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Improvement of the adhesion between CoCr and dental ceramics by laser surface structuring

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Abstract

The preparation of the interface between dental ceramics and non-precious metal alloy cobalt-chromium (CoCr) at veneered dental restorations is crucial to the durability of the bonding strength and thus to the lifetime of the prosthesis. Conventionally the surface finishing is carried out by manual sandblasting, which is a highly subjective process. Due to this fact, the reproducibility of the required surface roughness for the bonding is limited. In addition, embedded residues of the blasting material can result in failure of the bonding.
Laser based surface finishing represents a promising approach to condition dental prostheses. Through its reproducible working principle while avoiding the use of foreign particles, laser processing offers advantages over the conventional process. With laser ablation the creation of a determined surface roughness as well as the functionalization of surfaces by defined structures becomes feasible. Therefore surface structures that enhance the adhesion between CoCr and dental ceramics have been developed in the present study. The subject was to improve the metal-ceramic bonding strength by conditioning the CoCr surface. First, the structures were derived from natural models, abstracted to technical application and then implemented with laser ablation. The structures were ablated on CoCr test specimen with a nanosecond (ns) pulsed Yb fiber laser with maximal pulse energy of 1 mJ. After ceramic veneering, a Schwickerath test was performed. Overall, the laser structured surfaces show bonding strengths up to 57 MPa. These adhesive forces are significantly higher than those of conventionally treated surfaces. Thus, laser ablation appears to be an attractive technology for surface finishing of dental implants for reasons of reproducibility and enhanced surface properties.

Keywords: laser ablation; surface structures; adhesion of metal and ceramics; dental prosthesis; CoCr

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1. Introduction

Standard dental restorations are manufactured from CoCr alloy and veneered with specific dental ceramics (Kim et al., 2007; Mehulić et al., 2009; Henriques et al., 2012). Since ongoing research in material properties and production methods and contribute extensively to the optimization of artificial dentition, prostheses already provide satisfying results concerning long-term durability, biocompatibility and cost effectiveness. However, porcelain-fused-to-metal prostheses still show high risk of fracture (Henriques et al., 2012; Nieva et al., 2012; Xiang et al., 2012) which results in failure of the restoration (Jain et al., 2013). Due to the utilization of interacting materials, primarily the bonding between ceramic veneer and CoCr alloy framework affects durability (Henriques et al., 2012; Xiang et al., 2012).

Bonding forces occurring between framework surface and ceramics layer are established by chemical and mechanical mechanisms (Külünk et al., 2011). Chemical bonding is influenced by elemental composition of framework alloys and formation of an oxide layer on their surface (Xiang et al., 2012). Surface roughness enables mechanical fixation caused by increased surface area and microretentive topography (Kern and Thompson, 1993; Nergiz et al., 2004; Mehulić et al., 2009).

In order to prepare surfaces for veneering the framework is conventionally sandblasted with corundum (Al_2O_3) (Külünk et al., 2011; Henriques et al., 2012). This grants bonding mechanisms by modifying surface roughness, increasing surface energy as well as removing organic and metallic residues from the surface (Al Jabbari et al., 2012). Using common sandblasting methods surface roughness of $R_z = 4 - 12$ µm was realized (Nergiz et al., 2004).

However, resulting surfaces are hard to reproduce. They often form sandblasting-related low bonding forces and failure characteristics (Al Jabbari et al., 2012). This follows inter alia from unequal distribution of roughness, embedded corundum particles (Kern and Thompson, 1993) or remaining organic residues on the CoCr surface.

Using laser technology is a promising alternative to improve the metal-ceramic bonding. Through its reproducible working principle while avoiding the use of foreign particles laser processing offers advantages over the conventional process. Veneered prostheses can profit from adjusting surface topography through precise ablation of pulsed lasers and therefore control mechanical bonding mechanisms. Creation of a determined surface roughness as well as the functionalization of the surface of the framework by defined microstructures becomes feasible.

Applications for pulsed laser systems are found e.g. in fundamental research and material processing as well as medical procedures (Meijer et al., 2002). Due to their low acquisition cost and marginal effort for maintenance ns lasers have an economic benefit compared to lasers with shorter pulse duration (Fu et al., 2010). During the laser structuring process material is ablated by using high-intensity laser pulses at defined areas on the surface resulting in a specific surface topography. In particular by ablating with nanosecond pulses the process is dominated by heat conduction, melting, evaporation and plasma formation (Leitz et al., 2011). The irradiated energy of the ns-pulse is absorbed by the solid and the evolving thermal wave propagates into the material (Chichkov et al., 1996). Depending on the achieved temperature the material is molten up or a vapor plume is ejected above the irradiated zone which can become ionized producing plasma. The vapor can further absorb and disperse the laser beam, changing the actual flux received by the surface (Brown and Arnold, 2010). Vapor and plasma recoil pressure lead to a partial removal of material either in vapor or liquid phase whereas some melt remains at the surface due to tension forces (Leitz et al., 2011; Schäffer, 2012). The layer-by-layer removal of material with laser ablation is also suitable for very hard materials.

In the context of dental restorations and surface structuring by laser processing the present study aims at developing surface structures improving the bonding within the metal-ceramic composite structure by laser processing of the CoCr surface. For this purpose, surface structures from flora and fauna were collected, evaluated and the most promising ones were chosen. Structures in nature contain features in the range of nm to µm which establish characteristics like high adhesion forces when in close connection with other surfaces or facilitate mechanical interlocking. The chosen structures are abstracted to the technical application and implemented on test specimen with laser ablation. A three point bending test is performed to evaluate the bonding and new surfaces structures after ceramic veneering.

2. Material & Methods

Suitable surface structures for laser structuring are reviewed with regard to surface mechanisms which can improve metal-ceramic bonding strength. This research reveals functional structures like toe pad structures of different frog (Federle et al., 2006), bush cricket (Varenberg and Gorb, 2009) or gecko species (Spolenak et al., 2005; Abbott and Gaskell, 2007; Jeong et al., 2009; Boesel et al., 2010; Kamperman et al., 2010; Comanns et al., 2011; Tawfick et al., 2012; Stark et al., 2013). Furthermore, structures on leaf surfaces of numerous plants (Feng et al., 2008; Koch and Barthlott, 2009) provide beneficial characteristics for adhesion enhancement. It can be seen, that most of the investigated surfaces facilitate their bonding to contact material by establishing adhesive forces as well as mechanical retentions.

Since these mechanisms are assumed to be responsible for metal-ceramic bonding (Külünk et al., 2011) in conventional procedure, it is assumed that likewise similar effects are realizable when surface structures are deduced to dental applications. Reviewed structures have been rated individually based on VDI Guideline 2225 in terms of estimated adhesive strength, feasibility by laser ablation and cost effectiveness. Out of fifteen models the four best ranked are chosen to be used for laser structuring (Fig. 1). Moreover, due to the possibility of ablating stochastic surfaces with determined roughness, a laser processed surface structure with higher roughness than conventionally sandblasted is chosen for testing. Its realized surface roughness of S_a = 12.7 µm has been measured according to ISO 25178.

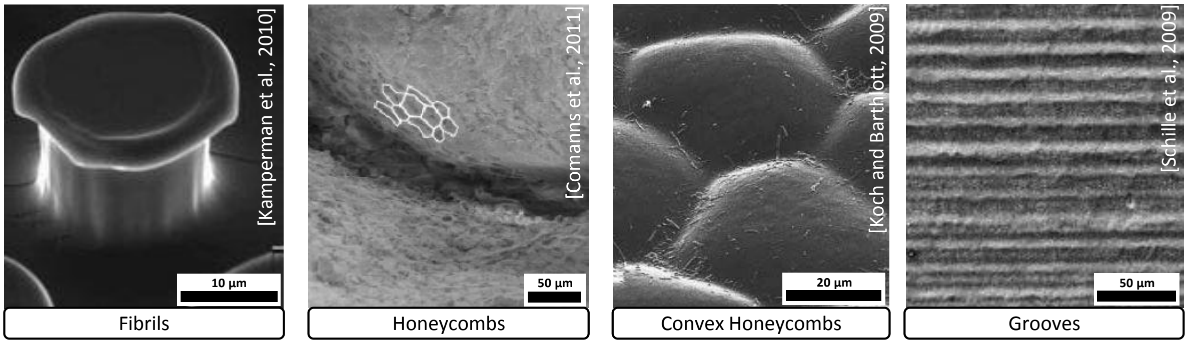

Fig. 1. Natural models of surface structures to be used as model for laser structuring

The surface structures from Fig. 1 are abstracted and scaled taking into account the possible resolution of laser processing with an approximated focal spot of 60 µm. First, unit cells are created by transferring the original surface topography into greyscale images (Fig. 2). Depending on the dimension of the target area these cells can be arranged multiple times side by side resulting in the defined area. The greyscale images provide topography characteristics where the diverse shades of grey contain the height information of the target structure. The brightest shade of grey determines the highest z-axis value whereas the darkest shade represents the lowest one. Finally, the images are converted into machine data containing laser vector information for each layer.

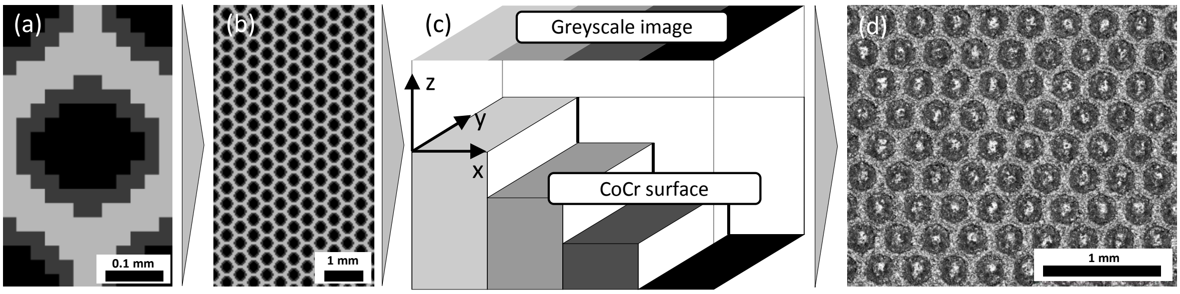

Fig. 2. Process chain of data preparation; (a) Unit cell of the Honeycomb structure; (b) Arranged unit cells to a defined area (c) Scheme of transferring greyscale image onto CoCr surface; (d) Laser ablated Honeycomb structure

For each of the five structures six test specimen were prepared according to ISO 9693-1 to carry out the composite structure test. Each one with a size of l x w x h = 25 x 3 x 0.5 mm (Fig. 3 a) is milled of a CoCr alloy with 61 % Co, 28.20 % Cr, 8.13 % W, 0.22 % Mn, 0.19 % Fe, 1.69 % Si and 0.06 % C. Modulus of elasticity is 190 GPa.

On each sample, an area with the dimensions 8.4 x 3 mm was laser ablated (Fig. 3 b; Fig. 4). Therefore a ns pulsed Yb fiber laser with 200 W average output power is used. For a precise positioning the machining setup consists of five CNC axes, three linear and two rotational. The scan head itself provides three additional optical axes. A focal length of 163 mm results in a maximum scan field size of 60 mm x 60 mm in the x-y-plane. Laser ablation of surface structures is conducted with pulse duration of 120 ns and pulse energy of 0.27 mJ. Furthermore, a scan speed of 2,000 mm/s and a track as well as pulse distance of 25 µm are set. Using the same laser und machining setup the roughened surface is ablated with pulse duration of 400 ns and pulse energy of 0.4 mJ. In this case the scan speed is fixed to 3,000 mm/s with a track and pulse distance of each 50 µm.

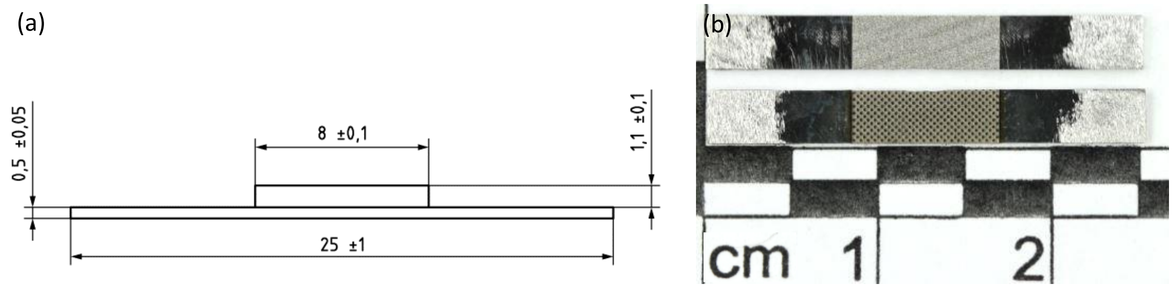

Fig. 3. (a) Dimension of test specimen according to ISO 9693-1; (b) Laser structured test specimen

After laser processing, a thin layer of wash opaque porcelain, a layer of opaque porcelain and of body porcelain were applied and fired onto structured areas (Fig. 5 a). To determine the bonding strength between ceramics and structured CoCr a three point bending test after Schwickerath is carried out (Fig. 5 b) according to ISO 9693. During the test the force-path-curve under axial load of the test specimen is measured until occurrence of crack formation at F_{max} [N] with a following reduction in force. Additionally, an acoustic analysis is executed including the measurement of the first microphone signal emitted by each test specimen.

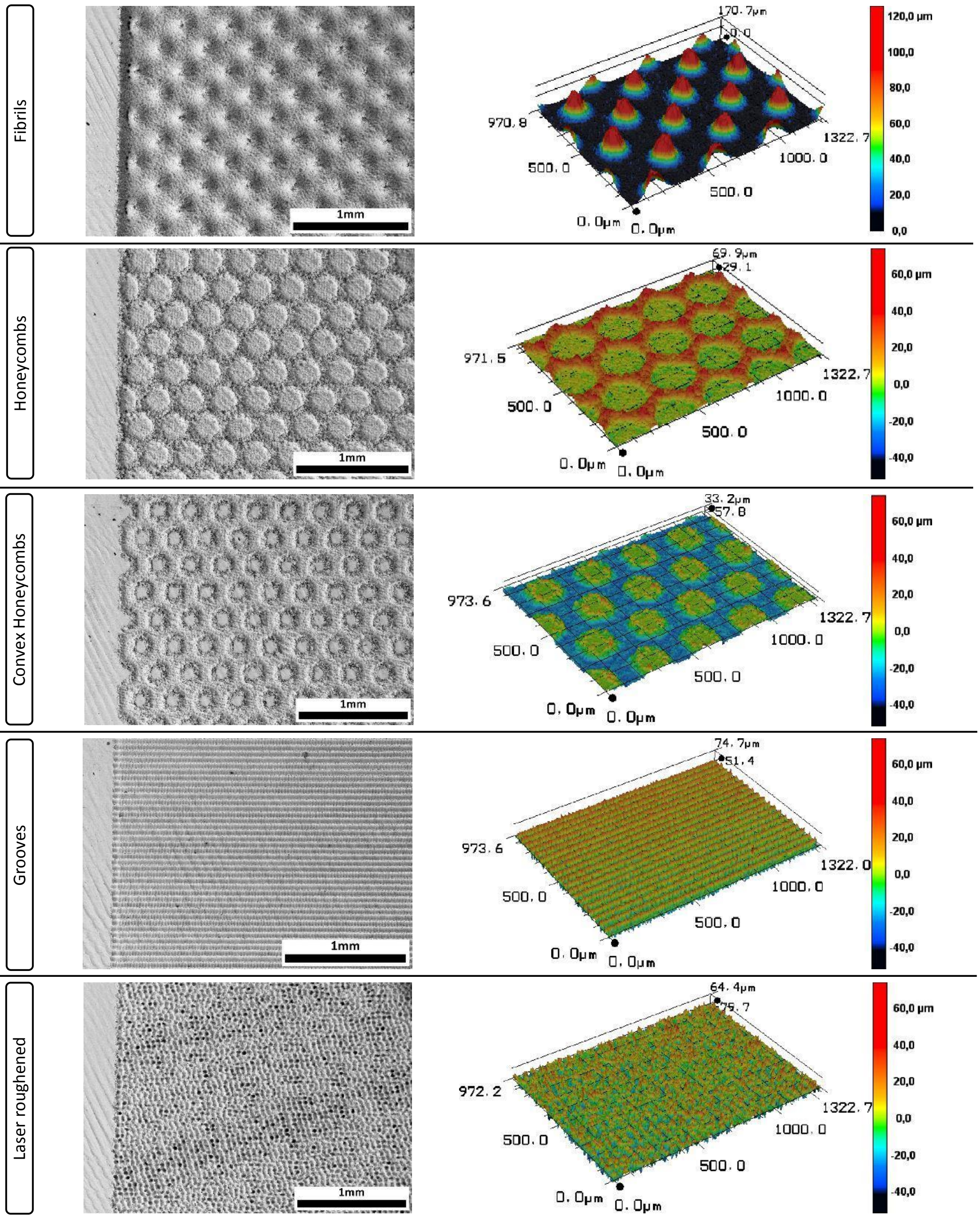

Fig. 4. Scanning electron microscope (left) and laser scanning microscope (right) images of the laser ablated surface structures

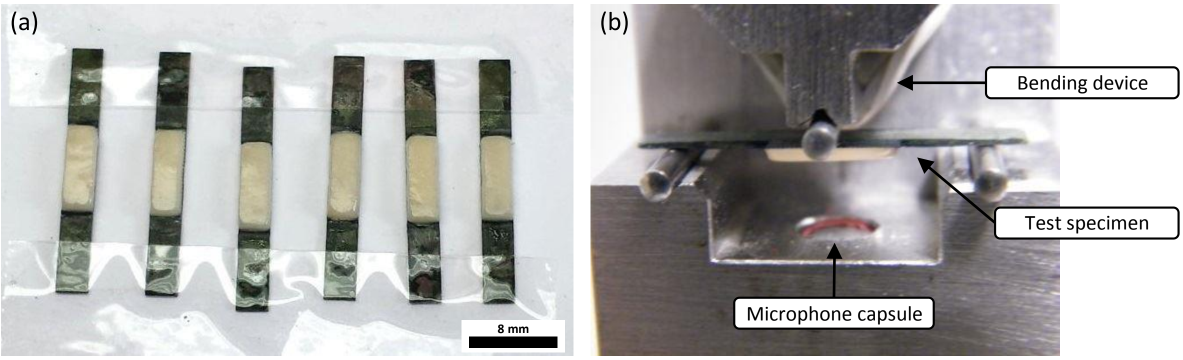

Fig. 5. (a) Group of completed test specimen; (b) Three point bending test with specimen

It is assumed, that the first signal indicates the initial formation of cracks. For each group and test specimen the adhesive bond τ_b [MPa] is calculated based on each F_{max} and the force at first acoustic signal. To check whether the mean values of adhesive bond differ statistically significant a nonparametric Mann-Whitney test is carried out ($p = 0.05$).

3. Results & Discussion

All natural models were successfully transferred to technical surfaces as well as reproducibly laser ablated on test specimen. The results of the Schwickerath test are shown in Fig. 6 on the basis of mean values and standard deviations. To be classified as suitable for dental prostheses, τ_b has to be at least 25 MPa according to ISO 9693-1 (horizontal line in Fig. 6). Values of conventionally sandblasted surfaces are 29 – 40 MPa. Considering F_{max}, the Schwickerath test shows that all validation groups reach mean adhesive bond values of 43 – 57 MPa (Fig. 6 a). This value clearly is above the minimum strength required. Here, the Fibrils feature the lowest (43 MPa) and the Grooves the highest value (57 MPa). The remaining structures show high values as well, which are similar, but slightly lower than the value of the Grooves. Adhesive bond of the Fibrils differs statistically significant from all other structures.

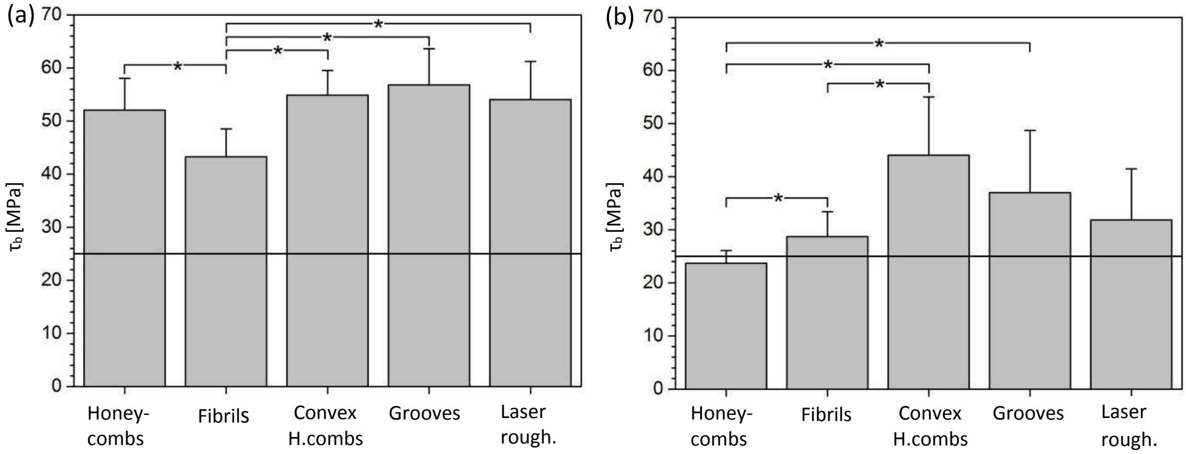

Fig. 6. (a) Mean adhesive bond at F_{max}; (b) Mean adhesive bond at F at first acoustic signal (*statistically significant different)

When the acoustic signal is additionally taken into account mean adhesion strength values are in range of 24 – 44 MPa (Fig. 6 b) and therefore for all groups lower than the F_{max} based values. In this case, the Honeycombs do not meet the requirements of minimum bonding strength and show statistical difference to the Fibril, Convex Honeycomb and Groove structure. The other surfaces still obtain sufficient values where the Fibrils are furthermore statistically different to the Convex Honeycombs. The Convex Honeycomb structure (44 MPa), which shows the minimum difference between both measurements, even exceeds the requirements clearly.

Beside unequal adhesive strength, all structures show specific failure mechanisms (Fig. 7). None of the ceramic veneers chipped from the metallic ground like usual during Schwickerath test. For Grooves and Laser roughened structure initial crack formation occurs at metal-ceramic interface. Crack propagation also takes place at the interface. The failure mechanisms of the other structures are characterized by an initial crack formation within the ceramics which propagates at the interface.

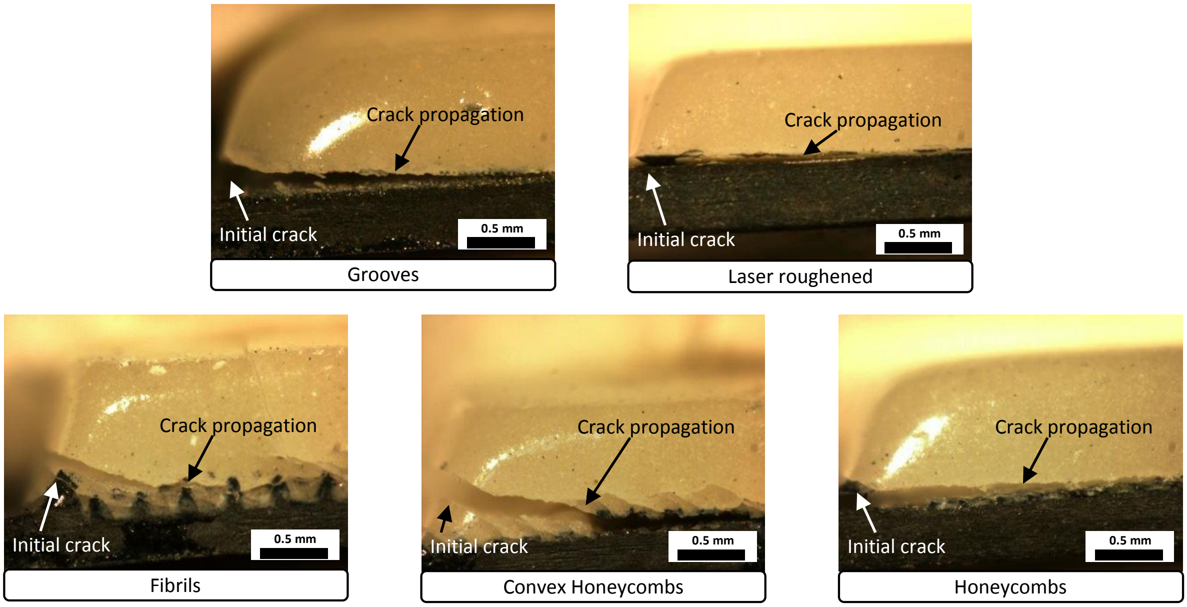

Fig. 7. Microscope images (32 x magnification) of the metal-ceramic interface after Schwickerath test and failure mechanisms

To investigate the effects of the detachment of ceramics from the metallic ground the relative surface enlargement of a conventionally sandblasted and laser structured surfaces were determined (Table 1). The surfaces were examined by laser confocal microscopy at an area of 2.25 x 3.00 mm² and set in relation to an ideally flat area of the same size (100 %). The conventionally roughened surface shows a relative surface of 157 % (57 % enlargement) compared to the reference value. Both Honeycomb structures and the Fibrils show an enlargement of 122 - 132 %. An increased surface of approximately 270 % is realized with laser roughened surface and Grooves.

Table 1. Relative enlargement of surface area depending on the structure

Structure	Relative surface enlargement in %
Ideal flat surface	0
Conventionally sandblasted	57
Convex Honeycombs	122
Honeycombs	130
Fibrils	132
Laser roughened	271
Grooves	275

All structures show bonding strength values which are significantly higher than the requirements described in ISO 9693-1. They even exceed usual values of sandblasted surfaces. Only in consideration of acoustic signals lower values can be observed, which are in range of usual strength.

The comparatively weak mean bonding strength of Fibrils, the deepest structure with approximately 170 µm, occurs due to crack propagation through fibril tips. Melt formation with structural change of CoCr as result from heat exposure during ns laser ablation seems to cause embrittlement and failing of the tips. For the bonding strength of the other structures melt formation does not show negative influence.

Furthermore, the crack initiation and propagation at the metal-ceramic interface as an adhesive failure is merely relevant at the laser roughened surface and Grooves. This represents the conventional mode of failure which can also be observed during Schwickerath test of sandblasted surfaces. Its occurrence is based on similar topography comparing the two structures with the conventional surface. However, mechanical bonding mechanisms might be stronger developed. Through an enlargement of the surface area by around 270 % and increased roughness, bonding strength based on F_{max} could be significantly enhanced.

The remaining structures, on the contrary, show initial cracks in dentine as a cohesive failure which is unusual for this type of test. Apparently, the bonding forces in the metal-ceramic interface exceed the inherent stability of the applied ceramics. Solely the crack propagation at the interface leads to failure of the test specimen. Here as well, however, the ceramics does not detach from the CoCr surface, so that total failure does not occur. The bonding strength is limited by inherent stability of the ceramics. Regarding the Convex Honeycombs, the ceramics is embedded into the structure similar a fixation through retentive topography.

3. Summary & Outlook

The aim of the presented investigations was to develop functional surface structures which improve the bonding of the metal-ceramic interface in the area of dental prostheses. Therefore, structures were successfully derived from natural models, transferred to technical application and implemented with laser ablation.

On the basis of the results obtained from Schwickerath test, it can be seen that the Convex Honeycomb structure yields the highest bonding forces. This is due to the fact that the measured values without as well as with consideration of acoustic signals result in high values which exceed values of conventionally sandblasted surfaces. By disregarding acoustic signals, all surfaces provide high bonding strength values. When acoustic signals are taken into account the values differ more. However, except for Honeycomb structure they are in range of conventional values and exceed minimum requirements.

In summary, defined laser structured surfaces are able to achieve technically superior properties compared to conventional sandblasted surfaces. The structures show great potential for further improvement in dental restoration since limiting factor is the inherent strength of ceramics. If ceramics with balanced inherent strength are used, it may be possible to increase bonding strength values significantly. Additionally, further shear and moist environment tests should be carried out. The present 2D study should be completed with further investigations in 3D laser structuring also considering different incident angles and structure information to freeform surfaces introduced to dental prostheses (Fig. 8).

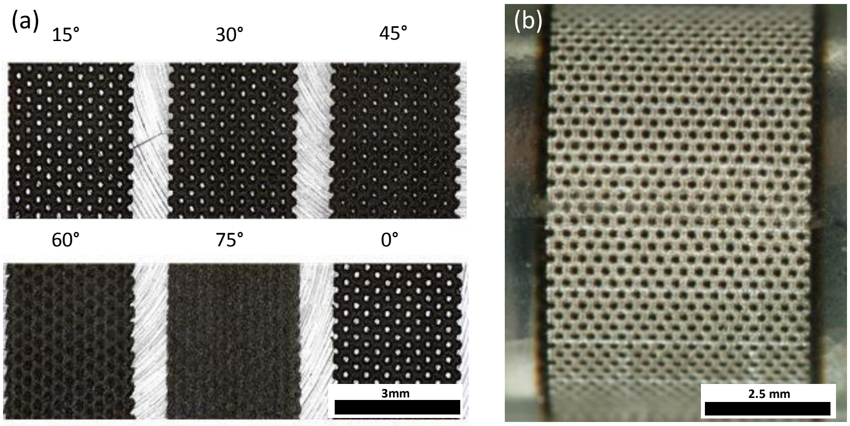

Fig. 8. Laser ablation of the Honeycomb structure with different incident angles (a) Structure ablated with angle to the normal vector of the flat surface; (b) 3D-laser ablation of the structure into an inner radius following real dental prostheses

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