ADHESION STRENGTH EVALUATION OF CERAMIC COATINGS ON CAST AND SELECTIVE LASER MELTED Co-Cr DENTAL ALLOYS USING TENSILE SPECIMENS

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***Abstract**: Studying the fracture characteristics of porcelain coatings plays a main role in selection of materials for metal-ceramic restorations. The aim of this work is to study the effect of the substrate manufacturing process on the adherence of the porcelain. The coatings of porcelain IPS.Inline (Ivoclar Vivadent) are fused onto dental Co-Cr alloys fabricated via casting (Biosil F) and Selective Laser Melting (SLM) (Co212-f). The adhesion strength of the ceramic coatings is studied under tensile load of flat specimens. The interfacial shear strength is determined using experimental results. The shear stress distributions in the metal-ceramic interface at the critical load are evaluated by analytical approach. It is established that the interfacial shear strength values of ceramic coating are 67.5 MPa for cast Biosil F alloy and 83.8 MPa for SLM Co212-f alloy. The higher shear strength of the porcelain to the SLM samples is due to the nearly two times higher surface roughness, which is reason for increasing both the mechanical and the chemical adhesion. The nature of the fracture of the ceramic coating on the Co-Cr alloys, produced by casting and SLM, is similar and is mixed adhesive–cohesive mode. The higher adhesion strength of the porcelain coating to the SLM dental alloy is a good precondition for the SLM application in production of metal-ceramic fixed partial dentures for areas with heavy loads*

Keywords: DENTAL Co-Cr ALLOYS, CASTING, SELECTIVE LASER MELTING, HARDNESS, ADHESION STRENGTH

1. Introduction

Metal ceramic dental construction consists of metal framework, covered with porcelain layers. For better aesthetics, the thickness of the porcelain layer should be higher - between 1.2-2.0 mm, while the metal framework should be thinner - about 0.5 mm [1]. That is why, the metal alloys, used for metal-ceramic dental restorations, have to possess high mechanical properties. The Co-Cr dental alloys are mostly used for manufacturing of metal frameworks due to their high hardness and strength, high corrosion and abrasive resistance. The properties of Co-Cr alloys depend on the microstructure, its morphology and composition, the γ-ε phases' ratio, the presence of carbides and intermetallic inclusions [2,3]. Cr and Mo are added for strengthening of the solid solution of Co-Cr alloys [4,5]. The chromium is a carbide-forming element and contributes to the formation of carbides in the microstructure, which lead to increase of the hardness and wear resistance. From the other hand, Cr additionally increases the corrosion resistance of Co-Cr alloys by forming of passive oxide layer on the surface of the detail.

The microstructure of metal alloys depends on the manufacturing process. Since the beginning of the last century, the lost-wax centrifugal casting is the technology mostly used for production of dental constructions from metal alloys. However, this technological process consists of many manual operations, thus leading to low dimensional accuracy and low quality of the restoration as a whole. The new CAD/CAM systems and additive technologies offer a number of advantages: digital design of the construction, simulation of the functions, fast and controllable manufacturing processes and no waste production from various materials [6]. Selective Laser Melting (SLM) is additive manufacturing process, characterizing with layer-by-layer building of the object from metal powder using laser beam. It is necessary to work with optimal technological regimes (laser power, layer's thickness, scanning speed and distance between individual melted traces) to obtain construction with high physical and mechanical properties. The high heating and cooling rates in the SLM process as well as the heating of the layers beneath the working surface above the transition temperatures lead to formation of the specific fine microstructure [7]. Meacock et al. [8] reported that the microstructure of biomedical Co-Cr-Mo alloy, produced by laser powder microdeposition, is homogeneous, comprised of fine cellular dendrites. The average hardness was 460 HV0.2, which is higher than the values obtained by the other fabrication process. Barucca et al. [9] investigated Co-Cr-Mo parts, produced by direct metal laser sintering. They established that microstructure consists of γ and ε phases. The ε phase is formed by athermal martensitic transformation and it is distributed as network of thin lamellae inside the γ phase. The higher hardness is attributed to the presence of the ε-lamellae grown on the $\{111\}_\gamma$ planes that restricts the dislocations movement in the γ phase.

In a metal-ceramic dental construction a good bond between the ceramic and metal is essential and it is achieved by the interactions of the ceramic with metal oxides on the surface of metal and by the roughness of the metal coping. There are two types of bonds on the metal-ceramic interface - chemical and mechanical [10,11]. The chemical bond is a result of chemisorption by diffusion between the surface oxides on the alloy and in the ceramic. The mechanical bond is carried out by the penetration of ceramic material into a rough metal surface, thus mechanically is interlocked with the metal. Therefore, the topography of a ceramic-metal interface plays an important role in the adhesion. The increased area, associated with a rougher interface, also provides larger area for chemical bonds to form. The minimum acceptable bond strength of metal-ceramic of 25 MPa is defined in the standard ISO 9693-1:2012 [12]. Most of the researchers confirm that the adhesion strength of the porcelain coating to the SLM Co-Cr dental alloys is comparable to that of the cast alloys and is higher than required in the standard [13-15]. Depending on the investigation method, the bond strength for the cast and the SLM Co-Cr dental alloys is 72.9 MPa and 67.0 MPa [14] or 54.17 MPa and 55.78 MPa accordingly [15]. Only Wang H. et al. [16] stated that there are statistically significant differences of the porcelain bond strength to the cast and SLM Co-Cr samples (37.7 ± 6.5 MPa and 46.8 ± 5.1 MPa respectively).

The SLM technological process is comparatively new and the data for the adhesion strength of the porcelain coating to the SLM Co-Cr dental alloys are insufficient and contradictory. The aim of the present paper is to study and evaluate the adhesion strength of ceramic coatings on cast and SLM Co-Cr dental alloys using tensile specimens.

2. Materials and methods

2.1. Samples manufacturing

Two groups of tensile test specimens (five samples in each group) were prepared by lost-wax casting and SLM using Co–Cr dental alloys. The first group was intended for tensile test, while the second – for adhesion strength evaluation. The cast samples were produced by centrifugal casting of Co-Cr alloy "Biosil" with chemical composition, given by the producer (Table 1). The SLM samples were fabricated directly from the virtual 3D models using SLM125 machine of the "SLM Solutions", Germany. The machine is equipped with continuous Nd:YAG laser which worked with power 100 W and laser spot diameter 0.2 mm. The metal powder of Co-Cr alloy Co212-f ASTM F75 (Table 1) was melted in layers with 0.03 mm thickness unless the desired construction was obtained. During manufacturing process, the laser at first scanned the outer contour of the layer of the first specimen's part; next, it hatched the area within the boundaries at an angle of 45° with a pitch of 0.13 mm. After that, it passed to the same layer of the next specimen's part, thus fabricating the whole layer. The SLM technological regime, recommended from the company producer was used. The specimens have a thickness of 2.2 mm for cast alloy and 2.07 mm for SLM.

Table 1.
Chemical composition of the alloys used.

Alloy	Chemical composition (wt %)							
	Co	Cr	Mo	Si	Mn	C	Fe	Ni
ASTM F75	Bal.	27–30	5–7	<1	<1	<0.35	<0.75	<0.5
Biosil, Degudent	64.8	28.5	5.3	0.5	0.5	0.4	–	–
SLM Co212-f ASTM F75	65.2	28.3	5.48	0.754	–	–	0.164	–

The both sides of the samples, intended for adhesion strength evaluation, were covered with 1.5 mm porcelain layer (IPS.Inline One, Ivoclar Vivadent) using the technology, recommended from the company producer of dental ceramic (Fig. 1). For better porcelain adhesion, the cast samples at first were sandblasted with SiO_2 particles (250 μm) and cleaned with steam jet. In order to maintain the original roughness, the SLM samples were only cleaned with steam jet. Five porcelain layers were put on the both sides of the samples: 1-st and 2-nd opaquers, 1-st and 2-nd dentcisal and a glaze. The samples were fired after each porcelain layer with regimes, given in Table 2.

Table 2.
Regimes of firing of different porcelain layers of one-layer metal-ceramic IPS.Inline One.

Ceramic layers	Firing temperature T (°C)	Closing time t (min)
1-st opaquer	930	6
2-nd opaquer	930	6
1-st dentcisal	910	4
2-nd dentcisal	900	4
Glaze	850	6

2.2. Surface roughness measurement

The arithmetic average of the surface profile R_a was measured in transverse and longitudinal directions of the samples with *Taylor Hobson Surtronik 3*. Five measurements in three areas of each direction on both sides of the samples were used for calculation the average value of R_a.

2.3. Adhesion strength evaluation

Uncoated specimens (pure substrate) and coated specimens were pulled uniaxially at room temperature using a testing machine (*FM*-1000) with a strain gauge attached to monitor the strain levels

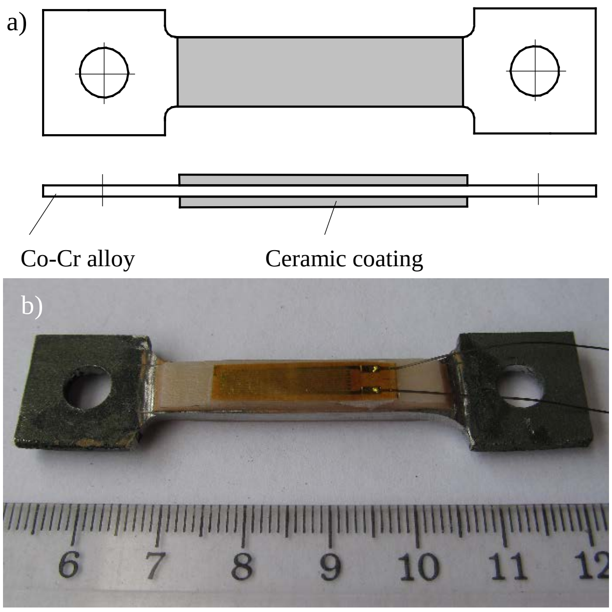

Fig. 1. *Scheme of the sample for evaluation the adhesion strength of ceramic coating to the Co-Cr alloys (a) and macroscopic photo of SLM tensile test specimen with porcelain coating and strain gage (b).*

(Fig. 1-b). The uniaxial tensile test allows the determination of Young's modulus of the porcelain layer and the substrate. The difference between the tensile response of coated specimen and uncoated one allows determining of the elastic modulus of the porcelain coating. Differences in Poisson's ratios between substrate and coating can be neglected [17]. The method for determining the elastic modulus of the coating is given in details in the previous investigations of Dolgov [18]. During the tensile test the coated specimens are subjected to an increasing tensile strain, causing cracking and delamination of the coating. Different analytical models exist to calculate the maximum interfacial shear strength [19]. In current study, the maximum interfacial shear strength τ (units of MPa) is calculated as [20]:

$$\tau = \frac{k\varepsilon}{1/(E_s H) + 1/(E_c h)} \tanh(kl)\,, \qquad (1)$$

where:

$$k = \sqrt{L \cdot \left(\frac{1}{E_s H} + \frac{1}{E_c h} \right)} \qquad (2)$$

$$L = 2\left(\frac{G_s}{H} \cdot \frac{G_c}{h} \right) \Big/ \left(\frac{G_s}{H} + \frac{G_c}{h} \right) \qquad (3)$$

E_s, E_c – elastic modulus of the substrate and the coating respectively; G_s, G_c – shear modulus of the substrate and the coating respectively; $2H$, h – thickness of the substrate and the coating respectively; ε – substrate strain at which occurs delamination of the coating; l – crack spacing in a fragmented coating.

The samples surface after manufacturing and adhesion testing was investigated by optical microscopies *Olympos SZ51* and *XJL-17A*.

3. Results obtained

3.1. Surface roughness

The data about the surface roughness of the samples, produced by casting and SLM, are given on Fig. 2. The surface of the SLM samples is nearly two times higher (R_a = 5.89 μm) comparing to the cast and sandblasted (R_a = 2.67 μm). The higher surface roughness of the SLM alloy is due to the specific features of the manufacturing technology.

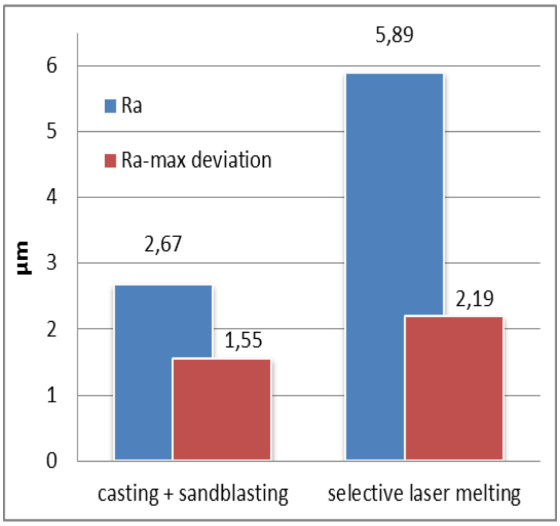

Fig. 2. *Arithmetic average of the surface profile R_a and its maximal deviation of Co-Cr samples produced by different technologies.*

3.2. Adhesion strength

Typical load versus strain graphs for samples with ceramic coating are shown in Fig. 3. The load–strain curves for the cast and SLM alloys is also shown for comparison.

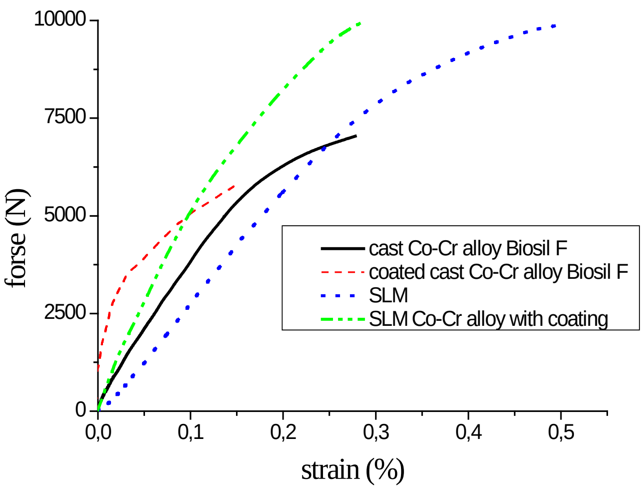

Fig. 3 *Typical load versus strain graphs for uncoated samples and samples with porcelain coatings.*

Due to the features of the casting process, the Co-Cr samples are characterized with the inhomogeneous microstructure, defining inhomogeneous properties. During the tensile test, with the load increase at first the network of multiple cracks appears in the coating, which is perpendicular to the direction of the applied force. After cracking of the coating, the delamination of the ceramic coating from the substrate occurs (Fig. 4). It should be noticed out that the coating is not completely detached from the cast alloy. There are islands of the porcelain on the surface of the sample. The uneven structure of the islands of the ceramic coating suggests uneven adhesion of the ceramics to the metal. After the test, the surface of the Biosil F alloy is cleaner than the surface of the SLM Co212-f alloy.

The fracture character of the SLM samples is similar. In the test process, after reaching the critical length of the crack spacing, the porcelain delamination occurs, followed by the adhesion failure of the coating from the substrate. However, these samples characterize with smaller cracks' spacing of the ceramic coating. A uniform network of lines with crack spacing of about 1 mm can be clearly seen. These are most likely opaque porcelain islands residues on the metal substrate. The network of lines, remained after the delamination of the ceramic coating, allows indirect evaluation of the adhesion strength. In the samples with smaller crack spacing, the adhesion strength is higher.

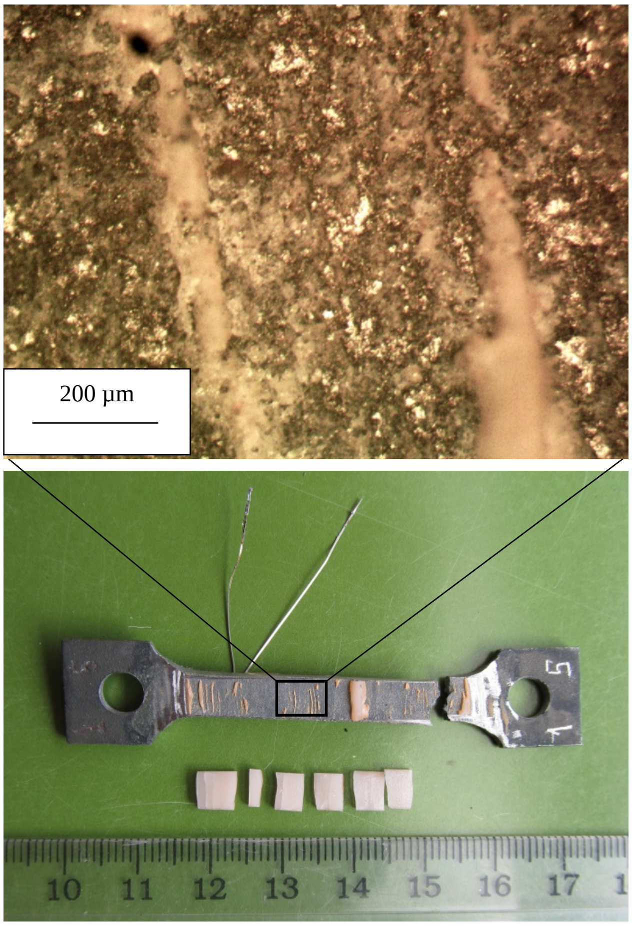

Fig. 4. *Cast sample with multiple cracking porcelain coating after tensile test.*

The results of the adhesion strength calculations and elastic characteristics of the metal-ceramic systems are given in Table 3. They show that the adhesion strength of the ceramic coating to the SLM Co212-f alloy is 23% higher than that of the ceramic to the cast Biosil F alloy (83,1 MPa and 67,5 MPa respectively), thus confirming the results of Lin Wu et al. [15] and Nan Xiang et al. [21].

Table 3.
Mean interfacial shear strength, elastic modulus and failure mode of metal-ceramic systems.

Substrate	Process	Modulus of elasticity *E* (GPa)		Interfacial shear strength τ, (MPa)	Coating failure mode
		Substrate	Coating		
Biosil F	Conventional casting	209	63	67,5	Cohesive or mixed cohesive-adhesive
Co212-f ASTM F75	SLM	213	72	83,1	Mixed cohesive-adhesive

4. Discussion

The bond between the ceramic and dental alloys is mainly two types – micro-mechanical and chemical [10,11,21]. Since the manufacturing technology of the porcelain coating to the cast and SLM dental alloys is the same, it is most probably that the stronger adhesion to the SLM substrate is due to the higher roughness of its surface. This hypothesis is confirmed by the surface examination of the samples after tensile testing. It is clearly seen that the non-melted alloy's powder acts as natural retentive beads. They retain a larger quantity of porcelain on the surface of the SLM sample, thus increasing the mechanical adhesion. Additionally, the higher surface roughness of the SLM specimens provides a larger surface area of ceramics interaction with the metal, which improves also the chemical adhesion. On the surface of the SLM detail, an intermediate layer is formed which consists of the elements of alloy and ceramic [15]. Since the chemical bond is decisive for the adhesion strength between the metal alloy and the ceramics, this boundary layer has a decisive impact on its enhancement. Ultimately, the adhesion strength of ceramic to the SLM Co-Cr alloy samples is significantly higher than that of the cast samples due to the increase in both the mechanical and the chemical components. Due to differences of the loading specimen configurations, used in the tensile testing and standard three-point bending (ISO 9693-1:2012), no direct comparison should be made of interface shear stress measuring by both tests.

5. Conclusion

The present study is focused on the evaluation of the adhesion strength of ceramic coating to CoCr alloy.

- Adhesion strength of a ceramic coating to a SLM Co212-f alloy is higher than the service requirements and 23% greater than that of ceramics to the Biosil F cast alloy (83.1 MPa and 67.5 MPa respectively). This is mainly due to the almost twice-higher roughness of the surface of the SLM samples, which leads to increase both mechanical and chemical components of the adhesion.

- The failure character of the ceramic coating to Co-Cr alloys, manufactured by casting and SLM, is similar and is of the adhesive-cohesive mode.

- The higher adhesion strength of the porcelain coating to the SLM Co-Cr dental alloys is a good prerequisite for their application in the production of metal-ceramic fixed partial dentures.

6. References

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