CERCETĂRI PRIVIND LEGĂTURA METALO - CERAMICĂ ÎN RESTAURĂRI PROTETICE CU COMPONENTĂ METALICĂ DIN TITAN ȘI ALIAJE DE TITAN
RESEARCHES REGARDING THE METALO - CERAMIC BONDING IN PROSTHETIC RESTORATIONS WITH TITAN AND TITAN ALLOYS METALLIC COMPONENT

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The quality of metal - ceramic restorations is closely related to the quality of the metal - ceramic bond, where the rigidity of the metallic structure that prevents the occurrence of the flexural forces in the plating ceramic and in the interface area is an essential condition. Typically cast, the metallic component is made up of various metals and noble alloys or non-noble alloys.

Titanium and titanium alloys are at present an ideal solution due to their exceptional properties such as: corrosion resistance and high mechanical strength, density, thermal conductivity and reduced thermal expansion coefficient.

The research carried out aimed at studying the behavior of a new titanium alloy in metal - ceramic technology (Ti10Zr), a preliminary study on metal - ceramic bonding compared to conventional alloys (Ti6Al4V) and pure titanium (TiCp). The evaluation of the Ti10Zr-ceramic bond T22 Noritake was performed by mechanical tests, namely the shear resistance measurement and the determination of the final value of the force at which the ceramic component of the metal substructure is detached.

Mechanical tests were complemented by indirect, non - destructive methods of assessing the strength of metal - ceramic bonding.

The experimental results obtained confirm some results from the literature on the behavior of non - alloying alloys as substructures in metal - ceramic restorations, and on the other hand they can constitute novelty elements regarding the behavior of a new titanium alloy (Ti10Zr) as a component metallic in metal - ceramic technology.

Calitatea restaurărilor metalo – ceramice este strâns legată de calitatea legăturii metal – ceramică, în care rigiditatea structurii metalice care împiedică apariţia forţelor de flexiune în ceramica de placare şi în zona de interfaţă, reprezintă o condiție esențială. De obicei turnată, componenta metalică este constituită din diferite metale și aliaje nobile precum aur , sau aliaje nenobile.

Titanul și aliajele de titan reprezintă la ora actuală o soluție ideală care se datorează proprietatilor de exceptie ale acestora cum ar fi: rezistență la coroziune și rezistență mecanică ridicată, densitate, conductibilitate termică și coeficient de dilatare termică reduse, s.a.

Cercetările efectuate au avut ca obiectiv studiul comportării unui nou aliaj de titan în tehnologia metalo - ceramică (Ti10Zr), studiu preliminar vizând cercetarea legăturii metalo – ceramică, comparativ cu aliajele convenționale (Ti6Al4V) și titan pur (TiCp). Evaluarea rezistenţei legăturii Ti10Zr - Ceramică T22 Noritake s-a efectuat prin teste mecanice, respectiv măsurarea rezistenței la forfecare și determinarea valorii finale a forței la care se produce desprinderea componentei ceramice de pe substructura metalică. Testele mecanice au fost completate de metode indirecte, nedistructive de evaluare a rezistenţei legăturii metalo – ceramice. Rezultatele experimentale obținute confirmă unele rezultate din literatura de specialitate cu privire la comportarea aliajelor nenobile ca și substructuri în restaurările metalo – ceramice, iar pe de altă parte pot constitui elemente de noutate cu privire la comportarea unui nou aliaj de titan (Ti10Zr) ca și componentă metalică în tehnologia metalo – ceramică.

Keywords: *non - noble alloys, Ti10Zr bioalloy, metal - ceramic connection, mechanical tests metal – ceramic (M – C) prosthetic restoration, oxide, layer thickness, SEM analysis.*

1. Introduction

After the competition between the metal-composite technique and the metal-ceramic technique, since the 1980s, metal-ceramic technology has enjoyed unprecedented use by combining the natural effect of a fragile material (dental ceramics) with mechanical strength and marginal adaptation of the metal component.

However, the success of metal-ceramic prosthesis depends essentially on the correct indication of these restorations, the compatibility of the two components (metal and ceramics) and, implicitly, the firmness of the bond.

The adhesion between the metallic component and the physionomic component is determined by the nature of the bond based on mechanical, physical and chemical mechanisms, the last from these being based on the formation of the ionic bond between the oxides on the surface of the alloy and the ceramic mass oxides [1 - 4].

In order to understand the nature of this link, all the application and sintering stages of ceramics on the alloy must be known, in which there is a complex multi-component adhesion system present (Fig.1), but also the phenomena occurring at the level of the interface area [5-9].

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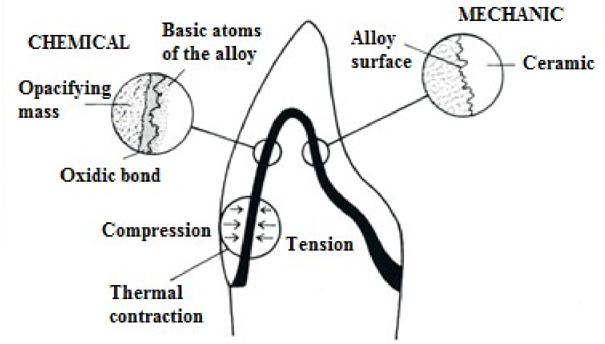


Fig.1 - The metal-ceramic bonding components (John W. McLean) / *Componentele legăturii metalo – ceramice.*

It is widely accepted in the literature, the theory that the adhesion of ceramics to the metallic component is the result of mechanical retention, Van der Waals forces and chemical bonds [5, 7, 10 - 12].

The mechanical adhesion of ceramic mass to metal increases the value of the metal-ceramic fusion (Phillips, McLean) and is influenced by the nature of the metal surface, surface contamination and rugosity, and measurements of the ceramic-metal contact angle indicate the role of the forces Van der Waals in the bonding of ceramics to metal. O'Brien and Ryge have shown that theoretically, the Van der Waals forces provide a sufficiently high resistance of this bond and that the fusion resistance is increased by the presence of the oxide layer.

The surface layer of ceramic mass saturated with metallic oxides, layer obtained during burning, is in thermodynamic equilibrium with the metal oxides on the surface of the metal. Through ionic exchange results in a continuous electronic structure from metal to ceramics, resulting a strong chemical bond (ionic, metallic and covalent) characterized on the one hand by the composition of the alloy and on the other by the humidity of the ceramic mass [13,14].

The basic components of dental ceramics are feldspar, quartz and kaolin, identical to porcelain, but in different proportions [1, p.65, 4]. In addition to the three basic components, dental ceramics contain pigments that will provide the color of ceramic mass and organic binders such as starch or glucose to facilitate prosthetic reconstruction modeling.

Over time, ceramic systems as a working technology have developed and evolved rapidly, bringing important changes in dental ceramic composition.

From ceramic with low sintering temperature, which allowed metal-ceramic restorations on noble metals (1958, Weinstein) or non-noble alloys (1970), it was switched to magnesium ceramic (1984, O'Brien) and then to ceramics with 85% alumina (1985, M.Sadoun). In 1987, Morman and Brandestini launched the CAD / CAM technique to perform prosthetic restorations in a computerized system, and in 1990 it is promoted the IPS.

A good bond between metal and ceramics mainly involves the transfer of stress acting on the ceramic to the metallic substructure. which has a mechanical resistance.

The basic characteristics of alloys used in metal-ceramic technology are as follows: the melting range greater than the ceramic sintering range, high mechanical strength at high temperatures to avoid deformation during ceramic firing, expansion coefficient higher or at least equal to that of the ceramic mass [2].

The large differences between the two thermal expansion coefficients can lead to the cracking of the ceramic and its detachment from the metal, the effect of the occurrence of compressive circumferential forces, along with the radial pulling forces. The latter generates tensions in the ceramic mass and implicitly generates circumferential fractures of the plating ceramic.

In the case of metal - ceramic prosthetics, however, very low values are somehow unfavorable, with ceramic with a coefficient of thermal expansion of 12 - 15x 10^{-6} / ^{0}C being preferred.

Lower values than these are found in the modern ceramic masses designed for titanium metal - ceramic mixed prosthetics , alloys which have low thermal expansion coefficients (9.6x10^{-6} / ^{0}C) [4,12].

Non-noble alloys commonly used have a thermal conductivity coefficient ten times lower than noble alloys and a lower specific weight, have higher values of mechanical strength, hardness and modulus of elasticity.

However, the non-noble alloys which have been imposed in metal-ceramic restoration technology due to practical advantages compared to the noble alloys are characterized by superior values of hardness, residual flow and modulus of elasticity, as elongation at breakage is approximately equal to that of noble alloys [4].

Table 1 presents the properties of base alloys used in metal-ceramic restorations.

The nickel and cobalt alloys contain large amounts of chromium to prevent the phenomena of clogging and corrosion. Aluminum and titanium form compounds like Ni_2Al or Ti_2Al_3 type, contributing to increased mechanical strength. Beryllium present in nickel alloys reduces melting temperature, but it has an essential contribution to making a strong bond between metal and ceramics.

Ceramic prosthetics made on titanium frame have appeared quite recently in dentistry.

Titanium and titanium alloys are currently an ideal solution of non-noble alloys due to their exceptional properties such as: corrosion

Table 1.
Properties of base alloys used in metal-ceramic restorations/*Proprietăți ale aliajelor frecvent utilizate în restaurările metalo ceramice* [4, p.657]

Alloy Type	Tensile Breaking Strength (MPa)	Yield Limit 0,2% (MPa)	Elasticity Module (MPa×10^3)	Elongation (%)	Hardness (DPH, kg/mm^2)	Density (g/cm^3)	Casting Temperature (°C)
Nickel	400-1000	255-730	150-210	8-20	210-380	7.5-7.7	1300-1450
Cobalt	520-820	460-640	145-220	6-15	330-465	7.5-7.6	1350-1450
Titanium	242-896	173-827	103-114	10-20	125-353	4.4-4.5	1760-1860

resistance and high mechanical strength, density, thermal conductivity and reduced thermal expansion coefficient, roentgen translucency, odorless and insipid character, low cost.

In general, limiting the use of titanium alloys in specialty maneuvers, such as prosthetics, has been linked to their processing difficulties [6].

By heating the metal component at relatively high temperatures, oxidation takes place at the surface of the alloy, which is beneficial to the metal-ceramic bonding through the formation of ionic networks, but obtaining a thick layer of oxides, in which case only polarized metal oxides are formed, leads to a decrease in adhesion strength (low binding force).

The most fragile area of this mixed metal - ceramic system is the metal - ceramic adhesion zone (interface).

Since all these inconveniences can be diminished by using CAD-CAM systems for making the metallic titanium alloy component, the present paper aims at studying the behavior of a new titanium alloy in metal ceramic technology (Ti10Zr) [15-21], a preliminary study to investigate the metal - ceramic bonding having a Ti10Zr metallic component compared to conventional alloys (Ti6Al4V) and pure titanium (TiCp), by assessing the strength of the metal - ceramic bond and preliminary investigations of the interface area.

The exact measurement of the metal-ceramic bond strength poses particular problems because the complexity of this link does not allow the realization of a single type of test experiment.

The evaluation of the mechanical tests that allow direct appreciation of the bond strength at the metal-ceramic interface.

These consist of the application on the test samples of traction, compression, flexion, shear forces until the ceramic component is detached, at which point the final value of the applied force is noted.

Of the commonly used tests, we mention: Voss's method (a metal-ceramic crown, inclined at 45 ° is required for compression), the bending test after Schwickerath (a metal plate on which ceramic is sintered is required at bending until the metal-ceramic bond cracks), the shear test after Schmitz and Schulmeyer (ceramic is burned on a metal cube, after which the interface is applied to the shear test until the link breaks) [4,6].

After the detachment of the ceramic component, the fracture characteristics are evaluated at the interface which can be of the adhesive type, cohesive type or adhesive-cohesive type.

The mechanical tests for the appreciation of the metal-ceramic bond strength are indicative tests, and today are preferred non-destructive methods of evaluation of the interface.

The non-invasive method of detecting defects at the interface allows an indirect assessment of the strength and quality of the metal-ceramic bonding and can prevent further flaws from occurring even since the laboratory phase, such as the separation of the ceramic veneer [1].

2.Materials, Method and Experimental Conditions

The research was conducted on samples of Ti grade4 plate or alloyed titanium, titanium alloy Ti6Al4V type chemically regulated by the standard specifications for titanium misaligned - Grade4 Ti (ASTM F67) and Ti6Al4V-Grade5 (ASTM F136) for surgical implant applications [22 - 26] and samples from the Ti10Zr experimental alloy. Characterization of the alloy chemically Ti10Zr is based on quantitative and qualitative chemical analysis of samples taken from the preform molding (cylinder with dimensions 70x18mm) obtained in special development conditions (cold crucible melting furnace in levitation). The alloy has 90% Ti and 10% Zr and no harmful elements [15,19 - 21].The purity of the raw material influence the content of impurities in the final alloy, including the gas (nitrogen, hydrogen), which are strictly limited.

Composition of raw materials:

- titanium metal, with chemical composition: 0.20% Fe 0.03% N_2, 0.18% O_2, max. 0.015% H_2, 0.08% C, Ti residue (according to ASTM F 67);
- 99,6% metal zirconium with the following chemical composition: 0,01% Fe; 0.035% Si; 0.03% Mo; 0.05% W; 0.01% Ti; 0.02% Ni; 0.02% O_2; 0.01% C; 0.0015% H_2; 0.01% N_2; 0.2% Nb; rest Zr.

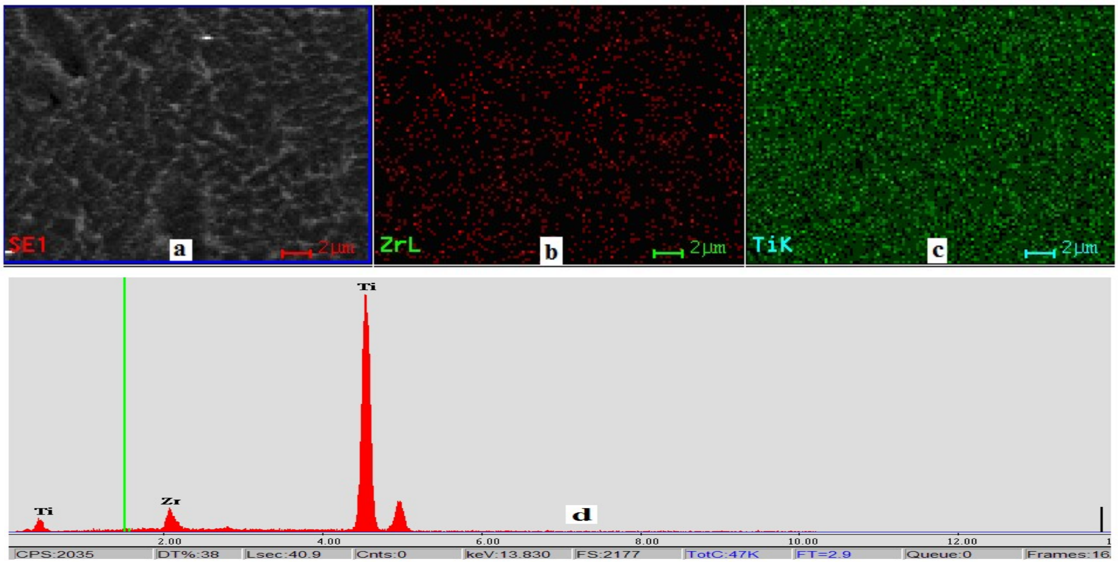


Fig.2 - The microscopic SEM aspect **(a),** the map of the chemical elements (**b** and **c**) and the Ti10Zr bioalloy specific spectra (d*)]/Aspecte de microscopie SEM (a),harta elementelor chimice (b și c) și spectrul de difracție specific bioaliajului (d) [15,19 - 21).*

Figure 2 presents the map of chemical elements and EDS spectra specific to the chemical elements present in Ti10Zr experimental bioalloy.

In the experiments we used ceramic with a composition specified by Noritake Japan manufacturer, specific for titanium and titanium alloys: type A30, A3B Noritake Super Porcelain Ti - 22 (ref 105 - 0121 EU), E3 Noritake Super Porcelain Ti - 22 (Ref. 105 - 0701 EU), BP Noritake Super Porcelain Ti - 22, Noritake Super Porcelain Ti - 22 BP Liquid (Ref 126 - 0161 EU), Noritake Super Porcelain Ti - 22 Forming Liquid (Ref 126 - 0171 EU), Noritake Super Porcelain Ti - 22 Opaque Liquid (Ref. 126 – 0181 EU). Ti-22 is designed to perfectly fit the thermal expansion of pure titanium. The use of Ti-22 together with titanium leads to very high adhesion forces (ISO9693-Part1-2012 / Dentistry Compatibility Testing / Metal-ceramic Systems), reducing the possibility of fracture in the oral cavity. Ceramic T22 has a good acid resistance, so good chemical stability in the intrathoral environment, and has a high coating power, so that the titanium-black black oxidized layer can be completely masked. The titanium metal structures to be applied to the ceramic must have a thickness of at least 0.5 mm over the entire surface to be coated to ensure marginal integrity and stability at the time of high temperature combustion inside the ceramic furnace. The oxide layer formed during the Ti-22 ceramic burning ensures precision and should not be removed in areas of minimum ceramic strength. Burning ceramics is performed at temperatures of up to 885^0C, which ensures stability of the titanium characteristics, guaranteeing durable substructures for the best clinical results. Generally, ceramic fracture resistance decreases when the thickness of the applied layer increases.

The sampling was carried out in accordance with titanium deposition technology in MC restorations, the Ti-22 ceramic work procedure including the following steps:

1. Sanding with aluminum oxide, particles of 50-70 microns, ultrasonic cleaning in acetone for 10 minutes, heating the metal from 500^0C to 800^0C with a heating rate of 50^0C / minute and keeping under vacuum for 3 minutes at the pressure of 99 kPa.

2. Application Bonding Porcelain (BP) in two stages; the second application in layer thickness 0.2 mm, followed by condensation.

3. Bonding Porcelain Burning (BP) followed by aluminum oxide sandblasting at 3Mpa pressure and acetone cleaning in the ultrasonic bath for 5 minutes.

4. Opaque application (liquid mix - powder, thickness 0.15 mm, oven drying 5-7 minutes and burning from 500^0C to 780^0C under 96kPa vacuum).

5. Dentine and enamel application (liquid-powder mix, thickness 0.8 mm minimum).

6. Burning the ceramic layers from 500^0C to 760^0C under vacuum, according to the burning programs.

Research on the phenomenon of adhesion of ceramic masses to titanium and titanium alloys was carried out by experimental tests which measured the shear strength values of specially made specimens embedded in devices designed and adapted to standardized mechanical test equipment traction or compression test). A number of 11 samples were made by metal-ceramic technology using titanium-specific Norytake ceramics (Table 2).

Table 2

Experimental metal-ceramic samples/ *Probe metal – ceramică experimentale*

Metal-Ceramic Samples	**No. Samples**
Ti grade 4+ Norytake	1
	2
	3
Ti6Al4V Alloy + Norytake	1
	2
	3
Ti10Zr Alloy* + Norytake	1

The appearance of the samples (the resulting shape) after the deposition of the ceramic on the metal substructure is shown in Figure 3.

Assuring the stability of the samples in the test equipment was done after their inclusion in acrylate and their attachment to a specially constructed device whose adaptive gripping mechanism allowed sample testing (Fig. 4).

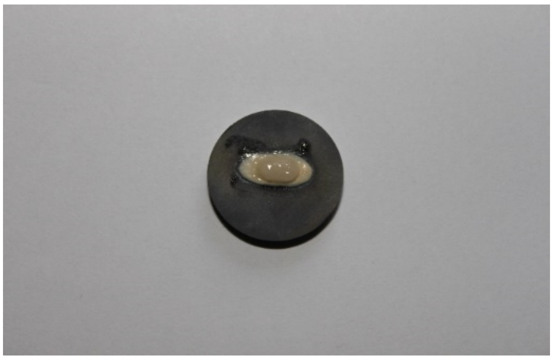


Fig.3.- Ti10Zr Alloy + Norytake/ *Aliaj Ti10Zr +ceramica Norytake*

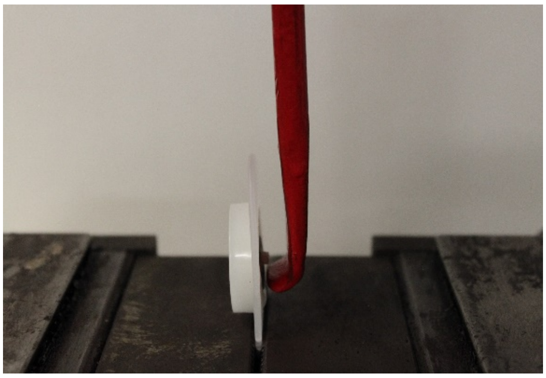


Fig.4 - Embedding grip in shape and in the test machine assembly */ Inglobarea probei în formă și în dispozitivul de testare al mașinii de încercare*

The equipment used for sample testing is the universal machine for static or dynamic for static or dynamic traction / compression testing, type UFP400 Germany. Tests were performed to determine shear resistance [MPa] in static regime, also recording the forces [N] at which the resistance values were determined. Each test is accompanied by the diagram represented with the test equipment processing software.

3. Experimental Results and Discussions

It is already known that in metal-ceramic technology the nature and characteristics of the metal structure decisively influence the adhesion after sintering of the overlying ceramic mass. Current research on the behavior of various metals and alloys used in metal-ceramic technology is concerned with the identification of those materials that diminish the negative effects and the factors favoring a poor resistance of the metal-ceramic bond.

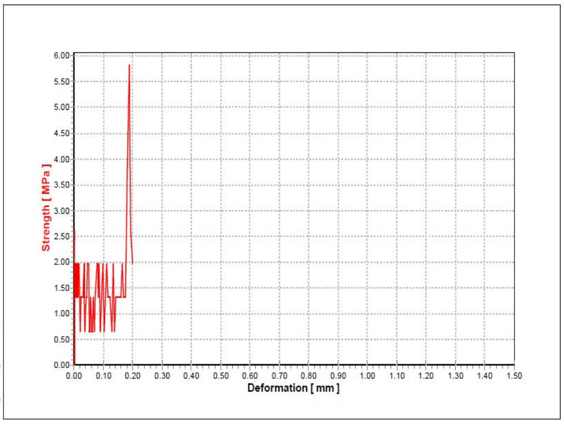
To test the link between the two components, researchers are currently using the following tests: measuring metal deformation after sintering the ceramic, measuring the strength of the bond between the two components, measuring the adhesion of ceramics, or measuring residual stress. These tests measure resistance to stresses applied by pressure, shear, bending, and so on.

The experimental researches focused on the analysis of Ti10Zr experimental bioalloy behavior compared to titanium and titanium alloys commonly used in dentistry (Ti6Al4V) as metal substructures in metal - ceramic restorations, using for the evaluation of the metal - ceramic bond the shear strength analysis and strength value at which the separation of the ceramic from the metal substructure is produced. The results obtained from testing the experimental samples are presented in the Table 3 and in the diagrams recorded during the test (Fig.5).

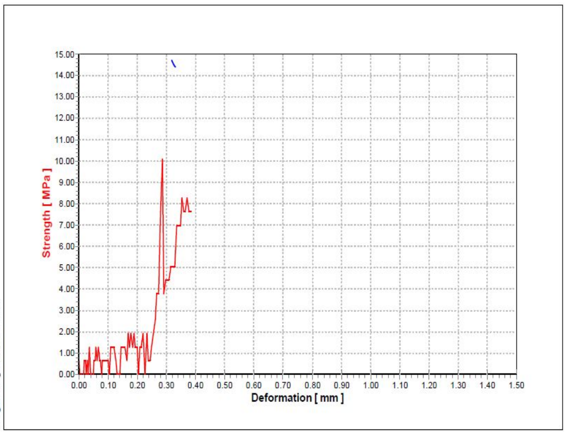
Table 3

Results obtained from experimental samples for shear resistance [MPa]/ *Rezultate privind rezistența la forfecare a probelor experimentale*

Alloys Substructure	No. Samples	Sample Dimensions [mm]	F [N]	Shear Resistance [MPa]
Ti Grade4	1	3.12x1.76	31.68	5.77
	2		32.51	5.92
	3		35.80	6.52
Ti6Al4V Alloy	1	3.14x1.79	57.44	10.22
	2		63.18	11.24
	3		82.68	14.71
Ti10Zr Alloy	1	3.11x1.71	92.43	17.38
	2		101.1	19.01
	3		104.02	19.56



a.



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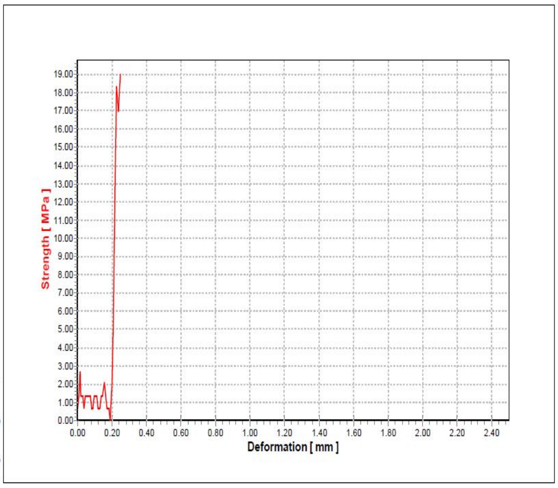

c.

Fig.5 - Diagram of shear resistance determination for some experimental samples with metallic substructure of: **a).** Ti grade 4, **b).** Ti6Al4V, **c).** Ti10Zr / *Diagrama determinarii rezistenței la forfecare pentru probe cu substructure metalică din:* ***a).****Ti grad4,* ***b).*** *Ti6Al4V,* ***c).*** *Ti10Zr.*

Although these are indicative values, as generally obtained in the mechanical tests for the evaluation of the metal-ceramic bond strength, the obtained results are considered useful information, which demonstrates, first of all, the superiority of the titanium alloys (Fig.5b and Fig.5c) to pure titanium (Fig. 5a), and the differences between the Ti6Al4V alloy (Fig.5b) and Ti10Zr alloy (Fig. 5c), although relatively small, require further experiments on a larger number of samples and deepening research to explain their behavior in relation to their composition and physico-mechanical properties. This is all the more necessary as the results of the electronic microscopy investigations of the interface have revealed a different behavior from the point of view well as of the compositional nature in the investigated areas of the interface.

In the literature little information is known about testing the resistance of the metal - ceramic bond having as its metal component the titanium and its alloys, there is no valid universal test and the tests elaborated so far do not offer a way of measuring the absolute value of the adhesion, but only a relative value of the adhesion resistance of the metal and ceramic couple under a load. Shell and Nielsen [26] have imagined a test in which a 1.63 mm diameter wire was inserted into a porcelain block, 2.5 mm deep, and then measuring the tension required to separate it.

The test invented by Lavine and Custer [27] uses a flat metal foil with sintered ceramics on the expandable face, which is then bent. Knapp and Ryge [28] propose tensioning a porcelain-coated alloy bar and measuring the energy needed to initiate and propagate the fracture. Sced and McLean [29] designed a testing machine which used a conical piece to put the link in the direction of the maximum shear stress. There is the view that, for a suitable bond, the breaking stress should be close to the tensile strength of the opaque porcelain, Nelly assigning it a value of 25N / mm^2 for a certain ceramic mass [30].

The values of the shear resistance obtained in experiments are indicative values, but the practical importance of these results is that they provide information on the behavior of the new bio-alloy (Ti10Zr) as a metallic structure in metal-ceramic restorations, and on the other hand allow the comparative analysis of adhesion force for titanium and titanium alloys studied, using Noritake ceramics.

The indicative results obtained in the mechanical tests for assessing the strength of the metal-ceramic bond are always complemented by indirect methods, which allow the study of the interface.

The metal - ceramic interface was studied, the Noritake ceramic detachment on the TiGrad4, Ti6Al4V and Ti10Zr substructures and the compositional nature evidenced by scanning electron microscopy analysis and EDS analysis with the MagnaRay on Common SEMs microscope - JEOL JSM-6490LV.

Microstructures indicate a different behavior of the materials in the interface area (Fig.6, Fig.7).

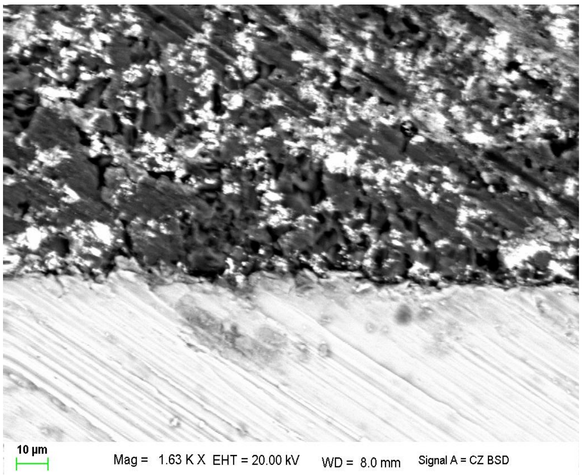

Fig.6 - Microscopic aspects of the metal – ceramic interfaceareas (Ti grad 4 substructure) / *Aspecte microscopice ale zonelor de interfață (substructură din Tigrad4).*

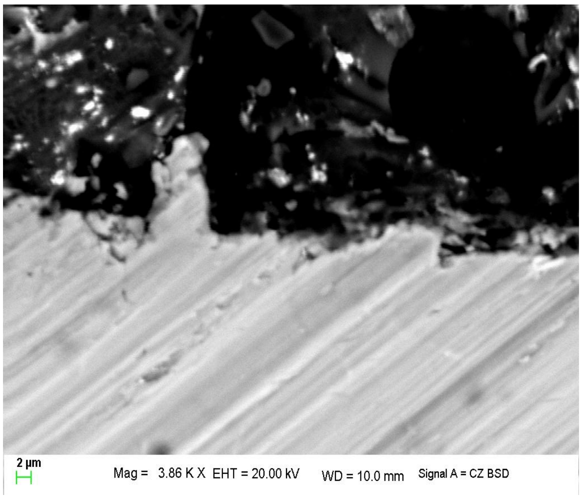

Fig.7 - Microscopic aspects of the metal - ceramic interface areas (Ti10Zr substructure) / / *Aspecte microscopice ale zonelor de interfață (substructură din Ti10Zr).*

Investigating the appearance of the surface when detaching ceramics from the metal substructure indicates an aspect of tenacious rupture in the case of titanium alloys (Fig.9) relative to pure titanium (Fig.8). The interface investigations continued through analysis that highlighted the link between the chemical composition of the interface area and the material specific to the metal substructure. EDS energy spectroscopic analysis showed the presence of oxides in the metal-ceramic interface area of the studied samples (exemplified with the Noritake Ti10Zr ceramic substructure). But the formed oxide layer and its characteristics, especially the thickness thereof, are depending on the metallic substructure of the samples.

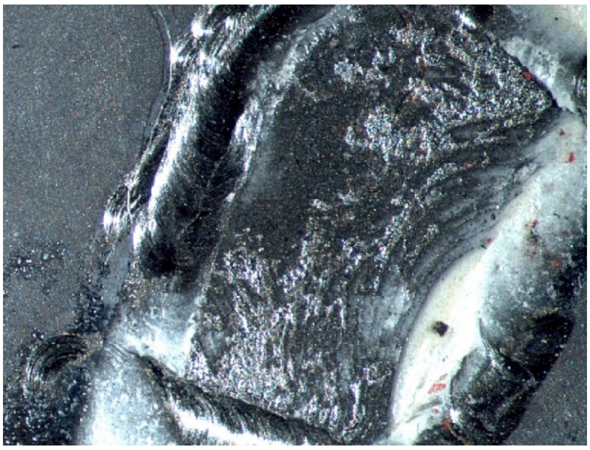

Fig.8 - Microscopic aspects of the metal - ceramic interface (Appearance of ductile rupture) at the detachment of ceramic on the metal substructure (Ti - grade4) / /*Aspecte microscopice ale zonelor de interfață metal – ceramic (Aspect de rupere ductilă la detașarea ceramicii de pe substructura metalică din Ti- grad4).*

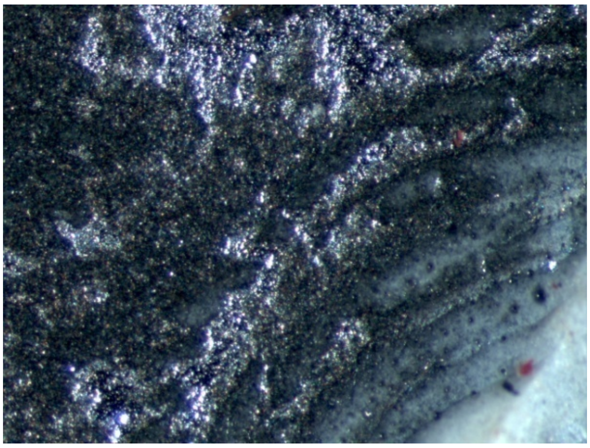

Fig.9. - Microscopic aspects of the metal - ceramic interface (breakage type/ Appearance of ductile rupture at the detachment of the ceramic on the metal substructure (Ti10Zr) / *Aspecte microscopice ale zonelor de interfață metal – ceramic (tipul de rupere/ Aspect de rupere ductilă la detașarea ceramicii de pe substructura metalică din Ti10Zr).*

It can be observed that the point analysis in the base metal mass of the field 2/ sample 3 indicates the composition of the experimental alloy (Ti10Zr metal alloy substructure, points 1, 2, 3, 4) (Fig.10).

In the case of the field 4 of the sample3, the composition analysis indicates the presence of oxygen in the interface area (Fig.11) as well as the line analysis (Fig.12).

Measurement of the thickness of the layer reveals, for some samples (especially those with a pure titanium metal substructure), non-adherent, discontinuous and high thickness (over 5 micrometers, Fig.13). Other samples, however, have continuous, adherent and uniform layers with a thickness of not more than 3.9, such as those obtained with the alloy substructure (Fig.14).

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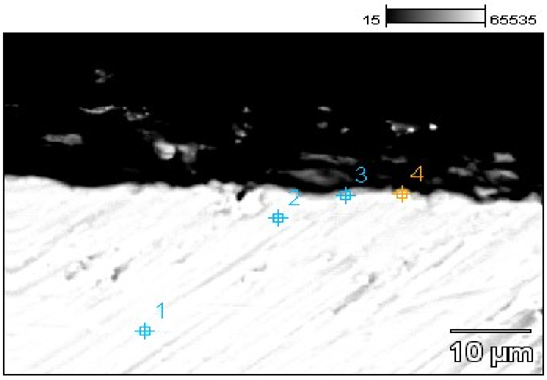
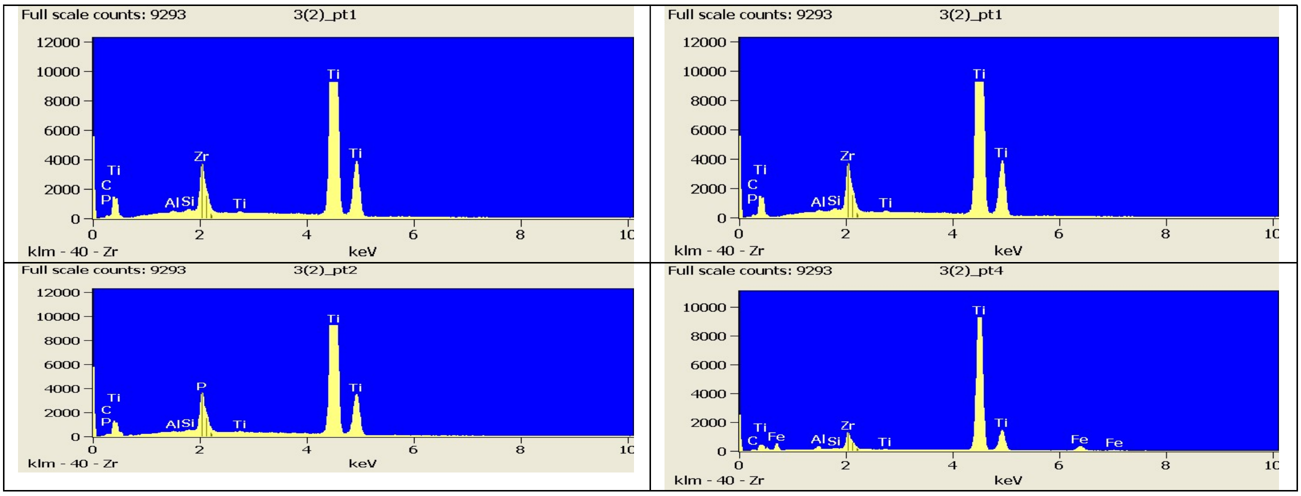
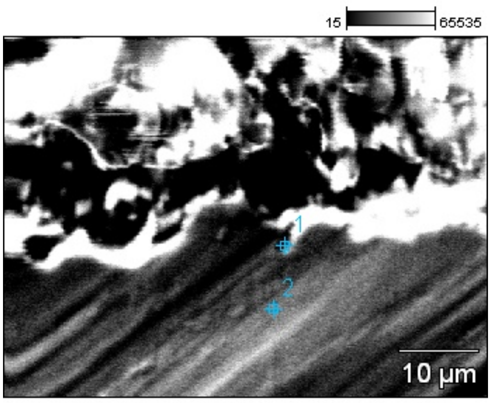


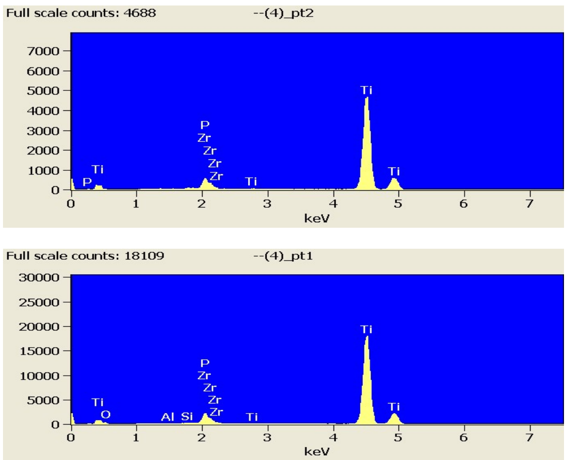


	C-K	Al-K	Si-K	P-K	Ti-K	Fe-K	Zr-L
3(2)_pt1	0.10	0.11	0.02	0.11	90.07		9.60
3(2)_pt2	0.35	0.09	0.21	4.03	95.33		
3(2)_pt3	1.23	0.56		3.56	88.68	5.96	
3(2)_pt4	0.99	0.69	0.05	0.00	84.22	5.32	8.73

Fig.10 - EDS Analysis of the Ti10Zr substructure - Norytake Ceramic - Interface Area (Sample no.3 /the field 2) */ Analiza EDS a zonei de interfață ceramică Noritake – substructură din Ti10Zr (proba3/camp de investigație2).*

--(4)





--(4)_pt1	0.43	0.11	0.36	3.88	95.22		
--(4)_pt2				0.00	90.13	9.87	

Fig. 11 – EDS Analysis of the Ti10Zr – Norytake interface area (Sample no. 3/ the field 4) / *Analiza EDS a zonei de interfață ceramică Noritake – substructură din Ti10Zr (proba3/camp de investigație4).*

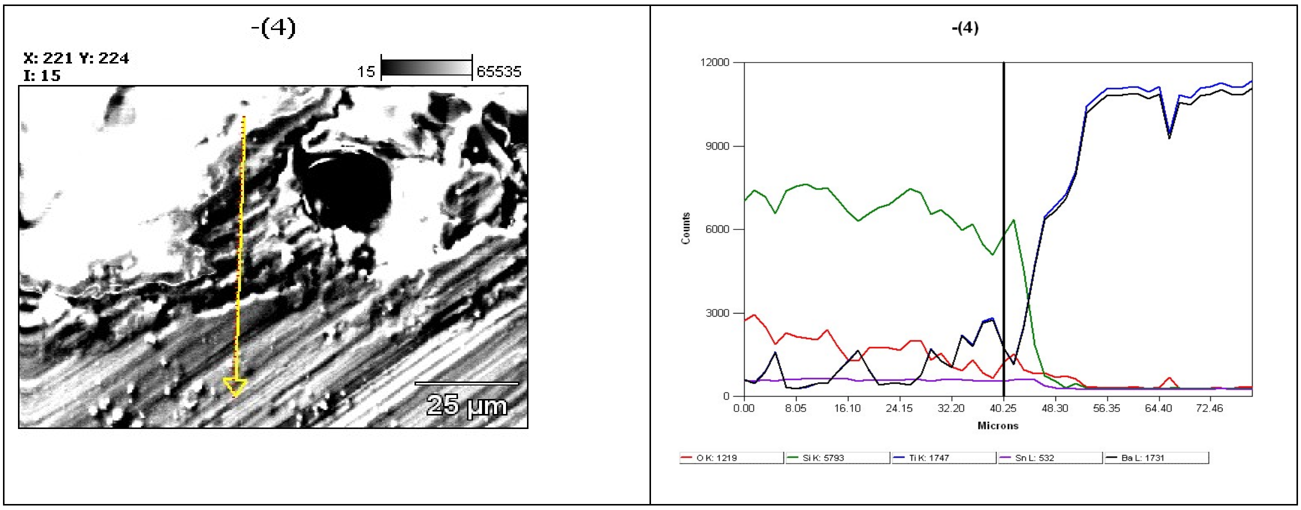


Fig. 12 – EDS/ the Line Scanning Analysis of the Ti10Zr substructure – Norytake Ceramic – Interface Area (Sample no. 3 / the field 4 the variations of oxygen content from ceramic to metallic substructure through the interface) / Analiză EDS de linie a zonei de interfață ceramică Noritake – substructură Ti10Zr (proba3/ câmp de investigație4, variația conținutului de oxygen de la ceramică la substructure metalică prin interfață).

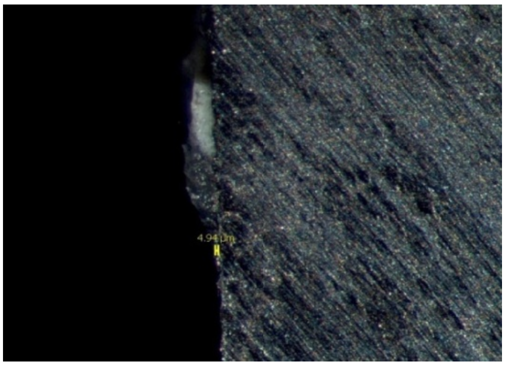


Fig. 13 - Oxide layer 4.94 microns (μm) thick on the Ti-Grade4 surface (LEICA stereomicroscope, X50 magnification) / Strat de oxid de 4,94 micrometri pe suprafața substructurii Tigrad4 (stereomicroscop LEICA, mărirea 50X).

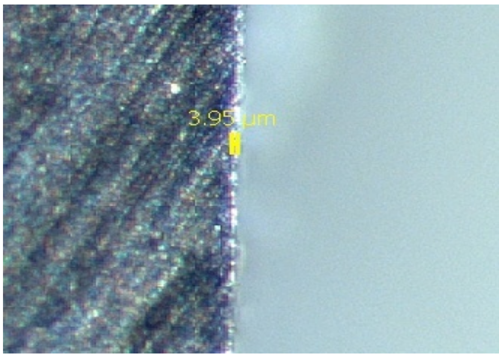


Fig.14 - Oxide layer 3.95 microns (μm) thick on the Ti10Zr surface (LEICA stereomicroscope, X50 magnification) / Strat de oxid de 3,95 micrometri pe suprafața substructurii Ti10Zr (stereomicroscop LEICA, mărirea 50X).

The experimental data obtained were the metal-ceramic bond, but obtaining a thick oxide layer can lead to a reduction in the adhesion reported to those in the literature, particularly those reported by McLean and Sced [31]. They have shown that the bond strength established between ceramic and non-alloy alloys is negatively influenced by oxides formation and showed that when these oxides are formed at the interface, they reduce the coefficient of thermal expansion of the ceramic mass, favoring the action of residual stresses and implicitly of fractures that may occur at this level. The fracture at the interface where the oxides are detached from the surface of the alloy and remains attached to the plated ceramic mass occurs in the case of non-alloying alloys when large oxides are formed. Although there is no established correlation between the pre-oxidation degree and the bond strength between non-alloy and superheated sintered ceramic masses, there are some authors (McLean and Sced) who claim that intense pre-oxidation favors increased resistance to this bond.

The characteristics of the metals and alloys indicated in the metal - ceramic technology are related to the fact that the formation of these metal oxides in the ceramic interface area must occur under certain conditions: oxides must be formed only in a very thin layer but allow the alloy to in atomic contact with the plated ceramic mass, the oxide layer has good adhesion to the surface of the alloy and reacts with the ceramic without altering the basic characteristics such as thermal expansion, strength, color and degree of translucency.

The thickness of the oxide layer is an important parameter, which controls the quality of the metal - ceramic bond strength. The formation of oxides at the surface of the alloy is beneficial to the practical importance of these results is that strength (in which case no ionic networks are formed, but only polarized metal oxides with a low binding force).

If we consider that the adhesion and friction between metal and ceramics depend on the thickness of the formed oxide films, and the soft metals generate by transferring continuous thick films, it results from this point of view that the titanium alloys are superior.

The experimental results obtained in the case of pure commercial titanium (Tigrade4), which demonstrate poor behavior in the evaluation of bond strength in relation to the other materials studied, are explained by the formation of a continuously non-continuous binder layer with a high thickness.

There are results which, on the one hand, confirm some results from the literature on the behavior of non - alloying alloys as substructures in metal - ceramic restorations, and on the other hand they can constitute novelty elements regarding the behavior of a new bioaliay (Ti10Zr), characterized so far as a high biocompatibility matrix for oral implants) as a metal component in metal - ceramic technology.

4. Conclusions

Current research on the behavior of various metals and alloys used in metal-ceramic technology refers to the identification of those materials which diminish the negative effects and the favorable factors which conduct to a weak resistance of the metal-ceramic bond.

Although the non-noble alloys have been imposed in metal-ceramic restoration technology due to advantages of great practical importance compared to noble alloys, ceramic works on titanium subframe have appeared quite recently in dentistry. Titanium and titanium alloys are currently an ideal solution of the non-noble category, due to their exceptional properties such as: corrosion resistance and high mechanical strength, density, thermal conductivity and reduced thermal expansion coefficient, roentgen translucency, odorless and insipid character, low cost.

The present study aims the behavior of a new titanium alloy (Ti10Zr) in metal ceramic technology by assessing the strength of metal - ceramic bonding and preliminary investigations on the interface area.

In order to evaluate the strength of the metal-ceramic bond, the shear strength and force value at which the ceramic detaches form the metal substructure were investigated, specially prepared samples and tested on the UFP400 static and dynamic compression / traction universal test machine,were measured.

The values of the shear resistance obtained in experiments are indicative values, but they provide information on the behavior of the new bioalloy (Ti10Zr) as a metallic substructure in metal-ceramic restorations, and on the other hand allow the comparative analysis of adhesion force for titanium and titanium alloys studied, using Noritake type ceramics.

Mechanical tests have been complemented by indirect methods for the evaluation of the metal - ceramic bond strength that allowed the study of the interface. SEM analysis and EDS analysis (using the Magna Ray on Common SEMs- JEOL JSM-6490LVmicroscope) allowed both components to be examined and provided information on the type of tear breakage of the ceramic form the metal substructure, the compositional nature, the presence and the characteristics of the oxide layer.

The appearance of the surface of detaching ceramics from the metallic substructure shows an aspect of tenacious rupture in the case of titanium alloys relative to pure titanium.

The experimental results obtained in the case of pure commercial titanium (Tigrade 4), which showed thicker layers of oxide, also showed a poor mechanical behavior in comparison to the titanium alloys studied (Ti6Al4V and Ti10Zr).

There are results which, on the one hand, confirm some results from the literature on the behavior of non-noble alloys as substructures in metal - ceramic restorations, and on the other hand they may constitute novelty elements regarding the behavior of a new bioalloy as a metal component in metal - ceramic technology (Ti10Zr, so far characterized only as a material for oral implants).

Even for a small number of samples, the results of the research have shown the superiority of the Ti10Zr alloy with high biocompatibility and high strength properties, with the highest shear strength values, which was agreed as to evaluate the strength of the metal - ceramic bond.

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MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS

This workshop is focused on the study of accelerated carbonation of recycled aggregates in laboratory and under realistic industrial conditions: Fast and Natural carbonation of RCA (experimental results and modelling, including improvement of RCA) **.**

Topics:

- Natural CO_2 uptake in concrete structures
- Fast and Natural carbonation of RCA (experimental results and modelling, including improvement of RCA), Life Cycle Analysis (LCA).

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