Ref: Ro J Stomatol. 2023;69(4)
DOI: 10.37897/RJS.2023.4.2

Adhesion evaluation of dental ceramics sintered on novel titanium alloys

Stefan Tudoran[1], Lucian Toma Ciocan[1], Tudor Spinu[2], Bogdan Mihai Galbinasu[3], Ion Patrascu[1], Vlad Gabriel Vasilescu[1]

[1]Technology of dental prostheses, Faculty of Dentistry, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania
[2]Prosthetic dentistry, Faculty of Dentistry, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania
[3]Discipline Morphology of teeth, dental arches and dental materials, Faculty of Dentistry, "Carol Davila" University of Medicine and Pharmacy, Bucharest, Romania

ABSTRACT

Metal-ceramics dental prosthetic restorations are clinically recommended for their advantages related to good aesthetic features along with strength and long-term clinical use. Given the importance of the quality of the metal-ceramic (M-C) bond, the metal substructure analysis has a major importance to the quality of the manufactured dental prosthesis. In the present study was analyzed the behavior of experimentally developed novel titanium alloys (TiZr, TiZrNbTa) comparatively with other frequently used titanium alloys (e.g., Ti Cp, Ti6Al4V) designated for the technology of mixed prosthetic restorations. All samples were been plated, simultaneously in the same conditions, with the same titanium specific compatible ceramic plating material (Ti22 Noritake). The examination of the surface of both components was performed by scanning electron microscopy SEM) analysis and EDS analysis, which showed differences in the characteristics of the oxide layer formed, depending on the composition of the metal substructure. The evaluation of the alloy-ceramic adhesion was performed by mechanical tests, which attest to the fact that the adhesion and the quality of the bond between metal and ceramic depend on the thickness of the oxide films formed. The results showed the superiority of titanium novel titanium alloys (TiZr, TiZrNbTa), having highest hardness values, highest values of shear strength, a continuous thin oxide films, and consequently, a better metal-ceramic adhesion. Comparatively, less ductile titanium alloys (TiZrNbTa/Ti3) are generating lower adhesion forces with values above 30MPa in some samples justifying less predictable clinical results.

Keywords: titanium alloys, metal-ceramic bond (M-C), interface, oxide layer, EDS analysis, microscopic analysis

INTRODUCTION

Metal-ceramic restorations are clinically recommended for patients who desire prostheses with special aesthetics (provided by the physiognomic component) but at the same time with a good resistance to mastication (provided by the metal component) [1,2]. The adhesion between the metal component and the physiognomic component is determined by the nature of the metal-ceramic bond. Is based on mechanical, physical, and chemical mechanisms, which will act insofar as the ceramic plating material covers the metal surface as intimately as possible, when optimal ratio between the alloy-ceramic contact surface and the coating size is provided [3-5]. The quality of the metal component depends on both the precision of execution and the good capacity to withstand stresses that will act on the ceramics. In other words, the good progress of specific processes, which ultimately contributes to the quality of metal-ceramic adhesion is also ensured by the optimal selection of alloys. It must have a number of basic characteristics, as follows: greater melting range than the sintering range of the ceramic, high

Corresponding authors:
Lucian Toma Ciocan, Tudor Spinu
E-mail: lucian.ciocan@umfcd.ro, tudor.spinu@umfcd.ro

Article History:
Received: 17 November 2023
Accepted: 28 November 2023

mechanical resistance at high temperatures in order to not deform during the firing of the ceramic, coefficient of thermal expansion greater or at least equal to the one of the ceramic plating material to avoid the appearance of stresses at the alloy-ceramic interface and therefore specific defects, such as cracks and or even fractures on cooling, after burning on the ceramics [6,7]. Commonly used non-noble alloys have a lower coefficient of thermal conductivity than noble alloys and a lower specific weight. Compared to noble alloys, they are characterized by higher values of hardness, residual yield strength and modulus of elasticity, given that the elongation at break is approximately equal to that of noble alloys [8-10]. During heating at relatively high temperatures (960-980°C in the case of noble alloys and about 1035°C in the case of non-noble alloys) oxidation occurs at the surface of the alloy, a process considered beneficial in terms of metal-ceramic bond, by forming of ionic networks. However, obtaining a thick layer of oxides (a situation in which only polarized metal oxides are formed) can lead to a decreased adhesion strength [11,12]. Non-noble alloys generally have a lower ductility than the noble alloys and the softer alloys are generating, by transfer, continuous thick films. The quality of the metal-ceramic adhesion is also affected by the thickness of the oxide films formed. Taking all these aspects into consideration, metal-ceramics (MC) bond is considered better in case of non-noble alloys comparatively noble alloys.

Another important aspect that must be taken into consideration from dental technician point of view, is that non-noble alloys have a higher hardness, are difficult to be processed (grinding surfaces is tough), have higher casting temperatures and higher values of the shrinkage coefficient. All this makes the resulting castings less accurate, and metallic components will be adapted with deficiencies on the dental prosthetic field [13,14].

However, due to advantages of significant clinical importance, such as exceptional resistance especially to high temperatures, non-noble alloys have prevailed in the technology of metal-ceramic restorations. From their category, titanium and titanium alloys [15-19] are currently an ideal solution due to their exceptional properties such as: biocompatibility, corrosion resistance and high mechanical strength, low density, lower values of the thermal conductivity coefficient (approx. 13 times lower than gold-based alloys and 3 times lower than that of Co-Cr alloys) and lower values of the thermal expansion coefficient.

MATERIALS AND METHODS

In this study was analyzed the behavior of experimentally developed novel titanium alloys: TiZr, TiZrNbTa (different chemical compositions/alloys marked Ti1, Ti2, Ti3) comparatively with other frequently used titanium alloys (e.g., Ti Cp, Ti6Al4V) [12] designated for the technology of mixed prosthetic restorations.

Table 1 shows, respectively, the chemical composition and the physical-mechanical properties (VH hardness) of the alloys taken into the experiments:

- The alloy TiZrNbTa1 has as alloying elements Nb (over 9%) and Zr (8%) and a hardness (average value of three determinations between the hardness value of the Ti2 alloy and the hardness value of the Ti3 alloy).
- Alloying by 14% Nb (increased the concentration in Nb from 9.26 to 14%) and additional alloying with Ta (4.68%), in the conditions of decreasing Zr content (from 8% to 4.53%) causes a decrease in hardness from 360HV to 319HV.
- The increase of Ta content from 4.68% (alloy 2) to 7.6% (alloy 3) associated with the addition of Zr (8%) and Nb (10%) led to an increase in hardness to 437HV.

It can be deduced that for the studied chemical compositions, the contribution of niobium to the increase of hardness is insignificant compared to the contribution of zirconium and tantalum (but these in proportion of over 5%).

All samples have been plated, simultaneously in the same conditions, with the same titanium specific compatible ceramic plating material (Ti22 Noritake). For the study of the metal-ceramic connection, samples were made using the technology of depositing ceramics on titanium in metal-ceramics restorations (see Figure 1). The working procedure for Ti-22 ceramics [12] includes the following steps: sandblasting, bonding application in two stages, the application of the opaque, the application of dentin and enamel and, finally, the firing of the ceramic layers under vacuum, according to the technology described in the previously published paper.

To determine the strength of the metal-ceramics connection by measuring the values of shear strength (axial load) the samples were embedded in acrylate and fixed in a device provided with a clamping mechanism (Figure 2a and Figure 2b), adapted to standardized mechanical equipment (universal machine for static tests or dynamic traction/compression, type UFP400 Germany).

The equipment used to determine the strength of the M-C connection is the universal machine for static / dynamic (axial) traction/compression testing. Each test is accompanied by the diagram drawn using the processing software also, recording the value of the force [N] at which the detachment of the ceramic from the metal substrate occurred (Figure 4).

a **b**

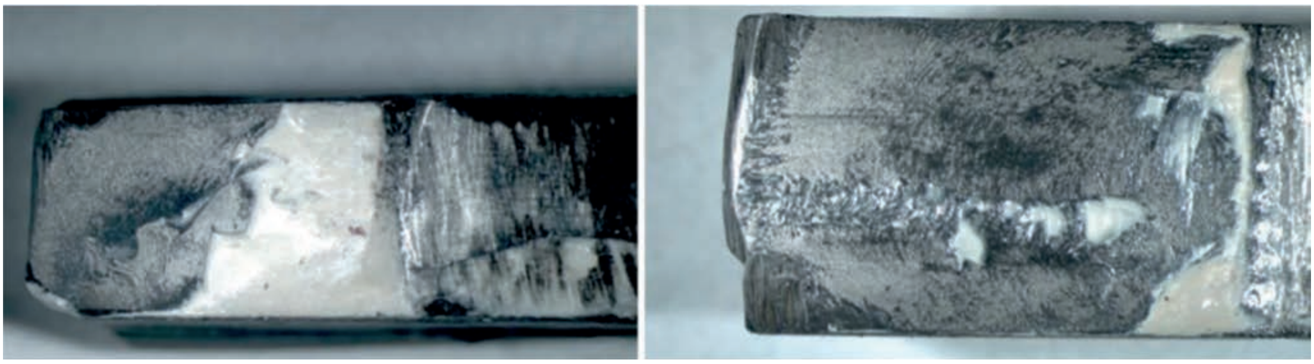
FIGURE 1. Appearance of samples after deposition of ceramics (Noritake T22) on the metal substructure of: (a). TiGrd4; Ti6Al4V, Ti10Zr; (b). TiZrNbTa (sample Ti1)

TABLE 1. Chemical composition of unalloyed titanium, Ti6Al4V alloy and novel experimental titanium alloys, %(*) [13], (**) [12], (***) [20]

Ti /Alloy	Al	V	Fe max.	H2 max.	O max.	N max.	C max.	Zr	Nb	Ta	Si	Cu	Ni	Ti	HV
TiGrd4(*)	-	-	0,30	0,013	0,45	0,05	0,1	-	-		-			rest	125-353
Ti6Al4V(*)	5,5-6,75	3,5-4,5	0,30	0,015	0,20	0,05	0,08	-	-		-			rest	330-390
Ti10Zr(**)	-	-	0,61	-	-	-	-	9,91	-		0,39	0,03	0,01	rest	212-330
Ti 1(***)	-	-	-	-	-	-	-	8	9,26	-	-	-	-	82,74	360
Ti 2(***)	-	-	-	-	-	-	-	4,53	14	4,68	-	-	-	76,79	319
Ti 3(***)	-	-	-	-	-	-	-	8	10	7,6	-	-	-	74,40	437

a **b** **c**

FIGURE 2. Holding mode of the sample in the support mechanism and in the grips of the testing machine: (a) - TiGrd4, Ti10Zr, Ti6Al4V, (b) - Ti1, Ti2, Ti3); (c) - Appearance of the sample after the axial traction test



a **b**

FIGURE 3. Macroscopic appearance (x5) of the sample surface Ti1 (a), Ti2(b), Ti3) after detachment of the ceramic from the metal substructure

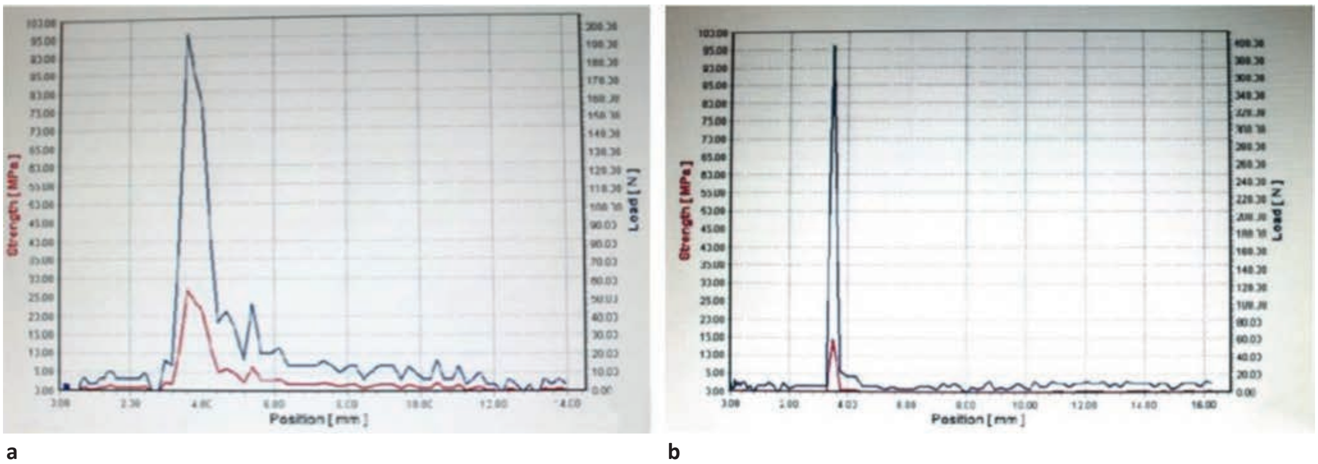


FIGURE 4. Diagram of shear resistance determination for some experimental samples with metallic substructure of: a) Ti1Alloy, b) Ti2Alloy. The blue curve: the evolution of the force applied to detach the ceramic material from the metal support. The red curve: the evolution of shear strength. The maximum values at which the detachment of the ceramic from the metal support occurs are noted (Table 2). Detachment occurs at a constant linear increase in the applied force, without plastic deformation

As the formation of metal oxides in the interface area must take place under certain conditions, which allow the alloy an atomic contact with the coated ceramic mass, a thorough study of the metal – ceramic interface has been carried out. The examination of the surface of both components was performed by scanning electron microscopy (SEM) analysis and EDS analysis.

RESULTS

Results obtained from the testing of experimental samples for the determination of shear strength are presented in Table 2.

TABLE 2. Comparative results of shear strength of the novel titanium alloys (TiZr, TiZrNbTa) comparatively with other frequently used titanium alloys, with the same testing conditions

Material/ bio alloy	Sample surface area) [mm²]	Force [N]	Shear strength [MPa]
Ti 1	7,43	199,20	26,79
Ti 2	27,50	398	14,47
Ti 3	12,91	396	30,67
TiGrad4 [12]	5,5	31.95	5,80
Ti6Al4V [12]	5,62	57.76	10,10
Ti10Zr [12]	5,24	99.68	19,02

In the experimental samples, the deposited ceramics detached off totally or partially, as indicated by the macroscopic appearance of the breaking surface, which differs depending on the type of metal substructure (sample). An in-depth analysis of the type of metal-ceramic fracture was performed by electron microscopy, investigating the interface area at the detachment of the ceramic, during the traction of the specimen (Figure 5).

The microstructural analysis (MagnaRay on Common SEMs electron microscope) of the metal-ceramic interface area after the detachment of the ceramics from the metal substructure reveals a different behavior of the researched materials. This highlights the appearance of a ductile fracture in some cases (e.g., TiGrade4 or Ti10Zr) and granular appearance, the effect of less tenacious fractures (e.g., TiZrNbTa).

The research on the interface area continued through EDS analysis which indicated the compositional nature of the detached surfaces.

The results obtained are highlighting the connection between the chemical composition of the interface area (signaling the presence of oxides in all experimental studied samples, oxide layer of different thicknesses depending on the material) and the specific material of the metallic substructure. The point analysis indicates the composition of the metal, of the transition area (at the interface), or in the deposited ceramics (Figures 6, 7, 8 and 9).

DISCUSSION

The initial composition of the metal substructure can be easily observed (points 1, 2, 3 for TiGrd4 or points 1, 2 for Ti10Zr), as well as the presence of oxygen in the interface area (point 3 of the sample with Ti10Zr alloy metal substructure). The analysis and interpretation of the experimental results have taken into considerations the existing literature regarding the nature and strength of the MC bond established between the alloys used as substructure and the ceramic plating materials. We noticed the benefits of a continuous thin oxide films upon the strength of the MC bond, unlike the supposition that intense preoxidation would promote the bond strength, McLean and Sced [7].

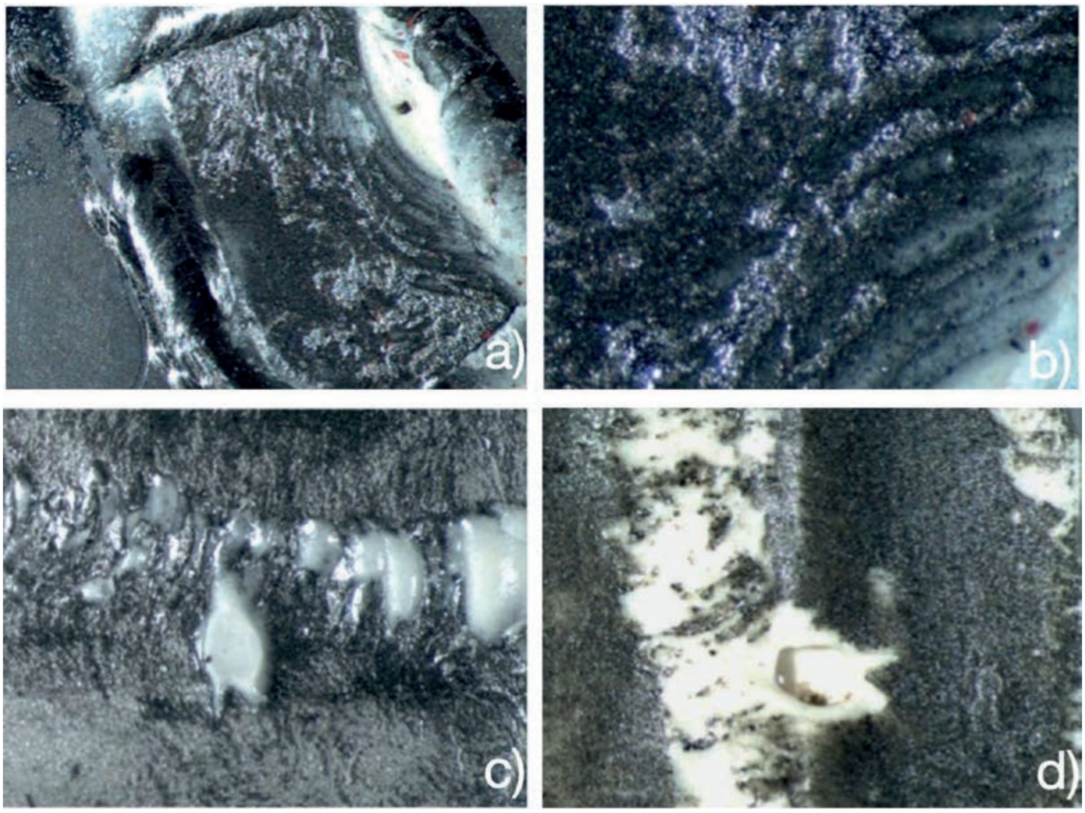
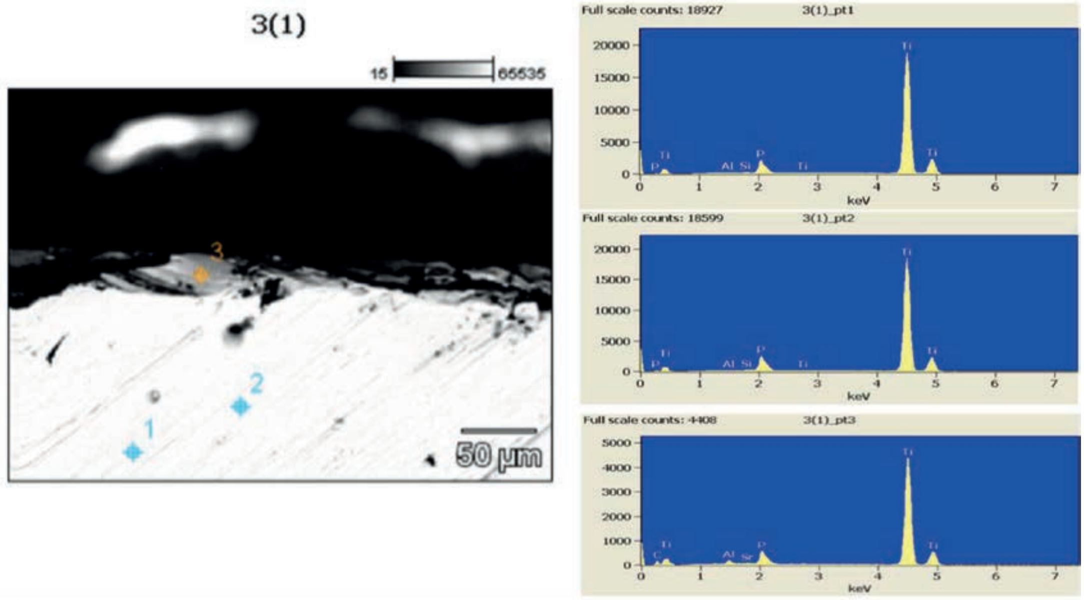
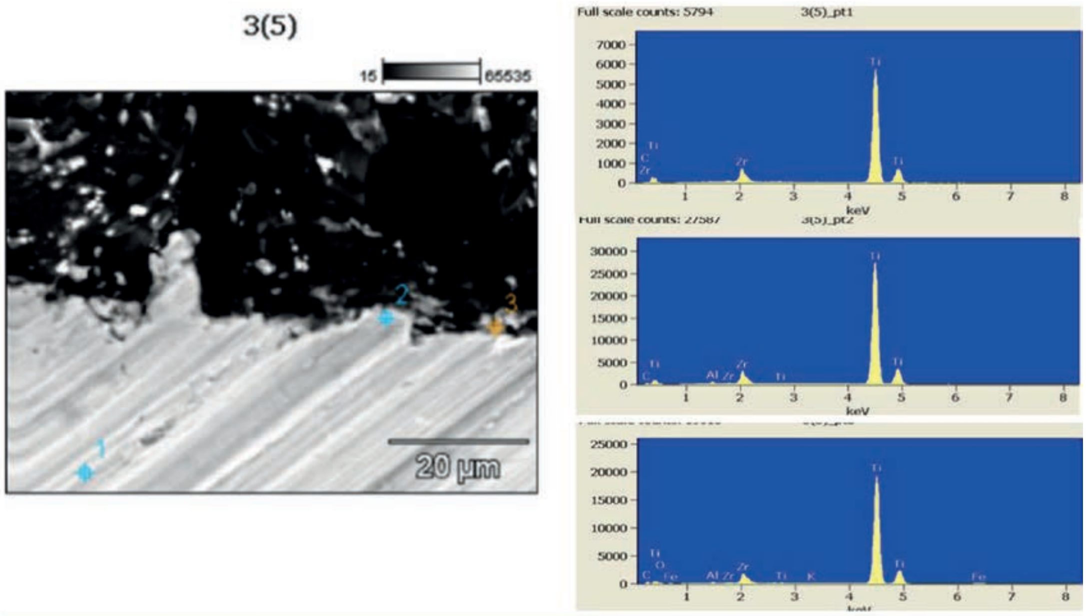


FIGURE 5. Macroscopic aspects (x50) of the metal-ceramic interface area after detachment of the ceramic plated material from the metal substructure: a. TiGrade4 [12], b. Ti10Zr [12], c. TiZrNbTa and d. TiZrNbTa. The aspect of the fracture in images c) and d) indicates a higher resistance to detachment compared with the images a) and b), as demonstrated by the residues of ceramic material (white color) present on the surface of the metal support. In images a) and b) these residues are not present



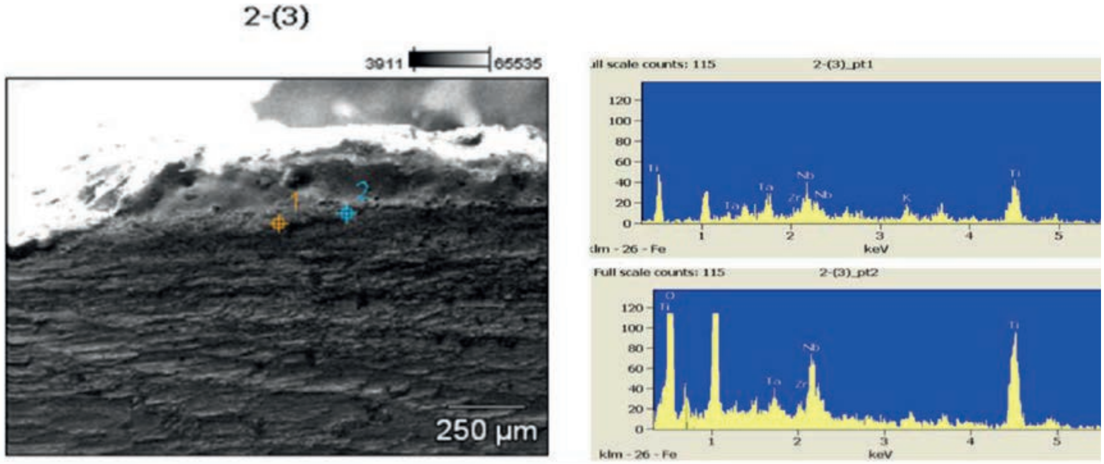
	C-K	Al-K	Si-K	P-K	Ti-K	Sr-L
3(1)_pt1		0.10	0.23	3.53	96.14	
3(1)_pt2		0.14	0.23	4.23	95.39	
3(1)_pt3	2.96	1.39		3.79	91.87	0.00

FIGURE 6. EDS Analysis of the TiGrd4 Substructure and T22 Noritake Ceramic Interface Areas (Sample no.3 / the field1). In field 3 located in the contact area between the two materials, the deviations of the elements C, Al, and Ti compared to fields 1 and 2, are due precisely to this contact area between the two materials affected by their detachment. The presence of carbon in this area may be due to the sample preparation process



	C-K	O-K	Al-K	K-K	Ti-K	Fe-K	Zr-L
3(5)_pt1	0.42				89.56		10.02
3(5)_pt2	1.23		0.57		89.39		8.81
3(5)_pt3	1.89	0.20	0.37	0.07	87.63	1.61	8.23

FIGURE 7. EDS Analysis of the Ti10Zr Substructure and T22 Noritake Ceramic Interface Areas (Sample no.3 / the field5)

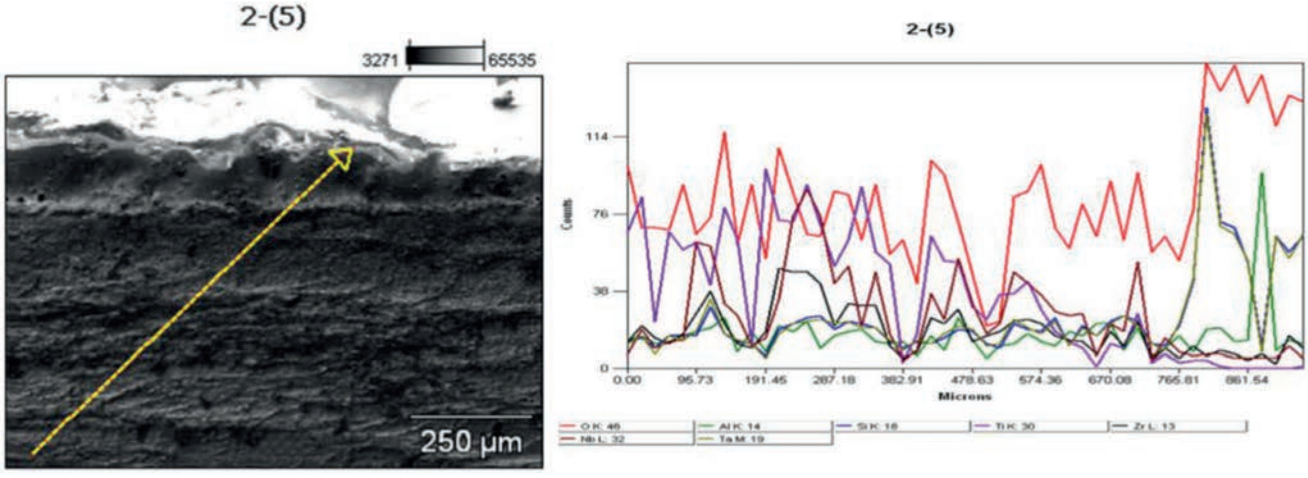


	O-K	Na-K	Al-K	K-K	Ca-K	Ti-K	Zr-L	Nb-L	Ta-M
2-(3)_pt1	20.63	4.34	1.78	4.45	5.08	69.84	4,19	12,24	4.45
2-(3)_pt2	41.93					69.28	4.11	13,59	4.10

FIGURE 8. EDS Analysis of the TiZrNbTa substructure - Noritake Ceramic - Interface Area (Sampleno.2 / the field 3)

The analysis of the experimental samples reveals discontinuous layers with large thicknesses (over 5 µm), especially in those with non-alloy titanium metal substructure [12]. However, uniform, continuous layers with smaller thicknesses were obtained in the samples with metallic component from titanium alloys, respectively of maximum 3.9µm for those with Ti10Zr and of 1.10-3.03 µm for those with TiZrNbTa (Figure 10).

In another studies, the authors show that the strength of the M-C bond is influenced by the characteristics of the oxide layer formed at the interface, which can reduce the coefficient of thermal expansion of the ceramic mass and can favor the action of residual stresses with implications in generating cracks or fractures at this level [8,10]. The fracture at the interface where the oxides detach from the surface of the metallic material and remain attached to the clad ceramic mass occurs especially in the case of unalloyed titanium, when large layers of oxides are formed. Confirming the data from the literature, the experimental results obtained in the case of non-alloy titanium (TiGrade4) [12] demonstrate a poor bonding behavior compared to the other mate-



a b

Figure 9. a) sample no. 2: ceramic plated TiZrNbTa alloy; b) EDS Analysis of the TiZrNbTa substructure - Noritake Ceramic - Interface Area (it can be noticed the variations of oxygen content from ceramic to metallic substructure through the interface)

a b

Figure 10. Oxide layer 1.10-3.03 microns (µm) thick on the TiZrNbTa surface (LEICA stereomicroscope, X50 magnification)

rials studied (e.g., Ti10Zr or TiZrNbTa), explained by the identification and highlighting of discontinuous and thick oxide layers.

Titanium is a chemically active element with a specific weight of 4.5 g/cm^3. It is 2 times lighter than Co-Cr-Mo alloys (8.3 g/cm^3), 3 times lighter than palladium-silver alloys or palladium-gold alloys and 4 times lighter than gold alloys (17.5 g/cm^3). Unalloyed titanium has a melting temperature of about 1660°C, is an allotropic element, presenting up to 882°C a compact hexagonal structure (allotropic form α), and above this temperature an internally centered cubic structure (allotropic form β). Depending on the content of impurities (oxygen, hydrogen, carbon, iron, nitrogen) there are four grades of unalloyed titanium. Hydrogen is considered the most harmful impurity because it produces cold brittleness by forming metal hydrides. The same negative effect has the carbon because is forming metal carbides at concentrations higher than 0.2%. The oxygen content in titanium greatly influences its mechanical properties leading to an increase in their values as the oxygen content increases. Thus, at a content of 0.18% O_2, the yield strength of titanium is about 170 MPa, and at a content of 0.40% O_2 the yield strength reaches values of 485 MPa. However, higher increases in oxygen content are not allowed as this worsens processability and decreases its chemical resistance. Titanium alloys with α structure include the following systems: Ti-Al, Ti-Al-Sn, Ti-Al-Zr, Ti-Al-Sn-Cu, Ti-Cu-Zr and others. Those in the Ti-Al system contain 2-7% Al, an element that raises the allotropic transformation temperature from 882 to 1100°C, favoring the formation of intermetallic compounds such as Ti6Al, Ti3Al and Ti2Al. They are alloys that can be easily processed by forging and molding and do not harden by thermal hardening treatments. Also, it is easy to weld them in argon atmosphere and have a special corrosion resistance. This type of alloys can have in their composition also other metals, such as Sn, Zr, Cu added in order to improve the mechanical properties, while maintaining the α structure. Titanium alloys with structure (α + β) are alloys from the systems: Ti-Al-Mn; Ti-Al-V; Ti-Al-Mo-V; Ti-Al-Mo-Cr etc., in practice those of the form Ti-Al-stabilizing β element are frequently encountered. The presence of aluminum in Ti-Al binary alloys contributes to raising the allotropic transformation temperature and increasing the solubility of β stabilizing elements, and the addition of elements such as Fe, Mn, Cr, Mo, V has the effect of eliminating brittleness, preventing the formation of α phase. The alloys from the Ti-Al-V ternary system have good mechanical and technological properties due to vanadium which, in a concentration of about 5%, increases plasticity, refractoriness and corrosion resistance [21].

The alloy with the widest use in dental prosthesis technology is Ti6Al4V, which has a particularly good corrosion resistance in specific corrosive environments and high mechanical properties. Due to the specific properties of titanium and its alloys, respectively the high melting temperature and the sudden increase of chemical activity with temperature, they are developed in electrical arch and induction furnaces, only in protective atmosphere with inert gases or vacuum. Also, special casting installations, materials and specific technologies are needed for the preparation of the mockup and the mold in dentistry. In general, the limitation of the use of titanium alloys in dentistry and orthodontics has been linked to the difficulties of processing them through casting, milling and electro-erosion, but advances today in processing technologies make it possible to use these alloys successfully [22].

Regarding the metal-ceramic technology, it is considered that the nature and characteristics of the metal structure decisively influence the adhesion after sintering of the overlying ceramic mass. In fact, this technology requires the use of specially developed alloys, with properties that vary depending on their chemical composition [23,24].

A previously published paper presented some experimental results regarding the study of the metal-ceramic bond, in restorations with metal component made of titanium and titanium alloys of the experimental Ti10Zr type [12]. The evaluation of the strength of the metal-ceramic bond was performed by mechanical tests that allowed the direct measurement of the strength of the bond at the metal-ceramic interface. The mechanical tests consist of application on the test samples of some forces of traction, compression, flexion, shear, until the detachment of the ceramic component, moment in which the final value of the applied force is noted. In all mechanical tests, after the detachment of the ceramic component, the aspect of the fracture at the interface is evaluated, which can be of the adhesive, cohesive or adhesive-cohesive type. Experimental research has shown superior values of M-C bond strength for Ti10Zr experimental alloy compared to those obtained in conventional Ti6Al4V alloy and pure commercial titanium (TiGrad4). This behavior was explained and related to the influence of the thickness of the oxide layer formed at the metal-ceramic interface. It was based on the experimental samples from the studied materials.

Research has continued and includes both the results obtained from the study of the behavior of new experimental titanium alloys, such as alloys from the TiZrNbTa system. The observations on the comparative study of the behavior of these alloys with those previously studied, respectively alloys from the Ti10Zr system, with the purpose of identifying and highlighting the influence of the chemical composition of the metal substructure on the alloy-ceramic adhesion processes and, finally, the strength (durability) of the MC bond.

In this research of the metal-ceramic connection, were mainly studied the conditions of ensuring a good adhesion, which would guarantee the optimal transfer of the stresses from the ceramic to the resistant metal substructure. The experimental results obtained when using titanium and titanium-based alloys (e.g., Tigrd4, Ti6Al4V, TiZrNbTa, Ti10Zr) as a metal substructure showed their behavior influenced by their physical-mechanical properties. Since the experimental tests were performed using the same technology and steps of the Ti-22 ceramic deposition procedure, the results obtained in evaluating the characteristics of the MC bond are comparable and provide information on the adhesion after sintering of the ceramic mass, decisively influenced by the nature and characteristics of the metallic structure. It is observed, for example, that for the studied TiZrNbTa alloys (Table 1), the contribution of zirconium and tantalum to increase the hardness is significant compared to the contribution of niobium, and this effect influences the characteristics of the oxide layer at the metal-ceramic interface. The study of the interface area and the examination of the surface of both components by scanning electron microscopy (SEM) analysis and EDS analysis identified differences in the characteristics of the oxide layer formed (thickness, uniformity, etc.), depending on the composition of the metal substructure. It turned out that the formation of metal oxides at the ceramic interface takes place under certain conditions and can be beneficial for the quality of the metal-ceramic bond. Although there is no established correlation between the degree of pre-oxidation and the strength of the bond between unalloyed titanium and sintered ceramic plating material, some researchers argued that intense pre-oxidation favors the strength of the bond [7]. Other authors [8,10] have shown that the strength of the MC bond is influenced by the formation of oxides at the interface, in the sense that they reduce the coefficient of thermal expansion of the ceramic mass, favor the action of residual stresses and contribute to crack formation or fractures that may occur at this level. However, what is confirmed experimentally is that the adhesion between metal and ceramic depends on the thickness of the oxide films formed and that metals or alloys with lower hardness, which generate thicker oxide films (e.g., TiGrd4) [12] have determined forces of adhesion to lower values, expressed by shear strength values [MPa]. The results of the experimental study demonstrated the superiority of some titanium alloys, namely those with higher hardness, in which case continuous and thinner oxide films were highlighted, and in which the highest values of shear strength were obtained. (Table 2, Ti1 and Ti3 Samples).

CONCLUSIONS

In the metal-ceramic technology, the nature and the characteristics of the metal structure decisively influences the adhesion of the overlying sintered ceramic mass. A good adhesion between metal and ceramics is mandatory for masticatory stress transfer from the plated ceramics to the metal substructure.

The characteristics of metals and alloys indicated for metal-ceramic technology are directly related to the formation of metal oxides at the ceramic interface area. This phenomenon happens under certain conditions and allows the alloy to obtain an atomic contact with the plated ceramic mass. The oxide layer formed has a good adhesion to the surface of the alloy and chemically reacts with the ceramics without changing its characteristics.

The formation of oxides on the surface of the alloy is beneficial to the metal-ceramic bond, but obtaining a thick layer of oxides can lead to decreased adhesion resistance (in which case no ionic networks are formed, but only polarized metal oxides with a low bonding strength/force).

Titanium and titanium alloys can be a good solution based on their exceptional properties, such as corrosion resistance and high mechanical strength, density, thermal conductivity and low coefficient of thermal expansion, X-ray translucency, odorless and tasteless nature.

The results presented in the paper illustrate the behavior of non-alloyed titanium, along with conventional alloys commonly used in dentistry and experimentally obtained titanium alloys, such as Ti10Zr and TiZrNbTa, towards their recommendation as substructures for titanium-specific ceramics in metal-ceramic restorations.

The results showed the superiority of titanium novel titanium alloys (TiZr, TiZrNbTa), having highest hardness values, highest values of shear strength, a continuous thin oxide films, and consequently, a better metal-ceramic adhesion. Comparatively, less ductile titanium alloys (TiZrNbTa/Ti3) are generating lower adhesion forces with values above 30MPa in some samples justifying less predictable clinical results.

Acknowledgments: all authors have read and agreed to the published version of the manuscript

Funding: this research received no external funding

Institutional Review Board Statement: not applicable

Informed Consent Statement: not applicable

Data Availability Statement: the data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy reasons

Conflicts of interest: the authors declare no conflict of interest

REFERENCES

1. Zhang Y, Kelly JR. Dental Ceramics for Restoration and Metal Veneering. *Dent Clin North Am.* 2017 Oct;61(4):797-819. doi: 10.1016/j.cden.2017.06.005. PMID: 28886769; PMCID: PMC5657342.
2. Naylor WP. Introduction to Metal-Ceramic Technology, Third Edition. Quintessence Publishing, 2018. p. 137-163.
3. Vasilescu E, Vasilescu VG, Pătrașcu I, Gălbinașu B. Researches regarding the metal-ceramic bonding in prosthetic restorations with titan and titan alloys metallic component. *Rom J Mat.* 2019;49(1):12-22. https://solacolu.chim.upb.ro/p12-22.pdf
4. Shen C, Rawls HR, Esquivel-Upshaw, J.F.Phillips' Science of Dental Materials, 13th Edition, Elsevier, 2021, p. 171-200.
5. Nicola C. Materiale dentare. Consideratii clinice si tehnologice. Cluj-Napoca: Casa Cărții de știință, 2009; p. 48-56, 177-180.
6. Sakaguchi RL, Powers JM. Craig´s Restorative dental materials, 13th ed. Philadelphia: Elsevier, 2012; p. 231-234.
7. Miculescu F, Ciocan LT, Miculescu M, Berbecaru A, Oliva J, Comăneanu RM. Failure Analysis of Dental Prosthesis. In: Antoniac I. (eds) Handbook of Bioceramics and Biocomposites. Springer, 2015, p. 1-30.
8. McLean J. The Science and Art of Dental Ceramics, vol. II: Bridge Design and Laboratory Procedures in Dental Ceramics. Denver: Quintessence Publ. Co., 1980.
9. Finnis MW. The theory of metal-ceramic interfaces. *J Phys Condensate Matter.* 1996;8(32):5811-36. doi: 10.1088/0953-8984/8/32/003
10. Sobczak N, Singh M, Asthana R. High-temperature wettability measurements in metal / ceramic systems - Some methodological Issues. *Curr Opin Solid State Mat Sci.* 2005;9:241-53. doi: 10.1016/j.cossms.2006.07.007
11. Giannarachis C, Marmandiu C, Vasilescu VG, Vasilescu E, Patrascu I. Studies on the importance of metal-ceramic bond in merging ceramic mass on metal component (review article). The Annals "Dunarea de Jos" University of Galati, 2013, XVII(2): 5-12.

12. Dorsch P. Thermal Compatibility of Materials for Porcelain Fused to Metal (PFM) Restorations, Ceramic Forum Int, Ber Dt Keram Ges, 1982, 59:1-5.
13. Fairhurst CW, Anusavice KJ, Hashinger DT, Ringle RD, Twiggs SW. Thermal expansion of dental alloys and porcelains. *J Biomed Mater Res.* 1980 Jul;14(4):435-46. doi: 10.1002/jbm.820140410. PMID: 6995461.
14. Patrascu I, Ciocan LT, Ghioghies C. Cercetări privind evoluarea legăturii metalo-ceramice la aliajele nenobile moderne. The Annals "Dunarea de Jos" University of Galati, V, 1999, 43-49.
15. Patrascu I, Patrascu D, Ciocan LT. Compatibility of Metal-Ceramics Bond. *Rom Bio Lett.* 2000;5(4):285-290.
16. Ghiban B. Metallic Biomaterials, Bucuresti: Ed. Printech, 1999; p. 124-40.
17. Lütjering G, Williams JC. Titanium. Berlin: Ed. Springer, 2003; p. 203-58.
18. Leyens C, Peters M. Titanium and Titanium Alloys - Fundamentals and Applications. Weinheim: WILEY-VCH, 2006; p. 4-16.
19. Khalid AW, Ibrahim AH. Bond strength of porcelain to titanium and titanium alloy. A comparative study with conventional metal-ceramic systems. *Egyptian Dent J.* 2005;51:1925-33.
20. Lütjering G, Williams JC. Titanium – Engineering Materials and Processes. Heidelberg: Springer, 2003; p 21-26.
21. Oshida Y. Bioscience and Bioengineering of Titanium Materials, 1st ed. Philadelphia: Elsevier, 2006, p. 79-103.
22. Oshida Y. Bioscience and Bioengineering of Titanium Materials, 2nd ed. Philadelphia: Elsevier, 2013, p. 255-281.
23. Albrecht J, Lütjering G. Microstructure and Mechanical Properties of Titanium Alloys, Titanium '99 Science and Technology, Vol I, St. Petersburg, 2000, p. 363-374.
24. Welsch G, Boyer R, Collings EW. Materials properties handbook - Titanium alloys, ASM International, 1993, p. 3-170, 483-609.
25. Rack HJ, Qazi JI. Titanium alloys for biomedical applications., Materials Science and Engineering C 26. Philadelphia: Elsevier, 2006, p. 1269-1277.
26. Tudoran S, Voiculescu I, Geanta V, Vizureanu P, Rosca I, Patrascu I et al. Effect of chemical composition on the microstructural characteristics of Ti-Nb-Ta-Zr alloys. In: IOP Conference Series: Materials Science and Engineering. IOP Publishing, 2019. S. 012022, p. 1-5.