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The role of mechanical, chemical and physical bonds in metal-ceramic bond strength

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ABSTRACT

Purpose: A review regarding the mechanisms of metal-ceramic join is presented.

Design/methodology/approach: The impact of the air-abrasion parameters on the mechanical bond strength of the ceramic crowns was discussed. The presence of opaque on the chemical bond was analysed. Research of the influence of the difference in the coefficient of thermal expansion values on the metal-ceramic bond was included. The methods of testing the bond strength were analysed.

Findings: The metal substructure-dental ceramic bond strength is affected by all types of bond. In bond strength, 3-point bending test and shear test are mainly used. Created samples simulate the ceramic crowns veneered on one side. The role of physical bond on ceramic crowns veneered around metal substructure is unknown.

Research limitations/implications: The prosthetic restorations with the ceramic surrounding whole the metal substructure are commonly used. The impact of shrinkage in the cylindrical deposition of the ceramic on metal substructure should be analysed.

Practical implications: Numerical analysis and FEM simulation can be helpful in the analysis of the physical bond between the metal substructure and the dental ceramic around it.

Originality/value: The impact of the type of the bond to metal-ceramic bond strength is presented, taking into account the cognitive gap in the influence of the coefficient of thermal expansion on the cylindrical placement of ceramic on the substructure.

Keywords: Metal-ceramic bond, Bond strength, Mechanical bond, Chemical bond, Physical bond

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MATERIALS

1. Introduction

Porcelain fused to metal crowns are common used restoration, because of aesthetic of ceramics and properties of dental alloys [1-5]. In clinical use, they indicate high strength and reliability, and in 94% cases, they achieve durability for up to 10 years of use [6]. This durability results from the strong join between dental ceramics and dental alloys, which is based on mechanical, chemical and physical bond [4,7,8].

Manufacturing permanent dental restorations, like crowns and bridges on metal substructures, is a precise process. It begins from forming metal substructure, which surface is treated to air-abrasion. Quality of performing this treatment depends to a large extent on the effectiveness of resulting connection. The last step is application and firing layers of dental ceramics on the surface of metal substructure to cope aesthetic and functional requirement of the future restoration [9-11].

Selection of compatible metal and ceramics materials in the manufacturing process of dental restoration is highly important. It is required for existing chemical and thermal compatibility between these materials [12]. Mismatched parameters can cause cracks of ceramics, distortion of metal substructure or unaesthetic appearance of dental crowns. [12-14]. Therefore join between dental ceramics and dental alloys is widely studied. In a mechanical aspect of bond parameters of air-abrasion are important and in chemical aspect- composition of opaque and type of metal oxides, which are formed on the metal surface. The physical aspect of the metal-ceramic bond depends on the selection of materials regarding the coefficient of thermal expansion. The aim of this paper is an analysis of the above mechanism occurring in porcelain fused to metal crowns and orderly literature review available in this space.

2. Metal-ceramic bond

In dental techniques is being used corrosion resistant metals and alloys, especially cobalt-chrome (Co-Cr), nickel-chrome (Ni-Cr), titanium alloys and precious metals (Tab. 1). Unfortunately in all listed materials occurs problem which effective and stable bond in join with ceramics. Hence in manufacturing process metal surface are air-abrasion to increase the number of mechanical bonds in connection.

Table 1.
Features of materials most commonly used in manufacturing permanent dental restorations [8,9,15-20]

Material	Advantages	Disadvantages
Au-Ag-Cu	Corrosion resistant	Low strength The difficulty of dental ceramic firing
Au-Pd	Stability in the wide temperature range Good mechanical properties (even possible manufacturing large dental restoration) Good corrosion resistant	Pd strongly absorbs hydrogen from air and cast can become porous Alloy sensitivity to overheating Pd can cause allergic reactions
Au-Pt	Strongly corrosion resistant in acidic, alkaline and oxide environment	High price
Pd-Ag	Good mechanical properties Good corrosion resistant	Susceptibility to corrosion, which causes permanent discoloration of the edges of the gums Difficulties in machining Pd can cause allergic reactions
Ni-Cr	Low price Corrosion resistant Hardness larger than the hardness of precious metal alloys Favourable value of elasticity modules (it's possible to execute structure in a thickness of 3 mm)	Allergic reactions caused by Ni Toxicity of the additive of beryllium during machining
Co-Cr	No nickel and beryllium additions Corrosion resistance	High elasticity modulus and hardness Difficulties during mechanical machining Difficult casting technology (temperatures>1300°C)

Material	Advantages	Disadvantages
Ti and titanium alloys	Biocompatibility Corrosion resistance Low specific weight Low thermal conductivity No allergic reactions No toxic effect No taste sensations in patients	Difficulties during casting and tooling The necessity of using low-fusing dental ceramics Low quality of the metal-ceramic bond

2.1. Mechanical bond

Surface for the mechanical bond is increased by air-abrasion, which depends on the use of air under pressure with particles of abrasion material. The kinetic energy of grains striking on the machined surface leads to its micro cutting and it results is surface extending. It can, therefore, be said that air-abrasion is abrasive method [21].

Air-abrasion improves the resistance of bond, because micro cutting of the machined surface depends to formation irregular surface, caused her extending and increase of her roughness. The result is increased mechanical retention and surface wettability of metal. Suitable wettability provides proper distribution of liquid ceramic, which in dental techniques is used in the form of water suspension. Influence ceramic mass in each nook and crannies of the metal surface at the stage of its application on metal substructure before firing in furnace determines good mechanical bond between dental ceramic and dental alloys. After the firing process, microcavities remain the places of attachment and locking up of ceramic grains [4,7,8]. Air-abrasion also cause purification of the metal surface from surface contamination, especially if metal substructure was made by a casting method. In this way is removed remains ceramic investment material, because its remains can disturb the metal-ceramic bond and lead to worsening corrosion resistance of the alloy [8,9,21,22-26]. Summarizing, air-abrasion change physical and chemical properties of the machining surface, e.g., electrostatic potential and surface energy [27]. Numerous studies show that metal surface not subjected to air-abrasion does not provide a proper bond with ceramic [9,22,23,28,29].

In a comparative study Ni-Cr and Co-Cr alloys, Melo et al. demonstrated that after air abrasion is no a statistically significant difference in forces of the metal-ceramic bond, between this alloys [30]. Bond force in both cases was in the range 54-71.7 MPa (Table 2), which is a value sufficient for the effective bond between crown with metal substructure [31]. These observations complement research [32], which show no a statistically significant difference between these alloys also using different grains (Al_2O_3, synthetic diamond particles, boron nitride) however, most durable bond was observed after air-abrasion of the metal surface with 110 µm Al_2O_3 grains and particles of boron nitride. (Table 2). Other Co-Cr alloy studies for bond strength with ceramic depending on parameters of air-abrasion showed that the best results are obtained for the surface, which was airborne-particle abraded with 110 µm Al_2O_3 particles, at 0.4 MPa, where the angle of incidence does not affect the strength of the bond (Table 2) [33].

Distinct material with high application in implantology and prosthetics is titanium, which has low density and good biocompatibility [34-36]. It is nontoxic and does not cause allergic reactions and taste sensations [8,18,19]. However fast formation oxides on titanium surface cause poor quality of his bond with dental ceramic. Hence titanium also is sandblasted for extending surface and improve the mechanic bond.

Testing of contact angle and surface free energy sandblasted titanium surfaces show the highest bond strength for surfaces air-abrasion with 110 µm Al_2O_3 particles, because for these parameters was observed the highest value of surface roughness and energy. The lowest value was obtained for samples sandblasted with 50 µm particles. Influence of pressure change (0.2, 0.4, 0.6 MPa) was noticed only in 250 µm grains, where when increasing this value, the examined parameters decreased [34].

Comparative study on extending titanium surface by air-abrasion (Al_2O_3 125 µm, 0.2 MPa) and electro-invasive treatment (65 W, 8 µs discharge impulse with 10 µs break between cycles) improve no statistically significant difference in bond strength of 3 points bending test. However, it was shown that titanium-ceramic bond (Vita Titankeramik, Vident, Brea) is significantly weaker than a Ni-Cr-ceramic bond (Vita Omega 900, VITA Zahnfabrik H. Rauter GmbH & Co., Bad Sackingen) [35].

A direct consequence of air-abrasion is sticking of abrasive particles in a machining surface, which remain in it during ceramic firing. Research Pietnicki et al. [37] show that in air-abrasion with Al_2O_3 Co-Cr alloys, the highest value of sticking grains occurs in sandblasting at an angle of 90° metal elements (30% of surface). Tests on Ni-Cr alloys confirm these results [38]. For tests of titanium amount of embedded particles are included in the range 13-30% of the metal surface [8,27,39,40].

Table 2.
Results of investigation of the impact of air-abrasion parameters on metal-ceramic bond strength in the shear test

Materials	Abrasive grains, µm	Pressure, MPa	Time, s	Angle, °	Nozzle distance, mm	Shear strength, MPa	Ref.
Ni-Cr/IPS d.SIGN	Al_2O_3, 100	0.200000	10	45	20	54.00-63.00	[30]
Co-Cr/IPS d.SIGN	Al_2O_3, 100	0.200000	10	45	20	55.20-71.70	[30]
Ni-Cr/IPS d.SIGN	Al_2O_3, 50	0.000315	15	N/A	10	40.48	[32]
Co-Cr/IPS d.SIGN	Al_2O_3, 50	0.000315	15	N/A	10	41.73	[32]
Ni-Cr/IPS d.SIGN	synthetic diamond particles, 30-50	0.000315	15	N/A	10	44.21	[32]
Co-Cr/IPS d.SIGN	synthetic diamond particles, 30-50	0.000315	15	N/A	10	45.39	[32]
Ni-Cr/IPS d.SIGN	boron nitride particles, 60-80	0.000315	15	N/A	10	51.87	[32]
Co-Cr/IPS d.SIGN	boron nitride particles, 60-80	0.000315	15	N/A	10	52.72	[32]
Ni-Cr/IPS d.SIGN	Al_2O_3, 110	0.000315	15	N/A	10	52.52	[32]
Co-Cr/IPS d.SIGN	Al_2O_3, 110	0.000315	15	N/A	10	54.55	[32]
Co-Cr/InLine	Al_2O_3, 50	0.400000	60	N/A	10	31.90	[33]
Co-Cr/InLine	Al_2O_3, 110	0.400000	45	N/A	10	45.20	[33]
Co-Cr/InLine	Al_2O_3, 110	0.400000	60	N/A	10	47.60	[33]
Co-Cr/InLine	Al_2O_3, 250	0.400000	60	N/A	10	30.40	[33]

Most of the literature reports suggest that embedded abrasive particles work unfavourably contributing to weakness bond strength between metal and dental ceramics. They generate local stresses and reduce metal surface necessary for creating bond [39,41,42]. In the case of titanium Gołebiowski et al. [27] reports that abrasive particles, which are present on the titanium surface decrease the smoothness of surface, change corrosion resistance and can reduce his biocompatibility. However, Wang et al. [10] report that impacts character (positive/negative) of abrasive grains on the titanium-ceramic bond is dependent on their fixing in the metal matrix. According to researchers in the case of loose fastening of Al_2O_3 comes to side effects, that is, stripping the ceramic layer from the titanium surface with abrasive particles. This detachment occurs adhesively. In case of very strong anchorage of Al_2O_3 particles, cohesive detachment occurs, which would suggest a positive effect of Al_2O_3 grains. However, the authors did not introduce reliable confirmation of the above hypotheses [10].

Research of Parchańska et al. [43] indicate that in the case of titanium Al_2O_3 particles can be effectively removed from the surface by subjecting it to chemical etching (30% HNO_3 aqueous solution + 3% HF, mixture of HNO_3+HF+ glycerine, 4% HF in H_2O_2 solution or 4% HF in H_2O solution) however, it cause statistically significant differences (about 50%) in bond strength relative to undigested surfaces. It follows that the removal of abrasive grains remaining in titanium surface after sandblasting decrease titanium-ceramic bond strength. The explanation of the phenomenon seems to be the fact that the etching factor causes erosion of surface irregularities after air-abrasion and thus the change of shape and alleviating irregularities in which ceramic grains may lock in the firing process.

2.2. Chemical bond

The metal alloys (Co-Cr, Ni-Cr) used in dental prosthetics are characterized by ease of oxide formation on their surfaces, which facilitates the formation of a chemical bond between the opaque and the metal. However, titanium behaves a bit differently than others metals and dental alloys commonly used as substructures. This is due to its structural structure because it is allotropic metal. The high tendency titanium to passivation (oxidation) in high temperatures cause formation too thick TiO_2 layer, which also is recognized like negative phenomenon [8,9,18,22,31,44].

The presence of the opaque has a positive effect on the quality of the metal-ceramic bond [45]. Research on Ni-Co and Ni-Cr alloys show diffusion occurs between the phases in samples with opaque during firing of the ceramic, where the oxidation of the surface before firing increase this effect [29,45,46]. Surowska indicates that in this process occurs sodium, potassium and barium diffusion from ceramic and formation of a bond with oxides [8]. However, it is believed that the form in which the layer of opaque is applied (spray, paste, powder with liquid) does not affect on metal-ceramic bond [47] or affects slightly better when using opaque in paste form [48].

In samples without opaque, the elements from metal do not pass or diffuse to ceramic in a small extent [45].

In the case of titanium substructures, except classical air-abrasion, sol-gel method or modification of the titanium surface composition using galvanization are used [34,49]. It has been shown that application of SiO_2 layer by sol-gel method on technically pure titanium, increase bond strength by 20% compared to using only air-abrasion [50].

Research of titanium galvanization (cover with a layer of chromium by applying 5% and 10% of chromium nitrate solution) show an improvement in bond shear strength in relation to air-abrasion, especially for short galvanization time (about 30 min) [49].

2.3. Physical bond

In addition to the mechanical and chemical bond, there is also a physical bond among components of the metal substructure-dental ceramic bond. The physical bond includes adhesion, which concerns to surface interactions and means bonding surface layers of physical bodies or phases. Thus, adhesion can be understood as a reversible thermodynamic process occurring in the layer of combining materials, resulting from the difference in the surface tension at the interface of the substance. Mutual adjustment coefficients of thermal expansion of metal and dental ceramic based on the physical bond are extremely important. Improper selection causes stress on the border of metal-ceramic bond followed by cracks [8,9,15,18,22,51-55].

In research on coefficients of thermal expansion of prosthetic materials, it was shown that difference between the coefficient of bonding materials higher than $0.5 \cdot 10^{-6} K^{-1}$ has a bad influence on bond strength [56]. In the shear strength test of the bond of air-abrasion metal elements (Al_2O_3, 50 µm, 30 s+ oxidation) with dental ceramic, the highest shear strength was observed for the Ni-Cr alloy with Ceramco II ceramic bond (25.3 MPa), where the difference between coefficient was $0.5 \cdot 10^{-6} K^{-1}$. The lowest shear strength noticed for a bond of Co-Cr and IPS d.SIGN, where the difference between coefficient was highest ($2.4 \cdot 10^{-6} K^{-1}$) (Tab. 3). For differences below $0.5 \cdot 10^{-6} K^{-1}$, the bond strength was in the range 15.4-18.3 MPa.

Table 3.
Coefficients of thermal expansion for selected metal and ceramic materials [56,57]

Material	Coefficient of thermal expansion ($\cdot 10^{-6}$ K^{-1})	Source
Ni-Cr	14.0	[56]
Ni-Cr	14.3	[57]
Co-Cr	14.4	[56]
Pd-Ag	14.5	[57]
Ti	8.5	[9]
Vita VMK68	15.2	[56]
IPS d.SIGN	12.0	[56]
Matchmaker	13.8	[56]
Finesse	14.5	[56]
CPC-MK (pressed ceramic)	13.0	[57]
Ceramco II	13.5	[56]
Ceramco II (feldspathic ceramic)	12.5	[57]

With coefficients of thermal expansion of bonding materials, the degree of shrinkage and the resulting shrinkage stress are associated. The phenomenon of shrinkage occurs independently of each other in both materials during cooling, as a result of the difference in the coefficients of thermal expansion. It seems that they have large meaning in metal substructure- dental ceramic bond. The difference between the thermal expansion of ceramic and metal causes as if ceramic were tighten on the metal element and formed the so-called shrink connection. On the micro scale, these type of connection also takes place when ceramic is tightened on the irregularities of the roughness. The situation is the most favourable when thermal expansion of metal is slightly higher than ceramic. When the difference is too large, generated stresses have high value and can lead to cracking. As mentioned earlier, the best-tolerated difference between this coefficient is $0.5 \cdot 10^{-6}$ K^{-1} [8,9,15,18,22,51-55]. Unfortunately, there are few scientific reports dealing with the analysis of this aspect. For this reason, it should be considered a cognitive gap.

3. Bond testing methods

For testing the strength of the metal substructure-dental ceramic bond, shear, bending, torsion, tensile and pull-through tests are used. Unfortunately, test results of shear, bending, torsion, tensile and pull-through strength are not comparable between each other. Of these methods, the most commonly used are shear and 3-point bending test, compliant with the PN-EN ISO 9693-1:2012 standard [8].

The bending test is carried out on rectangular samples, where ceramic is firing on the central part of the metal alloy. The sample is then loaded in half of the length and bend until the metal-ceramic bond are destroyed (Fig. 1). On this basis, the force, which caused separation ceramic from metal surface and place of separation and cracks, which may take place in the opaque layer, ceramic layer or directly on the boundary of bonding, are determinate. According to norm PN-EN ISO 9693-1:2012, the metal-ceramic bond must have to bend strength in the value of at least 25 MPa [8].

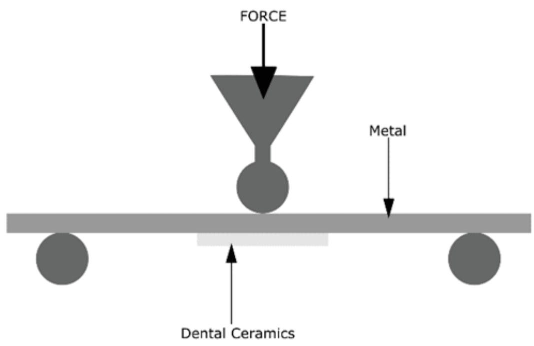

Fig. 1. Scheme of 3-point bending test in metal-ceramic bond strength test [own elaboration]

The shear strength test is used similarly common to the 3-point bending test (Fig. 2) [8]. Using this method, the value of tangential stresses at the boundary of the metal-ceramic bond is determined. Taking into account the shape of the sample and way of applying force in this method, the value of forces resulting from physical and chemical bonds and in minimal extend shrinkage bond (concerns only ceramic tightening on surface irregularities) are taken into account. In this method, it is impossible to take into account the values of forces arising as a result of shrinkage bond of the ceramic on the metal substructure. As for the 3-point bending test, despite its relatively widespread use, it can only be regarded as a comparative test. Considering the complex balance of forces, which occurs during this type of load, it's difficult to say which type of bond is tested and what is the reference to the real conditions. Can be clearly stated, that the same as the shear test, shrinkage bond of ceramic with metal substructure, is not taken into account.

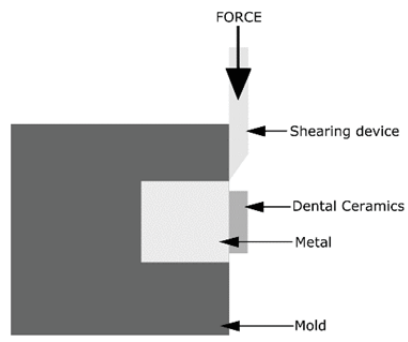

Fig. 2. Scheme of the shear test in metal-ceramic bond strength test [own elaboration]

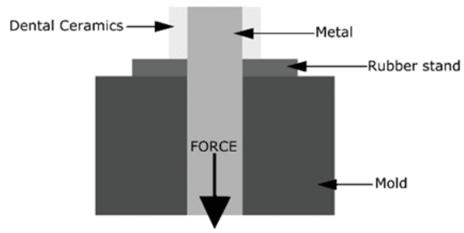

Fig. 3. Scheme of pull-through test In the metal-ceramic bond strength test [own elaboration]

In literature also exist a few mentions about tests based on a pull-through test (Fig. 3) and push-through test [58]. In this experiment is measurement force necessary to pulling out or pushing out metal rod from the ceramic hoop. Both of these methods are the same, differ only in the return of applied forces. Basing on researches from the 1960s, 1970s, and 1980s [59-61] created a few varieties of ways of conducting this test, from which all are considered to be incorrect. For the cause of the error was considered the influence of three factors: the texture of metal surface to bonding, residual stresses resulting from mismatch of coefficient of thermal expansion of materials and stresses formed in the rim [58]. However, researchers of this paper believe that with current calculation tools (simulation, numerical analysis, etc.) it is now possible to carry out methodologically correct pull-through and push-through test. Compared to previously discussed methods, there are only tests, which take into account shrinkage bond of metal substructure with veneering ceramic, as well as all other and is the closest to real conditions. All the allegations to this method related to the texture of metal surface on bond, residual stresses resulting from mismatch coefficients of thermal expansion of materials and stresses arising on the rim seem unfounded because all these factors occur in real bonds and they should be taken into account.

4. Comparison and remarks

Analysing the research on metal-ceramic bond in prosthetic applications carried out by listed methods (shear test and 3-point bending test), it can assume that the most important mechanism deciding about the effectiveness of the bond is a mechanical bond. Both apply to shrinkage bond of the ceramic-metal substructure, as well as ceramic tightening on irregularities. Selection of appropriate parameters of air-abrasion, thereby shape and size of irregularities are important. In case of so-called non-precious metal alloys important is also diffusion bond implemented through previous oxidation. However, the air-abrasion and surface oxidation for diffusion can turn out irrelevant, if on the boundary of metal-ceramic arise stresses and then cracking by inadequate adjustment of coefficients of thermal expansion of metal and ceramics [8].

In general terms for so-called non-precious alloys (Co-Cr, Ni-Cr), the metal-ceramic system is an adhesive-diffusion bond, and exactly there is a bond between ceramic and the oxide layer, which are formed on the metal surface during firing of ceramic [8,17].

5. Conclusions and outlook

The conclusions of the reviewed papers regarding analytical investigations of the metal-ceramic join as well as the results of experimental investigations are summarized, and an outlook is given.

5.1. Conclusions

Each of the discussed types of bonds influences the final mechanism and metal-ceramic bond strength. For Ni-Cr and Co-Cr alloys, this mechanism is similar, because no statistically significant differences were found between these materials in any of the research reports. Only titanium is material in which bond strength with ceramic is lower than strength obtained by the basic alloys used in dental techniques. It's mainly caused by easily formed oxide on titanium surface, which reach the limit thickness to usefulness at the temperature of 750°C [8]. Based on this, ceramic manufacturers create special kind of ceramics, which is adapted to the properties of titanium materials.

For all metal materials, it's necessary to surface extending before bond them with ceramic. In the case when using air-abrasion for this purpose, the selection of appropriate sandblasting parameters is crucial. The research related that the best results are obtained when the 110 μm Al_2O_3, at the 45° angle is used [43,62]. Extending of the surface by air-abrasion facilitates the attachment of the ceramic grains in arising irregularities. Additionally during heat treatment in firing temperature, the ceramic efficiently flows in the surface irregularities.

The occurrence of a chemical bond between metal alloys and ceramic has been confirmed by results showing the diffusion of elements at the border of the bond. Ion permeation is possible due to the presence of opaque, which not only provides coverage of metal and bridging the gray colour of the metal substructure but also strengthens the bond. In research, Hajdug and Zdziech confirmed the dependence of mechanical treatment, oxidation and diffusion on the durability of bond [46]. Then formation larger surface for mechanical bond works positively in case of a chemical bond, which depends on the diffusion of elements and creates a chemical bond in the border of connection. Extend surface increase the area of the formation of metal oxides, which additionally increases bond strength [4,8,12]. An important aspect is also the wettability of the material during firing. Good wettability facilitates the spreading of the ceramic on the surface and more accurately flowing it in the surface irregularities [4,12].

The physical bond is based on adhesion forces and the coefficient of thermal expansion. There are many types of ceramics and metal alloys, significantly differing in the coefficients values. Therefore it's advisable to select materials so that the difference between coefficients of thermal expansion is $0.5 \cdot 10^{-6}$ K^{-1} [4,8]. In the cooling process after ceramic firing, the alloy shrinkage to a lesser degree than fired ceramic, which results tightening of ceramic on metal substructure and creation so-called shrinkage bond. It increases metal-ceramic bond strength [4].

However, the role of material shrinkage, where ceramic cover the entire metal substructure, around its surface, has not been explained yet.

5.2. Outlook

To completely characterize the mechanism of metal-ceramic join further analytical and numerical investigations and especially their experimental validation are necessary. In all of the research, it was noted that the testing materials were prepared in the shape of rectangular tiles, or in the shape of cylinders. First are used in the bending test, second in the shear test. Each test checked the value of bond strength by simulating the dental restoration in the form of veneer, where the crown is covered with ceramic only on one side. In dental techniques are solutions, where ceramic covers entire metal substructure around. In that cases the impact of shrinkage on bond strength is unknown. However, it seems that development of research methods, such as numerical analysis and FEM simulations in the near future will enable further exploration of the topic of materials bond in prosthetic restorations, including the cylindrical seating of porcelain on the metal substructures.

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