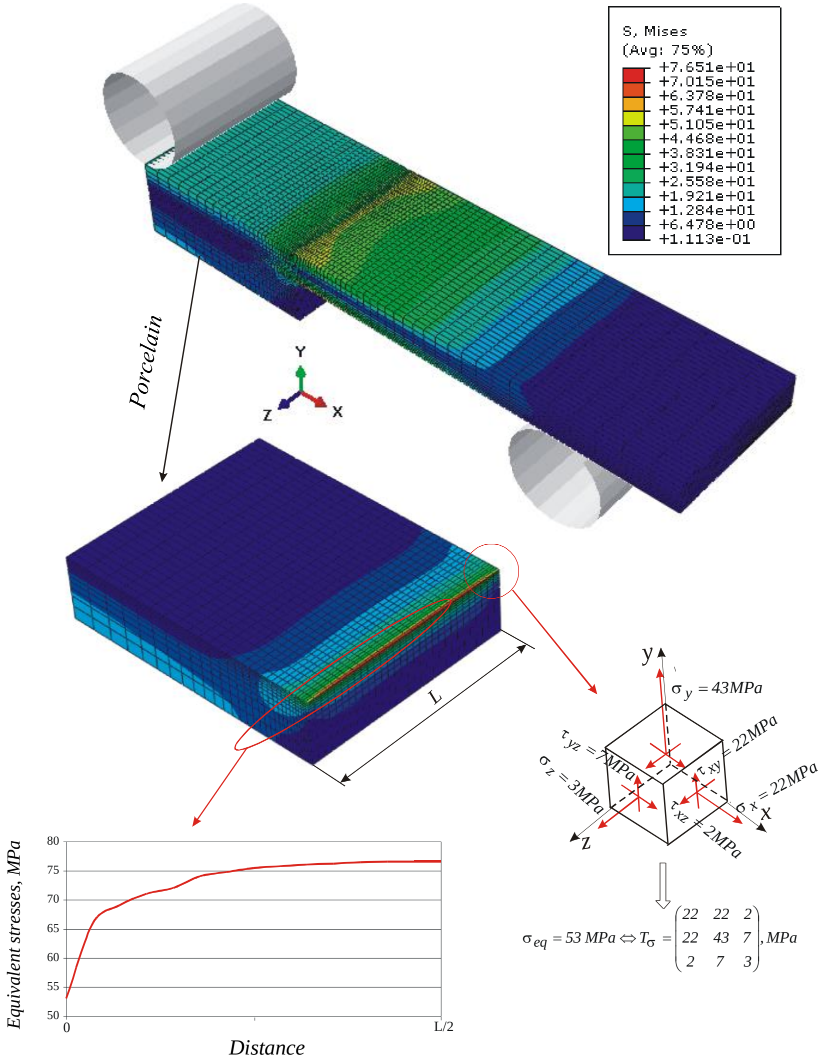


Fig. 5-1 Distribution of stresses in the metal and porcelain in the bending experiment of sample 1-5 of the control group of milled Ti6Al4V alloy.

The normal stresses along Y-axis possess the highest values (Table 5-1) and they act perpendicular to the porcelain/metal interface. The high Y-axis normal stresses are the main reason for the failure of the coating from the metal surface to become adhesive by delamination from the milled and laser-built specimens without bond.

Table 5-1

Stresses, MPa: maximum and minimum equivalent, respectively in the middle and at the end of the upper edge of the porcelain; components of the stress tensor at the point at the end of the porcelain edge (Fig. 5-1).

Samples with no bond		$min\,\sigma_{eq}$	$max\,\sigma_{eq}$	σ_x	σ_y	σ_z	τ_{xy}	τ_{xz}	τ_{yz}
Milled alloy	1-5 control	53	76	22	43	3	22	2	7
	2-6 sandblasted	67	97	27	56	4	28	3	9
SLM alloy	1-3 control	68	113	30	47	1	28	4	14
	2-5 sandblasted	60	101	26	41	0.8	25	3.5	12.5

5.2 Stresses in samples with sublayer with bonding agent

Combined treatment of milled alloy was found to generate the highest equivalent and normal stresses in the bond sublayer (Fig. 5-2, Fig. 5-3, Fig. 5-4, and Fig. 5-5). If they are higher than the cohesive strength of the ceramic, the porcelain coating is destroyed cohesively by the appearance of cracks.

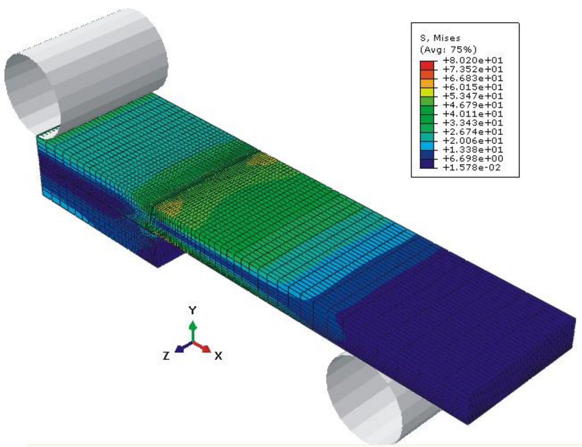


Fig. 5-2 General view of the stress state in bending of a milled Ti6Al4V alloy specimen with a porcelain coating and a bond interlayer.

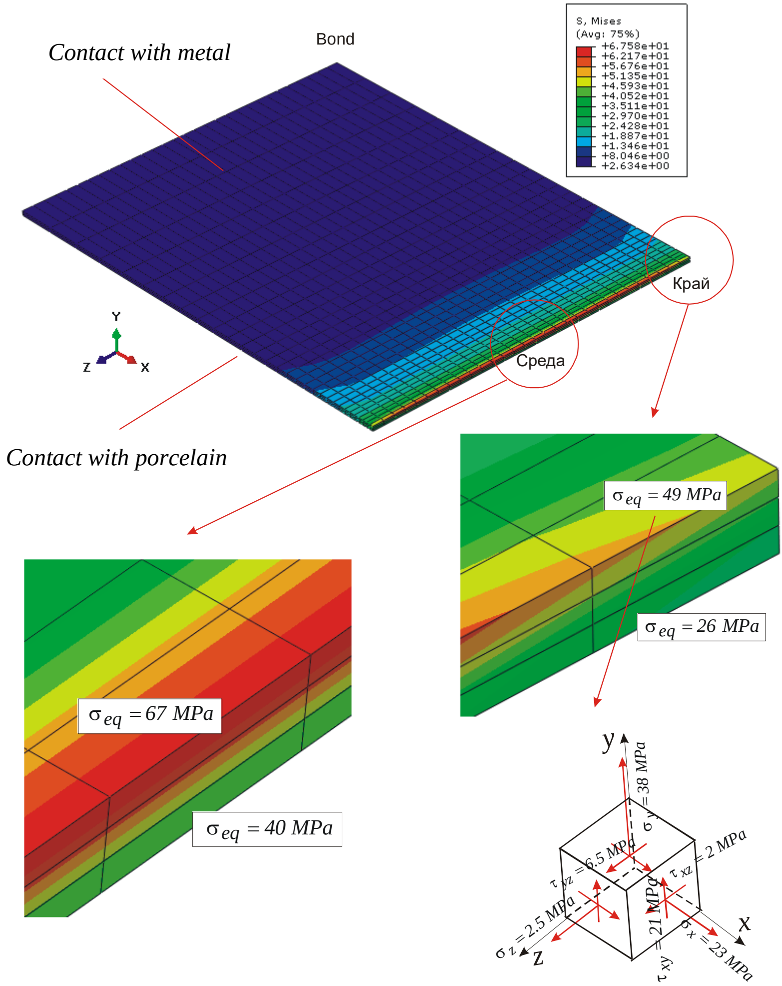


Fig. 5-3 Stress state in the intermediate bond layer.

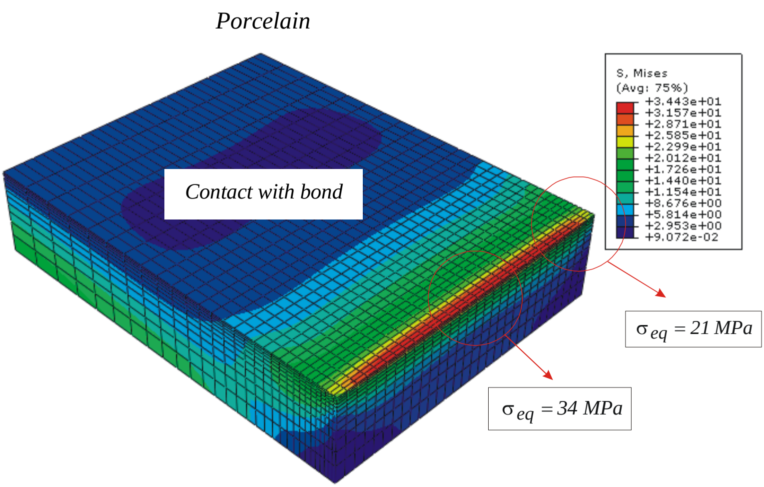
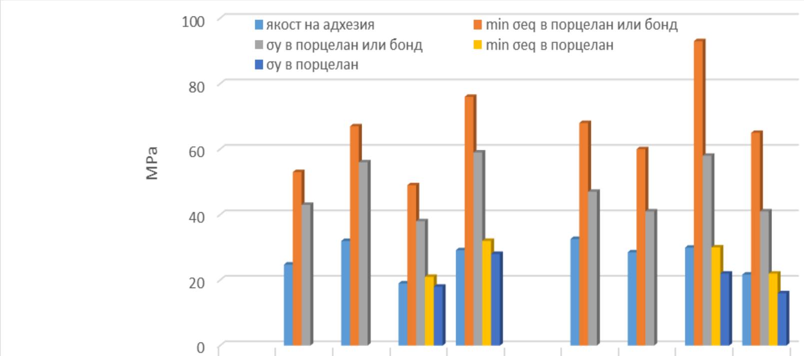


Fig. 5-4 Stress state in the porcelain coating.

In the milled alloy group, the stress trend follows the bond strength trend—sandblasting increases the stress values and bond-only treatment decreases them (Fig. 5-5).

For the SLM fabricated specimens, the bond treatment increased the stresses at the bond/metal interface, and the stresses at the bond/porcelain interface were commensurate with the experimental adhesion strength (Fig. 5-5).

SLM samples are characterized by high roughness and the presence of partially melted powder particles on the surface (Figs. 3-5 and 3-11 of Chapter 3), which increases the mechanical adhesion of the bonding agent to the metal. On the other hand, the firing of the porcelain was done at temperatures 150 °C lower than those of the bond firing, which is the reason for the lower chemical adhesion between them. This causes the destruction of the coating to occur by delamination of the porcelain from the bonding agent. It takes place at significantly smaller normal and equivalent stresses shown in the graph of Fig. 5-5. The values of these stresses agree very well with the adhesion strength obtained in the experiment.



Образец	Фрезовани образци	1-5 контрол	2-6 пясъкоструен	3-2 бонд	4-5 комбинирана	СЛС образци	1-3 контрол	2-5 пясъкоструен	3-3 бонд	4-2 комбинирана
якост на адхезия		25	32	19	29		33	29	30	22
min σ_{eq} в порцелан или бонд		53	67	49	76		68	60	93	65
σ_y в порцелан или бонд		43	56	38	59		47	41	58	41
min σ_{eq} в порцелан				21	32				30	22
σ_y в порцелан				18	28				22	16

Fig. 5-5 Adhesion strength from the experiment, minimum equivalent (min σ_{eq}) and normal (σ_y) stresses in porcelain (specimens 1-5, 2-6, 1-3 and 2-5) or in bond (specimens 3-2, 4-5 , 3-3 and 4-2) and only in the porcelain in samples 3-2, 4-5, 3-3 and 4-2.

Comparing the all stresses, the normal stresses along Y-axis have the highest values (Table 5-1 and Fig. 5-5) and act perpendicular to the porcelain/metal, bond/metal, or porcelain/bond interface. Actually, they determine the failure of the coating to become adhesive by delamination.

It has been confirmed that the influence of the morphology and surface roughness of the laser-built samples, which increase the mechanical adhesion of the bond to the metal and lead to delamination of the porcelain from the bond, cannot be accounted for in the FEA research.

Despite the limitations of the methodology used, the present study elucidates the failure mechanisms of a titanium alloy porcelain coating fabricated by milling and selective laser melting.

CHAPTER 6

LABORATORY PROTOCOL FOR MANUFACTURING OF METALCERAMIC OF Ti6Al4V ALLOY, FABRICATED BY CAD/CAM TECHNOLOGIES

In this chapter, on the basis of the obtained results for adhesion strength, a laboratory protocol for the fabrication of metal-ceramic fixed dental prostheses, the infrastructure of which is produced from Ti6Al4V alloy by milling and selective laser melting, is developed.

6.1 Laboratory protocol for manufacturing of metalceramic of Ti6Al4V alloy, fabricated by CAD/CAM technologies

Our research shows that the milled and sandblasted samples (30.89 MPa) and SLM samples without surface treatment (31.04 MPa) are characterized by the highest adhesion strength (Fig. 4-3 of Chapter 4). Therefore, the milled metal skeleton of the bridge must be sandblasted. In the case of bridge infrastructure made by SLM, after heat treatment, not only high roughness is observed, but also uncleaned parts of the supports on the occlusal surface and the presence of an oxide layer, most likely of uneven thickness. For these reasons, it is imperative to clean the rest of the supports of the metal skeleton and sandblast it after the heat treatment. After such treatment, the adhesion strength of the porcelain is 27.91 MPa (Fig. 4-3 of Chapter 4) and meets the requirements of the standard.

Regarding the application of a bonding agent sub-layer between the metal substrate and the ceramic, our research shows that the adhesion strength is reduced in both cases – in unsandblasted and sandblasted surfaces (Fig. 4-3 of Chapter 4). Therefore, when manufacturing metal-ceramic constructions, it is not recommended to apply VITA NP BOND PASTE bond on the surface of milled and SLM metal frameworks made of Ti6Al4V alloy, when VITA LUMEX AC is used for porcelain coating.

Based on the synthesized results of the present study, two laboratory protocols were developed for the production of metal-ceramic fixed prosthetic structures from Ti6Al4V alloy, made by CAD/CAM milling and selective laser melting:

6.1.1 Laboratory protocol for manufacturing of metalceramic of Ti6Al4V alloy, fabricated by milling;

6.1.2 Laboratory protocol for manufacturing of metalceramic of Ti6Al4V alloy, fabricated by SLM

Following the recommendations in the newly developed protocols, two three-unit metal-ceramic bridges were prepared, the metal infrastructures of which were fabricated from Ti6Al4V alloy by milling and selective laser melting (Figs. 6-7).

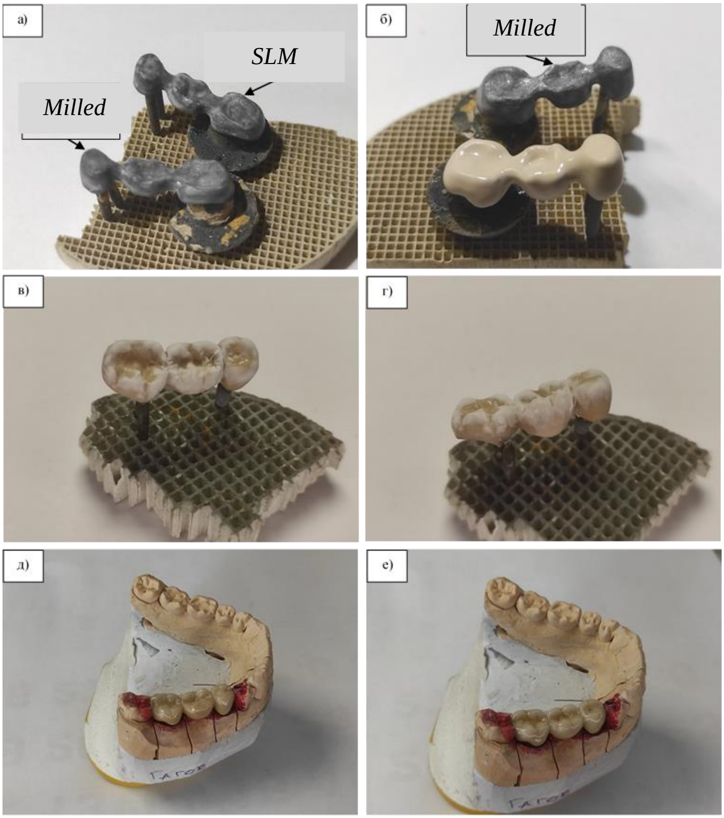


Fig. 6-7 Stages of manufacturing the porcelain coating on Ti6Al4V alloy infrastructures made by milling and SLM – а), б), в), г). Ready to use metal-ceramic bridges, whose metal frameworks are made of Ti6Al4V alloy by milling – д) and SLM – е).

CONTRIBUTIONS

1. **Scientific-applied contributions**

   1.1. Original

- A new methodology for determining the modulus of elasticity has been developed, which is based on a bending experiment and finite element analysis;
- For the first time, the topography of a Ti6Al4V alloy was investigated using ADC (amplitude distribution curve) curves of the surface profile of the samples.
- The features of the topography of the surface of milled and laser-built Ti6Al4V alloy before and after sandblasting were established.
- The values of the modulus of elasticity of the Ti6Al4V alloy were determined according to the newly developed methodology: 180 GPa for the milled and 120 GPa for the SLM manufactured samples.
- A different influence of the surface treatments of the metal base on the adhesion strength was found: sandblasting and combined treatment increased the adhesion strength of the porcelain to the milled samples, but reduced it to those made by SLM.
- The normal, tangential and equivalent von Mises stresses at a point at the edge of the porcelain coating and the bonding agent sublayer were determined.
- The normal stresses along Y-axis, acting perpendicular to the interface between porcelain/metal, bond/metal or porcelain/bond, were found to be the highest and lead to predominantly adhesive failure of the coating from the metal surface.

   1.2. Confirmatory

- It has been confirmed that the roughness of the samples produced by SLM (Ra=6.7 μm and Rz=36.36 μm) is several times higher than the milled ones (Ra=0.86 μm and Rz=4.61 μm). Sandblasting reduces the roughness of laser-built parts by about 10%, but almost doubles the roughness of milled parts.

- The microhardness of Ti6Al4V alloy was confirmed to be higher in the laser built samples (396 HV) compared to the milled ones (347 HV).
- It has been confirmed that the adhesion strength of the porcelain coating to the titanium alloy produced by both methods has close values: 17.63 - 30.89 MPa for the milled and 22.12 - 31.04 MPa for the laser-built alloy.
- It has been confirmed that the destruction of the ceramics occurs by a mixed adhesion-cohesion mechanism, with a difference in the layer in which the adhesion or cohesion failure occurs.

2. Applied contributions

- For metal-ceramic constructions of Ti6Al4V alloy, fabricated by milling/SLM and coated with VITA LUMEX AC porcelain, the application of a VITA NP BOND PASTE bond sublayer is not recommended because it reduces adhesion.
- Two laboratory protocols were developed for the production of metal-ceramic fixed dental prostheses from Ti6Al4V alloy, fabricated by CAD/CAM milling and selective laser melting.

PUBLICATIONS ON DISSERTATION

1. Dikova T, Dzhendov D, Gagov Y. Surface morphology and roughness of Ti6Al4V alloy manufactured by milling and selective laser melting. Proceedings of INNOVATIONS 2022, 20-23 June 2022, Varna, Bulgaria; Vol 1(6): p. 48-55;

2. Dikova T, Dunchev V, Gagov Y. Investigation of Hardness and Elastic Modulus of Milled and SLM Ti6Al4V alloy. Journal of the Technical University of Gabrovo, 2022 Nov 11; 65:1-6.

3. Dikova T., Anchev A., Dunchev V., Gagov Y., Dzhendov D. Experimental investigation of adhesion strength of dental ceramic to Ti6Al4V alloy fabricated by milling and selective laser melting, Procedia Structural Integrity 42 (2022) 1520–1528. https://doi.org/10.1016/j.prostr.2022.12.193.