Universitatea Națională de Știință și Tehnologie POLITEHNICA BUCUREȘTI

DOCTORAL SCHOOL MATERIALS SCIENCE AND ENGINEERING
DEPARTMENT OF METAL MATERIALS SCIENCE, PHYSICAL METALLURGY

Summary of the doctoral thesis

Contribuții privind tehnologiile de obținere și procesare a aliajelor Co-Cr utilizate în restaurări metalo-ceramice

Contributions regarding technologies for obtaining and processing Co-Cr alloys used in metal-ceramic restorations

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Doctoral Student: DAWOD NAZEM
Scientific Coordinator: Prof.Univ.Habil.Dr.Ing. ANTONIAC VASILE-IULIAN

Bucharest 2023

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DOCTORAL THESIS

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Bucharest 2023

Thanks

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Thank you!

Sincerely,
DAWOD NAZEM

Contained

ABSTRACT

Metal-ceramic restorations are prosthetic restorations that combine mechanical strength and physiognomy formed by a metal substructure that supports a ceramic structure. Metal-ceramic systems are used for dental restorations that aim to combine the properties of metal alloys, such as tensile strength, compressive strength, wear resistance, respectively corrosion resistance, with the aesthetic appearance, naturally possessed by ceramic materials. The systems obtained from these two types of materials have been significantly successful in recent years, thanks to their ability to meet the functional requirements of dental restorations, while also providing excellent aesthetic results. Good corrosion behavior, especially under the influence of liquids in the oral cavity, but also biocompatibility with oral tissues, have made them become one of the most demanded options on the market.

Regarding their vast applicability in the dental field, one of the main applications of metal-ceramic systems in dentistry is their usefulness in the manufacture of dental crowns and bridges. The subadjacent metal alloy provides structural stability and a robust character, while the ceramic layer, through various combinations of shades, reproduces the natural appearance of the teeth, solving the problem from an aesthetic point of view. The combination of metal and ceramics allows precise control over the hue, translucency and texture of the restoration surface, making the restoration result blend perfectly with the patient's natural dentition.

Another application satisfied by these systems is the construction of prostheses on implants. The metal substructure provides the strength needed to withstand occlusal forces, while the ceramic layer provides a natural look, imitating the optical properties of neighboring teeth. In addition to these benefits, metal-ceramic biocompatibility minimizes the risk of allergic reactions and adverse tissue responses, ensuring long-term success and patient satisfaction.

The connection between metal and ceramic ensures the simultaneous operation of the two materials to provide the strength and durability necessary for a dental restoration, so that it can be subjected to cutting and mastication forces in the oral cavity. A strong bond prevents chipping or cracking of ceramics, which can lead to failure of restoration over time.

In addition, the connection between metal and ceramics gives a natural and aesthetically appropriate look. When it is strong, ceramics can be layered and shaped to fit perfectly with surrounding natural teeth. This is essential to create a realistic and visually attractive restoration that blends harmoniously with the rest of the patient's dentition.

An important aspect to consider for a good functioning of metal-ceramic systems, but also for the long-term success of the restoration depends on the strength of the bond between the two materials.

The retention or adhesion of metal to various substrates such as enamel, dentin, ceramics, old resins and other metals is crucial in ensuring a successful restoration, and in today's aesthetic-focused dental practice, clinicians demand multifunctional primers or adhesives that can provide a strong and durable adhesion.

Chapter 1
Introduction

Metal-ceramic restorations are prosthetic restorations that combine mechanical strength and physiognomy formed by a metal substructure that supports a ceramic structure. Metal-ceramic systems are used for dental restorations that aim to combine the properties of metal alloys, such as tensile strength, compressive strength, wear resistance, respectively corrosion resistance, with the aesthetic appearance, naturally possessed by ceramic materials. The systems obtained from these two types of materials have been significantly successful in recent years, thanks to their ability to meet the functional requirements of dental restorations, while also providing excellent aesthetic results. Good corrosion behavior, especially under the influence of liquids in the oral cavity, but also biocompatibility with oral tissues, have made them become one of the most demanded options on the market.

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In addition, the connection between metal and ceramics gives a natural and aesthetically appropriate look. When it is strong, ceramics can be layered and shaped to fit perfectly with surrounding natural teeth. This is essential to create a realistic and visually attractive restoration that blends harmoniously with the rest of the patient's dentition.

Currently, the most widely used non-noble metal alloys for metal-ceramic restorations are nickel-chromium (Ni-Cr) materials. But the potential health problems associated with nickel have led to the preponderant development of research into cobalt-chromium alloys (Co-Cr) [8, 10].

Chapter 2
Materials used in dental prosthetic restorations of metal-ceramic type

In dentistry, metal alloys can be classified according to the number of constituent elements, when this number of components involves only two elements combined in different proportions, they are called binary systems, and when they involve three or more elements, they are called ternary systems [5, 6].

Depending on the chemical composition of noble dental alloys, three categories are identified: ultra-noble alloys (HN), noble alloys (N) and predominantly base metal alloys (PB). This classification is shown in Table 2.2. [9]. Noble metals comprise a group of seven metals that are resistant to the highly corrosive environment in the oral cavity. In order of increasing melting temperature, these include: gold, palladium, platinum, rhodium, ruthenium, iridium and osmium. Only gold, palladium and platinum, which have the lowest melting temperatures of the seven noble metals, are currently of major importance in dental alloys [10, 11]. The noble metals mentioned above and silver are sometimes called precious metals, due to their high economic values, the term precious not being synonymous with noble. Silver is reactive in the oral cavity and is not considered a noble metal.

Table 2.2. Classification of dental alloys according to their noble metal content [9]

Type of dental alloy	Content of noble metals
Ultra-noble (HN)	≥40% Au and ≥60% of the total weight of the alloy
Noble (N)	≥25% of the total weight of the alloy
Metal-based (PB)	<25% of the total weight of the alloy

In dental prosthetics, Cr-Co alloys were used by Prange and Renge in 1933 under the name of Vitalium, due to its special anticorrosive qualities and good fluidity, ideal for osteosynthesis. They have applications in the manufacture of cast metal housings, skeletal prostheses, bridges, but also in the immobilization of teeth. More than 100 varieties of these alloys are currently being used and new ones with improved qualities are being developed [26, 27, 28]. All alloys used over time have been shown to comply with the requirements of ISO 6871-1:1994,[10] which dictate that the sum of the percentages by mass of Co, Cr and Ni should not be less than 85 (%wt, percentage by weight), whereas that of Cr and Mo should not be less than 25%.

Table 2.7. Elemental composition of commercial alloys [7]

Elements	Wironit LA	Wironium plus	Suprachrome	Vitalium	BrealloyF400
Co	63,5	62,5	63,6	63,4	64,7
Cr	5,0	29,5	28,5	29,0	29,0
Mo	1,2	5,0	6,0	5,2	5,0
Si	<1,0	<1,0	<1,0	<1,0	0,5
Mn	-	<1,0	<1,0	<1,0	0,4
Fe	<1,0	<1,0	-	-	-
Ta	<1,0	<1,0	-	-	-
C	<1,0	<1,0	<1,0	<1,0	0,4
N	<1,0	<1,0	-	<1,0	-

The ceramic masses originally used in dentistry, respectively dental porcelain, revolutionized dental prosthetics a few decades ago. The bath components of dental porcelain are: kaolin, feldspar, quartz, which are used in different proportions. In addition to these basic components, a number of other substances are added to the composition of dental ceramics, such as: fondant, metal oxides, additional or flux agents [10, 11, 12, 22, 23].

Chapter 3
Technologies and methods for obtaining, characterizing and testing dental prosthetic restorations of metal-ceramic type

Currently, the metal components made of Co-Cr alloys of metal-ceramic dental prosthetic restorations can be manufactured mainly using three different production technologies: conventional casting, milling or selective laser melting (SLM). However, there are other methods of obtaining dental alloys available and used in dental prosthetics. Each modality has both advantages and disadvantages, being chosen in relation to the possibilities of each laboratory.

Chapter 4: STUDY 1 - Identification of existing limits regarding obtaining the metal component of metal-ceramic dental prosthetic restorations, from commercial Co-Cr alloys, through casting technology

A first method of evaluating the correctness of cast prosthetic works is represented by macroscopic analysis of the obtained samples. The macroscopic examination was performed with the naked eye and magnifying glass, under conditions of illumination of the examined surfaces, with sources allowing the orientation of light perpendicular to them.

First of all, we made sure that the metal skeleton is not modified in relation to the model made initially. This defect could occur if the model method has generated significant wax contractions after cooling or the stress relief step has not been performed (Figure 4.11).

Figure 4.11. Identification of defects in the package

Another aspect that can be observed at surface level is represented by macroscopic homogeneity defects, namely gas inclusions, sulfides or packaging mass. The castings obtained in dental laboratories are made according to high precision technologies, which has the effect of eliminating these inclusions; Failure to comply with technological parameters can sometimes lead to the appearance of gas inclusions, known as pores. The pores are microcavities of spherical shape, filled or not with gases, arranged inside the metal mass or on the surface of the prosthetic work.

The pores are determined by the following causes: overheating of the alloy, inefficient heat source, the molten alloy tank with small diameter unable to provide the required amount of alloy in the pattern, the isthmus between the liquid alloy tank and the pattern cavity with a diameter of less than 2.2 – 2.5 mm, the molten alloy tank incorrectly placed in the center of the print, the casting force of the molten alloy in the pattern reduced in intensity and duration (Figure 4.12).

Figure 4.12. Detecting the presence of pores

The shape and volume of the casting can be changed due to *shortages*, which are partial or total.

Partial shortages are caused by insufficient amount of alloy used for melting, inefficient casting force, heat source did not properly melt the alloy, pattern was not heated to optimum temperature so as to favor fluid alloy flow, the pattern showed a very small area which was an obstacle to the liquid alloy, the presence of gases in the pattern as a result of failure to make or incorrect application of exhaust channels (Figure 4.13.).

Figure 4.13. Partial gaps in cast metal frames

The shape and volume of the prosthetic part modified due to pluses by the presence of a small amount of alloy, solidified on the surfaces of the part can have different shapes: spherical, lamellar or aciform cones, these representing the defect called plus material.

These changes occur at two different times in the technological process: when packaging the mock-up and when heating the mold for casting.

By the shape of the plus, the cause that caused the defect is deduced. The spherical shape of the plus is the consequence of the non-intimate application of the packaging mass to the surface of the model or the presence of air inclusions during the pattern (Figure 4.14).

Figure 4.14. Spherical pluses at the level of cast metal skeletons

Chapter 5: STUDY 2 – Experimental obtaining of new Co-Cr alloys alloyed with precious metals, through casting technology, for the metal component of metal-ceramic dental prosthetic restorations

5.3. Results and discussions of experimental study 2

The results of optical microscopy investigations are shown in Figure 5.4.

Experimental alloys have a dendritic structure formed by solid solution of Co, and in the interdendritic space, the presence of eutectic can be observed. These aspects are specific to cast Co-Cr alloys. Alloying elements are generally positioned in interdendritic spaces.

All experimental alloys showed a dendritic structure, from a microstructural point of view.

Gold-based microstructural compounds have a globular appearance and relatively uniform distribution.

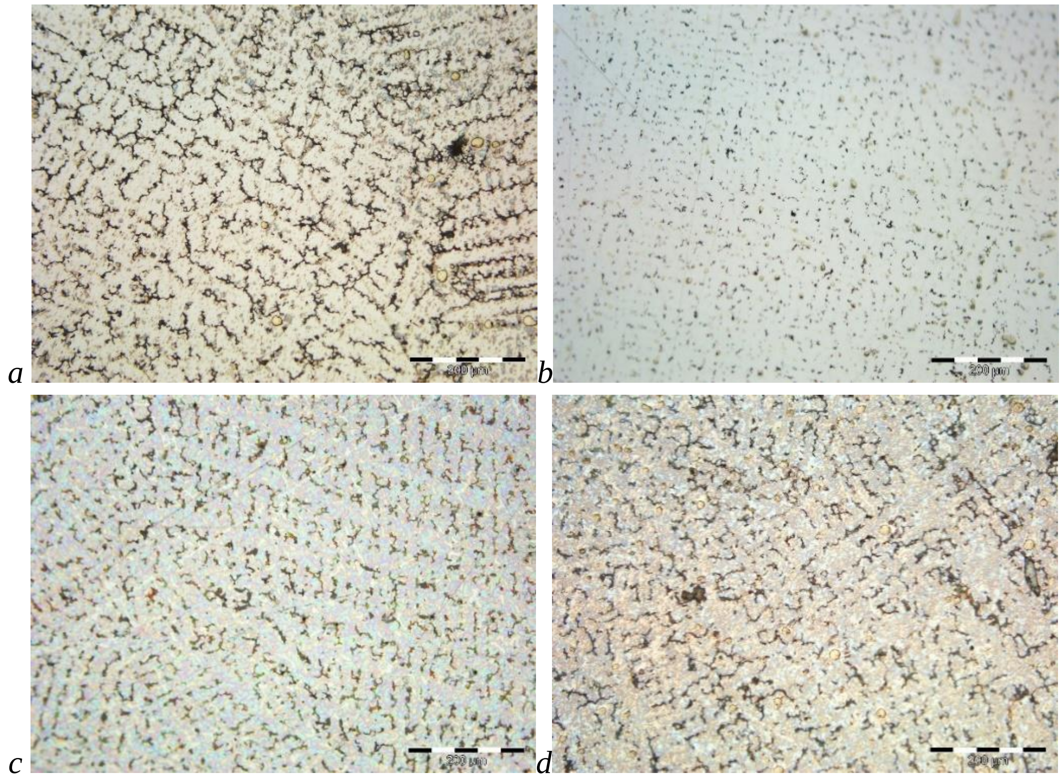


Figure 5.4. Microstructural aspects obtained with the help of optical microscopy, corresponding to each experimental dental alloy based on Co-Cr: a) Alloy #1, b) Alloy #2, c) Alloy #3, d) Alloy #4

In Figure 5.4.b, the addition of alloying elements refines dendrite size but maintains a low degree of porosity. In Figure 4.c, the dendritic structure is uniform, and in Figure 5.4.d, the dendritic structure is disturbed, the porosities being smaller but bulkier.

In the case of experimental dental alloys, particularly complex from a compositional and microstructural point of view, it is recommended to use SEM scanning electron microscopy coupled with energy dispersion X-ray spectrometry (EDS) to highlight microstructural details. Figure 5.5 shows the experimental results obtained for the 4 experimental alloys.

As can be seen in Figure 5.5., in Alloy #1 and Alloy #4, containing 7% Au and 14% Au, it is not evenly distributed, generating globular inclusions (highlighted in Figure 5.5a and Figure 5.5d) and may influence the mechanical properties of the biomaterial. These areas are composed primarily of gold, according to chemical analysis. In Figure 5.5.b, alloys containing 2% Ag and 5% Au do not exhibit dendritic structure specific to the structure of Co-Cr alloys. Sample #3 (Figure 5.5.c) shows the best homogeneous structure and the alloying elements are evenly distributed. Figure 5.5.c (Alloy #3) shows a globular formation that (according to the spectrum indicated by the arrow) has a predominant composition of Zr and Nb.

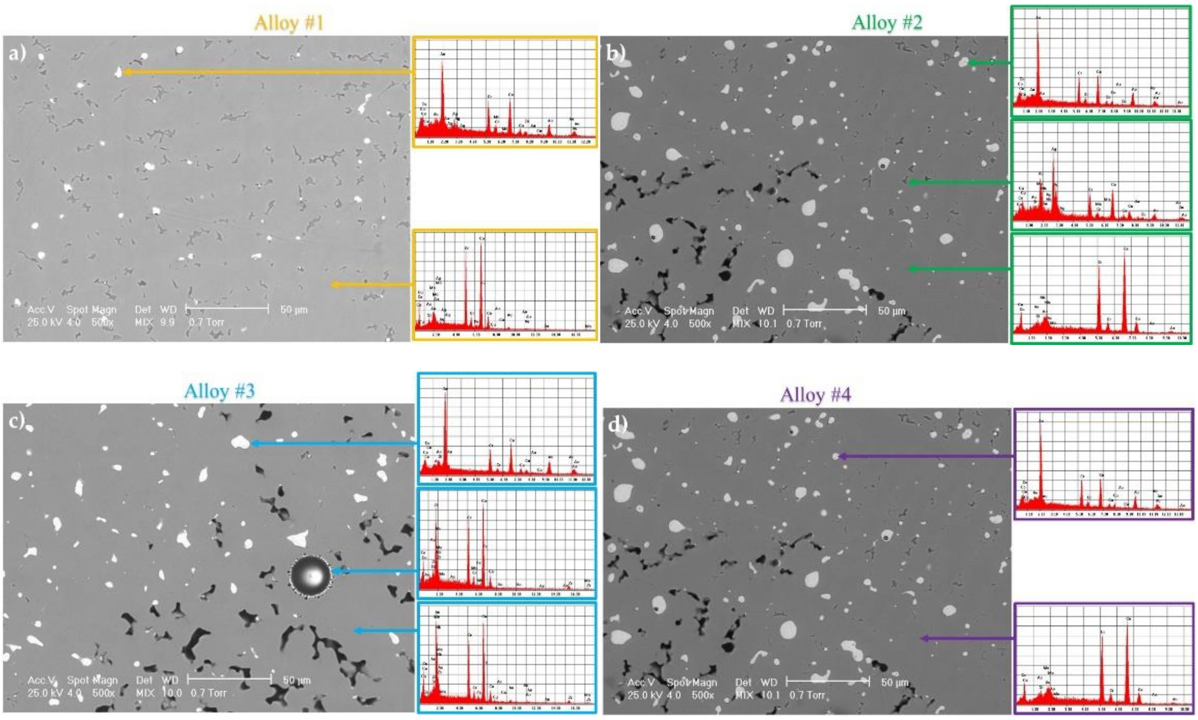


Figure 5.5. Microstructural aspects obtained by SEM associated with EDS in each Co-Cr-based dental experimental alloy: a) Alloy #1, b) Alloy #2, c) Alloy #3, d) Alloy #4

Table 5.2. Nominal sample compositions (% by weight) of the experimental alloys obtained

	Reference Co-Cr	**Alloy #1**	**Alloy #2**	**Alloy #3**	**Alloy #4**
Co	60,51	55,36	56,07	36,15	57,39
Cr	28,66	25,96	26,62	16,23	25,26
Mo	4,89	8,66	7,83	14,85	-
Si	2,61	1,15	0,89	1,13	1,01
Au	-	7,41	5,39	7,68	14,81
Ag	-	-	2,07	-	-
Zr	-	-	-	20,59	-
Nb	-	-	-	1,97	-
Cu, Fe	Balance				

Following the analysis, the same composition was identified as the one initially estimated for the formation of experimental optimized dental alloys in the Co-Cr system.

Good corrosion resistance of the material implies an electropositive corrosion potential value (Ecorr). From this point of view, it can be seen that Alloy #4 has the most electropositive corrosion current value. Corrosion current density (icorr) is the most important electrochemical parameter, with better behavior corresponding to more positive value. Among the alloys tested, it can be seen that Alloy #3 has the lowest value of this parameter (44.65 nA/cm2), highlighting a better anti-corrosion character than the other alloys tested.

Table 5.4. The main parameters of the electrochemical corrosion process

Nr.	**Coding of samples**	**E_{corr} (mV)**	**i_{corr} (nA/cm^2)**	**β_c (mV)**	**β_a (mV)**	**R_p (kΩxcm^2)**
1	Aliaj #1	105.16	76.75	113.72	350.59	486.41
2	Aliaj #2	54.21	532.43	215.48	556.83	126.86
3	Aliaj #3	66.08	44.65	172.46	76.87	517.71
4	Aliaj #4	118.48	259.48	285.54	101.47	125.44

In terms of polarization resistance (Rp), it can be seen that the material with the highest value is Alloy #3 (517.71 kΩxcm2), thus demonstrating that it has the best corrosion behavior among the tested alloys.

The alloy showing the best corrosion resistance is Alloy #3 (with 7% Au, 20% Zr and 2% Nb) - with icor of 44.65 nA/cm2 and Rp of 517.71 kΩxcm2 followed by Alloy #1 (with 7% Au) with icor of 76.75 nA/cm2 and Rp of 486.41kΩxcm2.

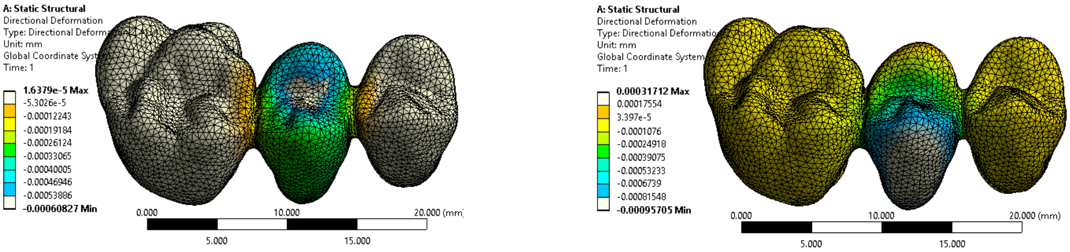
The other two alloys have much higher icor values, respectively 259.48 nA/cm2 Alloy #4 and 535.43 nA/cm2 Alloy #2 and much lower values of Rp (125.44 kΩxcm2 for Alloy #4 and 126.86 kΩxcm2 for Alloy #2).

Chapter 6: STUDY 3 - Finite element analysis of stress and deformation state in metal-ceramic dental prosthetic restorations, with metal support made of Co-Cr alloys obtained by different manufacturing technologies

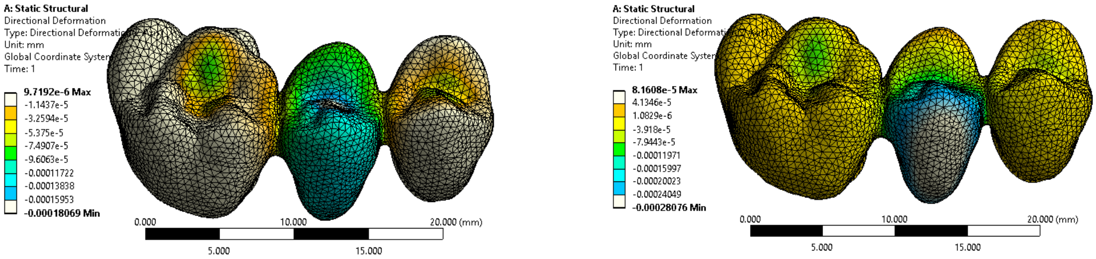
6.3. Results and discussion of experimental study 3

Displacement of the dental bridge under the action of mechanical stress

The displacement of the deck qualitatively and quantitatively highlights how the structure loaded with stress and fixed by means of metal inserts will deform. Two types of displacement of the structure are shown below: vertical displacement (Z) in Figure 6.8. and total displacement in Figure 6.9.

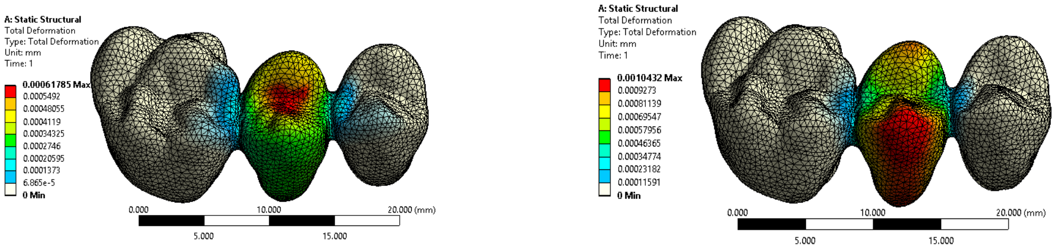


a) Focused, vertical load *b) Focused, oblique stress*

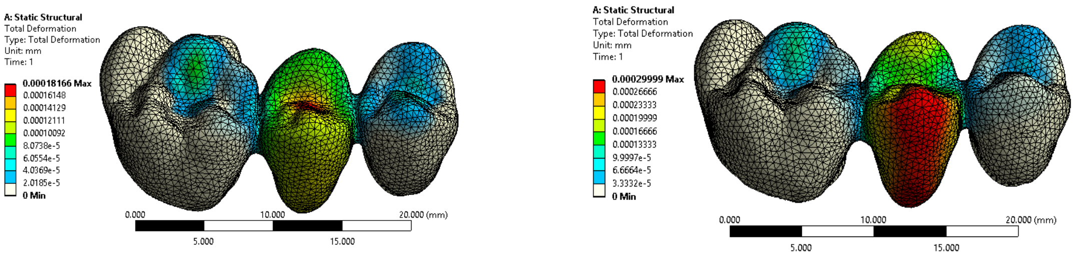


c) *Distributed, vertical request* d) *Distributed, skewed request*

Figure 6.8. Deformation of the dental bridge in the vertical direction



a) *Focused, vertical load* b) *Focused, oblique stress*



c) *Distributed, vertical request* d) *Solicitare distribuită, oblică*

Figure 6.9. Total deformation of the dental bridge

As for the directional displacement of the insert, it is at values of the order 10-5- 10-6 mm, i.e. very small (Figure 6.11). These values are found regardless of the type of obtaining of the Co-Cr alloy because in any way of obtaining it (cast, sintered or milled CAM), its rigidity is similar and at a very high level. Contributing to this is the fact that the metal insert is trapped between the ceramic crown and the simulated surface of the dental structure.

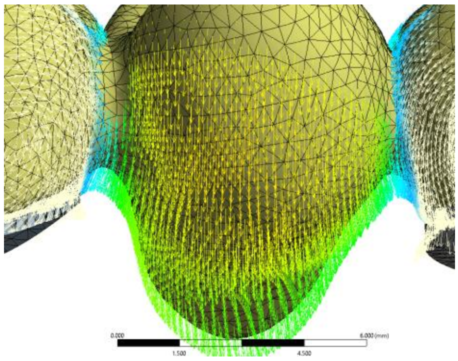


Figure 6.10. Total deformation, vector view

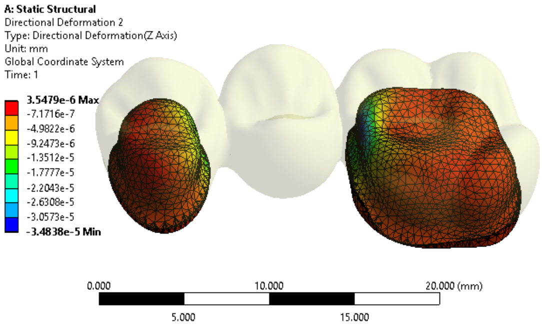


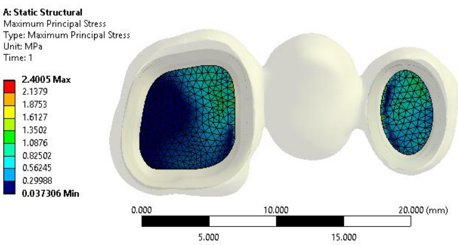
Figure 6.11. Directional displacement of the metal insert

<u>Equivalent and shear stresses of the dental bridge</u>

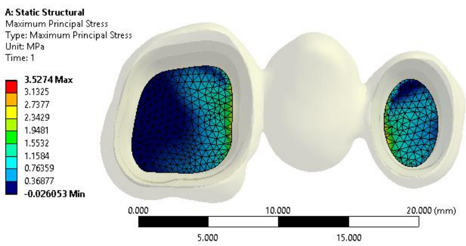
Shear stresses refer to stresses that arise in the structure to oppose the tendency to move relative rotation, or slip of two surfaces. In Figure 6.12. observe the distribution mode of these voltages in close connection with the direction of stress and the mode of distribution. The maximum values recorded at the level of the whole structure range from 1 to 12 MPa, which is little compared to the mechanical strength of dental ceramics and Co-Cr alloy. This indicates that the structure will remain integral for physiological stress values, both in terms of insert and ceramics.

The main maximum stresses are tracked because they are a predictor of surface fracture. Thus, if a model with brittle material properties is subjected to a multiaxial state of tension, then breakage will occur when the maximum main voltages anywhere in the component exceed the local mechanical resistance [10].

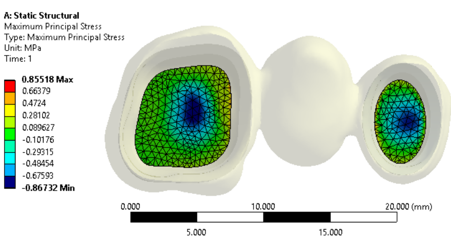
In Figure 6.14. The maximum main stresses in the surfaces of the engagement elements (metal insert) shall be shown. A circular distribution of them is observed under evenly distributed stress, with increased values towards the extremities of the sections. In the case of point forces, the bending effect leads to a loading of the inserts facing the middle crown. The stress values are very low compared to the yield and Rm limit of the Co-Cr alloy and therefore the structure does not pose any risk of mechanical failure.



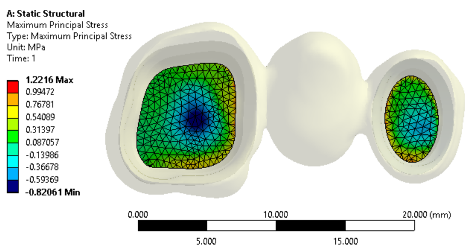
a) Focused, vertical load



b) Focused, oblique stress



c) Distributed, vertical request



d) Focused, oblique stress

Figure 6.14. Maximum main tensions in the surface of the engagement elements

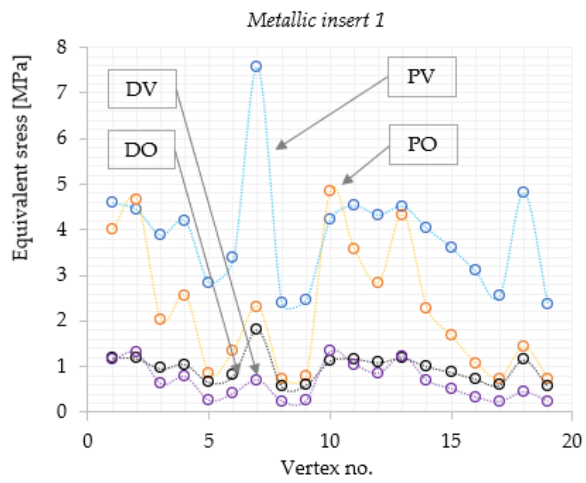
Axle performance depending on how the Co-Cr alloy is obtained

The performance of the dental bridge in terms of the type of Co-Cr alloy used is shown below, as values of the maximum tension in the metal insert.

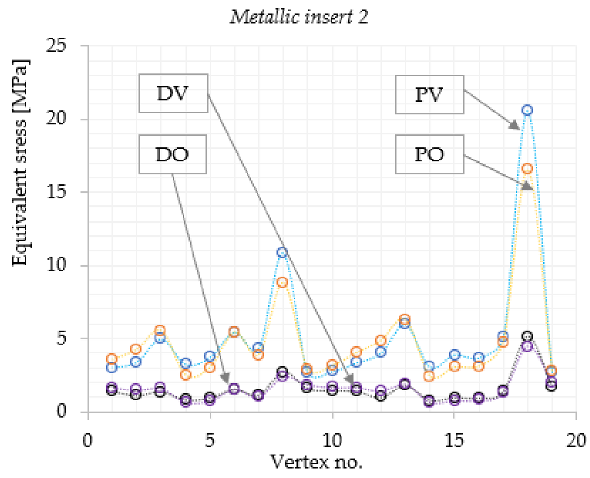
When comparing voltage values according to the 3 types of materials, a trend of similarity is observed, regardless of the mode of stress. Thus, the sintered Co-Cr alloy appears with the highest voltage values, followed by the milled alloy CAM and ending with the cast one. This indicates that the sintered alloy's stiffness is superior, allowing it to better handle the load.

However, the differences in voltage variation are very small between the 3 alloys, of the order of magnitude < 1MPa, which leads us to the conclusion that in terms of how to take over and transmit the load the 3 alloys are very similar. In Figure 6.16. Variations in voltage values in the area of maximum stress of metal elements are presented.

Figure 6.17. presents in the form of a circular representation the values of 12 knots taken circularly and equidistantly on the two contours of the ceramic element of the deck. And in the area of ceramic sections, the decisive dependence of tensions is on the type of stress, and not on the type of material from which the insert is made. The lowest voltage values shall be recorded for evenly distributed stress.



a) Metal insert 1



b) Metal insert 2

Figure 6.16. Variation of voltages in the metal insert on the maximum load line

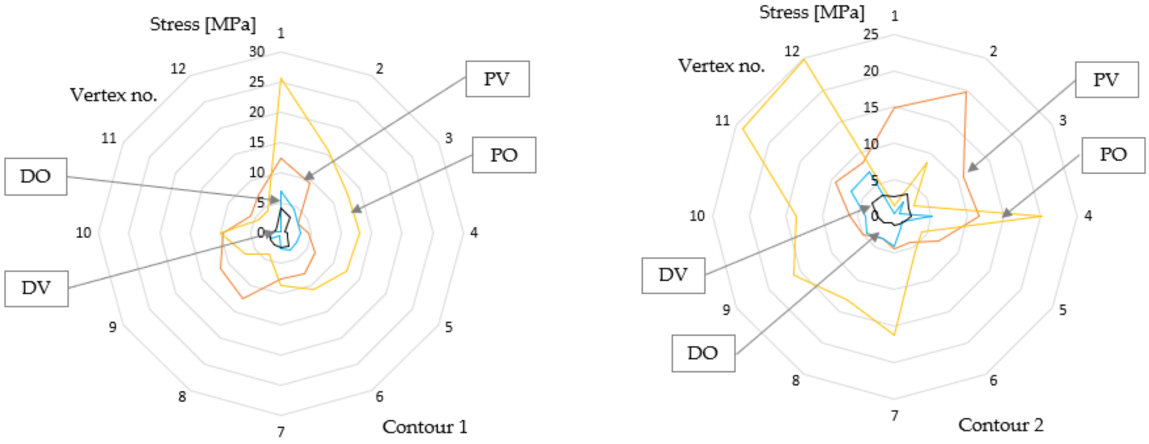


Figure 6.17. Variation of tensions in the contours of the dental crown

6.4. Conclusions on the eperimental study 3

The numerical simulation was performed on a 3D model of dental bridge built on a metal Co-Cr support (insert). The crown materializes 3 molars and was simulated with the generic mechanical properties of dental ceramics. The simulation conditions were physiological both in terms of modules and loading directions, but also in terms of constraints.

- The results of the analysis refer to the state of tension and deformation in the dental crown and in the metal insert in the case of 3 different mechanical properties of the Co-Cr insert, corresponding to its manufacturing technology: sintered, milled CAM and cast. Following the numerical analysis, the following conclusions can be highlighted:
- The metal insert plays a decisive role in obtaining a mechanical behavior of tenacity of the denar bridge assembly;
- The differences in mechanical strength of a dental bridge construction on a sintered, molded or milled CAM Co-Cr insert are insignificant in terms of mechanical strength;
- The rigidity of a construction using sintered Co-Cr is 2-3% higher than in the case of the alloy obtained by the other two manufacturing technologies;
- The method of obtaining the metal insert is particularly important in terms of initiation and propagation of cracks, this directly influencing the fatigue behavior of the structure.
- The presence of metal inset reduces the risk of fracture of the dental crown, due to the toughness of the alloy.

Chapter 7: STUDY 4 - Study on component compatibility in case of dental prosthetic restorations of metal-ceramic type, with metal support made of Co-Cr alloys obtained by different manufacturing technologies

7.3. Results and discussion of experimental study 4

<u>Results obtained by stereomicroscopy</u>

Set 1 of results – surface analysis

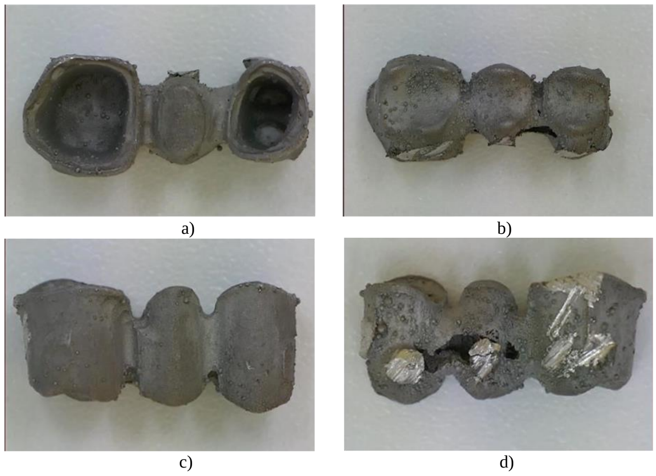


Figure 7.8. Macroscopic image of the experimental sample obtained by classical casting: a) upper vision; b) lower view; c), d) side view

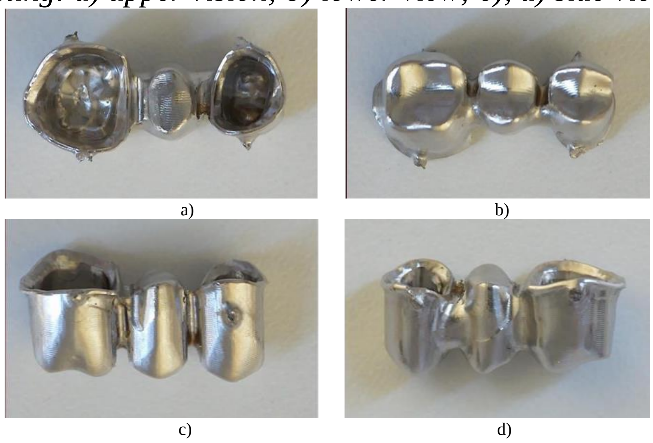


Figure 7.9. Macroscopic image of the experimental sample obtained by milling: a) upper vision; b) lower view; c), d) side view

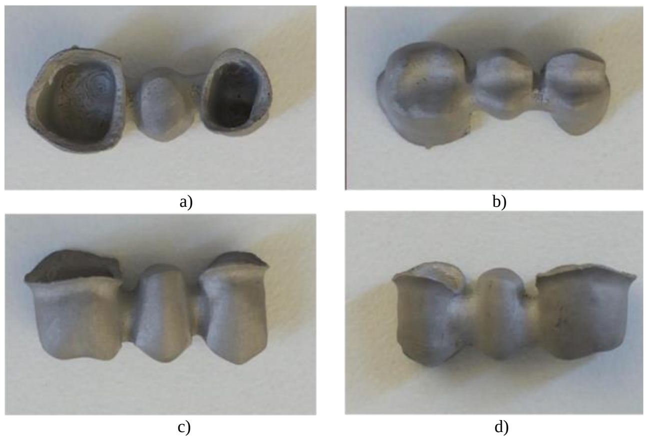
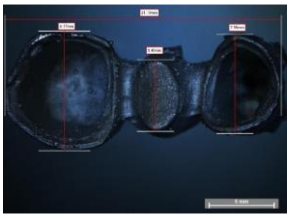
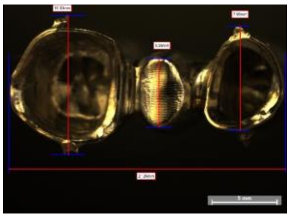


Figure 7.10. Macroscopic image of the experimental sample obtained by selective laser melting: a) upper vision; b) lower view; c), d) side view

Also with the help of stereomicroscopy, besides surface images, measurements of experimental samples could be made for dimensional analysis.

a)  b) 

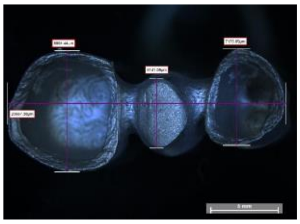
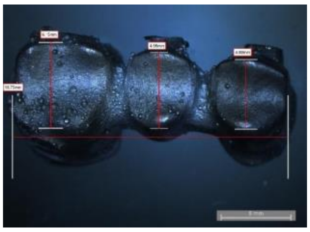
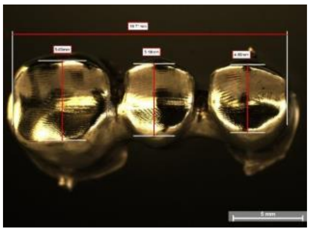
c) 

Figure 7.11. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c) selective laser melting – superior view

a) b)

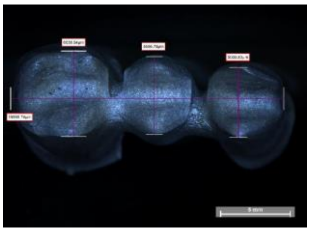
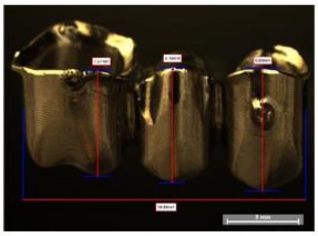
c) 

Figure 7.12. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c) selective laser melting – lower view

a)  b) 

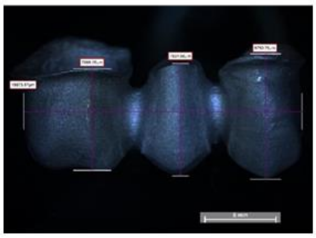
c) 

Figure 7.13. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c) selective laser melting – side view

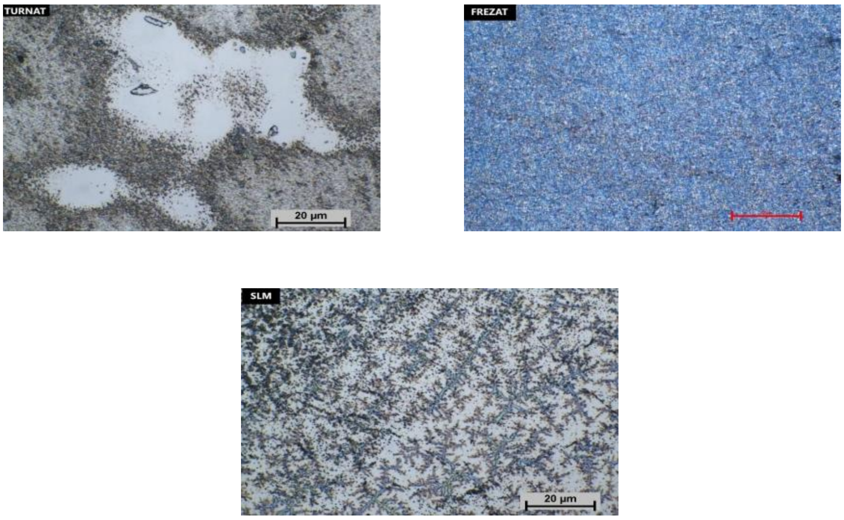


Figure 7.18. Optical microscopy images for experimental samples obtained by classical casting, milling and selective laser melting, 100x

In the case of specimens obtained by casting, there is a heterogeneous, dendritic microstructure, with a multitude of defects, following the obtaining process. There is also a large volume of pores, which can be a precursor to internal stresses, causing the bending strength of the cast Co-Cr alloy to be low.

For specimens obtained by milling, an improvement in the appearance of the micrography is observed, through a slightly more homogeneous structure, compared to that of the cast samples. However, the same dendritic appearance is preserved, accompanied by random black dots marking the presence of microgrids.

Chemical attack at the particle limit (n.a. they are not grains, but sintered particles) is easiest to visualize in the case of sintered alloys (attack parameters may have been extended, particle limits are slightly over-attacked). The dimensions of the particles are completely uneven, they range from 20 to 150 microns. Due to sintering, particles occupy a smaller volume, conglomerates appear, but also some areas that are not fully sintered, in terms of voids.

Results obtained by 3-point bending test

Modulus of elasticity of Co-Cr alloys with low values were obtained after studying the slopes, which gives them a more elastic character.

Depending on the obtaining technology, three data sets were operated, the curves having quite small differences between them.

The results of the 3-point bending tests were shown as force-displacement curves as shown in Figure 7.22. and compared according to Figure 7.23. The shades of red were rendered those corresponding to the parts obtained by the conventional casting method, shades of blue marked the curves related to the parts obtained by milling, and the shades of green characterize the parts obtained by selective laser sintering.

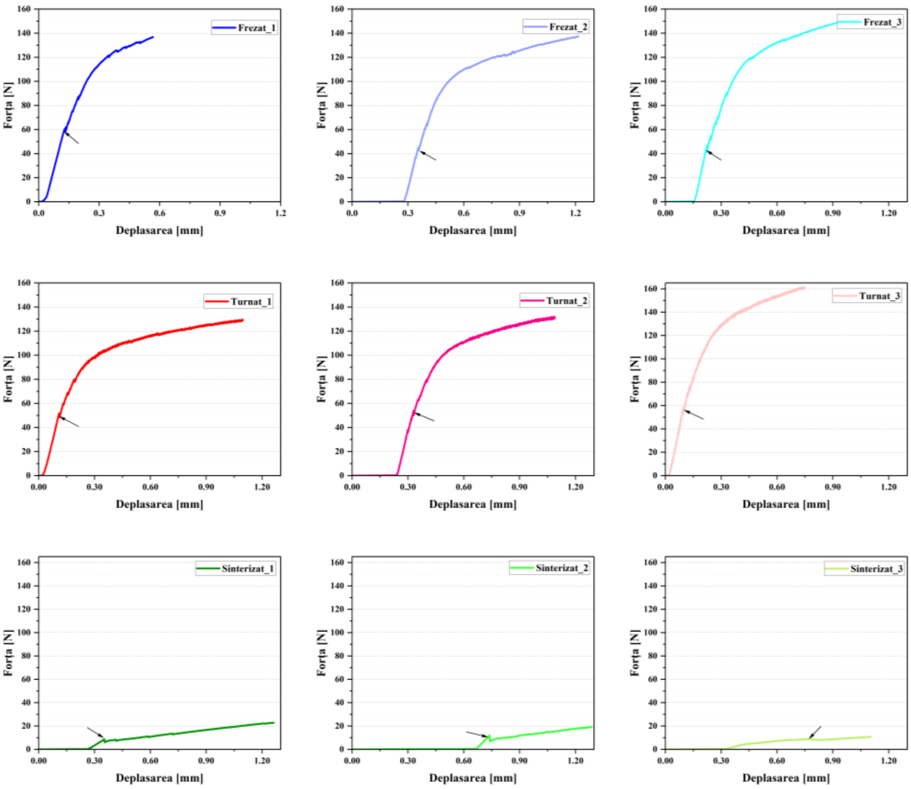


Figure 7.22. 3-point bending test graphs

Chapter 8
Conclusions, own contributions and future research directions

8.1. Conclusions

The conclusions issued in this study, entitled "Contributions to Co-Cr alloy production and processing technologies used in metal-ceramic restorations," reflect a comprehensive and integrative approach to scientific research in the field of dental prostheses. The thorough analysis of theoretical and practical studies and experiments reveals a special attention paid to the information gaps existing at the intersection between the medical and engineering fields.

The results obtained and their interpretation indicate not only a consolidation of existing knowledge, but also an expansion of the frontier of knowledge through significant original contributions. Through the careful orientation of theoretical and experimental research, the aim was not only to obtain theoretical understanding, but also to bring substantial practical contributions. These contributions can be outlined as follows:

1. Contributions to the content of global and national research on metal-ceramic restorations and materials used.
2. Contributions regarding the establishment of the experimental program and research methodology, according to European Union standards and unconventional methods.
3. Contributions to the understanding of processes at the metal-ceramic interface.
4. Contributions to identifying the possibilities of realizing and modifying the characteristics of the metal support.

In a synthetic and theoretical perspective, this work is distinguished by original contributions of the author, encompassing the issues approached in a broader context of knowledge in the field of medical engineering. Thus, this doctoral thesis not only fills in the informational gaps, but also strengthens the theoretical and practical basis of research in the field of dental prostheses, thus contributing to scientific and applicative progress in this interdiscipline.

- **STUDY 1 - Identification of existing limits regarding obtaining the metal component of metal-ceramic dental prosthetic restorations, from commercial Co-Cr alloys, through casting technology**

The Critical Importance of Casting Technology: The study highlights that the casting process is an essential aspect in obtaining the metal component of metal-ceramic dental prosthetic restorations made from commercial Co-Cr alloys. The results indicate that the use of temperature-adjustable fusion source is imperative to achieve precise fusion and convenient structure, essential for the durability and final quality of prosthetic constructions.

The Determining Role of Choosing Dental Alloy: The study emphasizes the importance of choosing the appropriate dental alloy according to essential characteristics such as mechanical strength, chemical stability, low thermal conductivity, biotolerance and affordable cost. These criteria directly influence the performance and durability of metal-ceramic restorations, thus reinforcing the relevance of alloy selection in the context of mixed prosthetic restorations.

Complex Levels of Study in Mechanical Properties of Alloys: The study brings to attention the complexity of evaluating the mechanical properties of alloys used in prosthetic elements. The assessment of these properties is not limited to the superficial level of observation, but requires an understanding of internal reactions and interactions at the microscopic level, thus highlighting the importance of a detailed and multidimensional study of the alloys used.

Key Factors in the Quality of Cast Prosthetic Restorations: The study identifies a number of key factors influencing the quality of cast prosthetic restorations, including how to preserve and prepare the packaging masses, dimensional accuracy of the pattern, alloy casting composition and temperature, and the conduct of the solidification and cooling process. These factors, when properly managed, contribute significantly to avoiding defects in the metal skeleton and ensure the integrity of prosthetic restorations.

Necessary Convergence of Aesthetics and Durability: By mentioning mixed prosthetic constructions, the study highlights the need for a convergent approach between the strength offered by the metal infrastructure and the aesthetic component made of ceramic or composite. This synergy is essential to ensure both longevity over time and optimal aesthetic restoration in accordance with the functional and aesthetic requirements of the dental system.

- **STUDY 2 – Experimental obtaining of new Co-Cr alloys alloyed with precious metals, through casting technology, for the metal component of metal-ceramic dental prosthetic restorations**

Innovation in Co-Cr Alloy Composition: The study demonstrates an innovative approach to obtaining the metal component of metal-ceramic dental prosthetic restorations by developing and testing new Co-Cr alloys alloyed with precious metals. This initiative highlights the ever-changing direction and adaptation of the chemical composition of dental alloys to improve corrosion resistance and machinability.

Benefits of Adding Nb and Zr: The study highlights the benefits of adding niobium (Nb) and zirconium (Zr) to Co-Cr alloys, highlighting significant improvements in corrosion, microstructure, and mechanical properties. The research also highlights that the addition of Nb may contribute to osteogenesis, thus providing integrated insight into the multiple benefits of new dental alloy formulations.

Relevance of Globular Particulate Matter in Corrosion Behavior: The observation of the presence of globular particles and the uneven distribution of gold in the alloys tested suggests a direct correlation with corrosion behavior. This finding makes a significant contribution to understanding the microscopic-level phenomena that influence the durability and stability of Co-Cr alloys in corrosive environments.

Optimization of Corrosive Performance of Alloys: The findings reveal that alloy #3, containing 7% Au, exhibits superior corrosion resistance compared to the other samples studied. This optimization of corrosive performance, evidenced by the lowest current density and the best resistance to polarization, represents a significant step towards improving the durability of dental alloys used in prosthetic restorations.

Significant Contribution to Technological Progress: The study makes a significant contribution to technological progress in the field of dental materials, highlighting that Co-Cr alloys with specific additions, such as 7% Au or 7% Au, 20% Zr and 2% Nb, represent a significant improvement in corrosion behavior compared to conventional Co-Cr alloys. This result offers new perspectives for the development and implementation of better dental materials in dental practice.

STUDY 3 - Finite element analysis of stress and deformation state in metal-ceramic dental prosthetic restorations, with metal support made of Co-Cr alloys obtained by different manufacturing technologies

The Decisive Role of the Metal Insert: The finite element analysis reveals that the metal insert has a crucial role in determining the mechanical tenacity behavior of the metal-ceramic dental bridge assembly. This finding underlines the inherent importance of the metal support in influencing the integrity and strength of the prosthetic assembly.

Significant Similarities in Mechanical Strength: The results of the analysis indicate that the differences in mechanical strength between dental bridge constructions on sintered, molded or milled Co-Cr insert by CAM technology are insignificant. This finding suggests that, in terms of mechanical strength, all three Co-Cr metal support manufacturing technologies are comparable.

Increased Rigidity in the case of Sintered Co-Cr: The study highlights that the rigidity of a construction using sintered Co-Cr is approximately 2-3% higher than in the case of alloy obtained by the other two manufacturing technologies (cast and milled by CAM). This observation highlights the specific advantages of the sintering process in terms of stiffness of the prosthetic assembly.

Physiological Conditions and Implications: The numerical simulation was carried out under physiological conditions, both in terms of load modules and directions, as well as in terms of constraints. This approach ensures clinical relevance and transferability of results in the functional context of the stomatognathic system, thus emphasizing the applicability of the findings in dental practice.

Equivalent Perspectives in Prosthetic Construction Efficiency: Overall, the findings indicate that, in terms of mechanical strength, Co-Cr-based dental bridge constructions, regardless of manufacturing technology (cast, sintered or milled by CAM), exhibit equivalent efficiency. This equivalence can serve as a guide for the choice of manufacturing technology according to practical and economic considerations.

- **STUDY 4 - Study on component compatibility in case of dental prosthetic restorations of metal-ceramic type, with metal support made of Co-Cr alloys obtained by different manufacturing technologies**

The importance of Mechanical and Chemical Compatibility: The study reveals that mechanical, chemical compatibility and adequate stress distribution in metal-ceramic systems are essential factors for the successful integration of different materials into metal-ceramic dental prosthetic restorations. This compatibility is essential to ensure coexistence without significant adverse interactions between the metallic and ceramic components.

Modulus Elasticity Assessment: The three-point bending test reveals that the elasticity moduli of Co-Cr alloys showed low values. This finding underlines the need to adapt metal-ceramic systems to achieve superior bending strength, which is essential to withstand mechanical stress and ensure durability in the context of mastication forces.

Efficiency of Different Manufacturing Technologies: The results of experiments indicate that the casting method gives the best results in terms of three-point bending strength, followed by milling and finally sintering. This hierarchy of efficiency of manufacturing technologies provides valuable information for choosing the right method according to the specific requirements of metal-ceramic dental prosthetic restorations.

8.2. Own contributions

The experimental researches carried out brought a series of original contributions obtained also through their theoretical interpretation. The original contributions and the most important results obtained are:

- Contributions regarding the establishment of applicative possibilities for achieving and modifying the characteristics of metal alloys used in the execution of metal-ceramic dental restorations.
- Contributions regarding the design of the working protocol in determining the coefficients of linear thermal expansion for the components of the metal-ceramic system.

The researches carried out have brought a series of novelty contributions through the original results obtained and through their theoretical interpretation. The original contributions will be presented below together with the most important results obtained:

- A complex synthesis of scientific documentation was carried out, which led to obtaining many new results and interpretations, some of them being novel and original.
- The technology for making ceramic cladding of experimental alloys was conceived and experimentally verified;
- The structural characteristics of the experimental metal alloys were highlighted by thorough research conducted by optical microscopy and scanning electron microscopy.
- Using the set of imaging and thermal methods in evaluating the behavior of metal-ceramic couple at dental prosthetic restorations;
- Determination of variation of linear thermal expansion coefficients for experimental alloys; observation and determination of temperature variation of the average coefficient of thermal expansion;

- Analysis of experimental data on thermal expansion and their processing;
- Correlating the thermophysical properties of support materials and ceramics with the standard process of manufacturing ceramic deposits;
- Highlighting and interpreting microstructural aspects related to studied Co-Cr alloys.
- Influence of structure on thermal expansion reproducibility of selected alloys.
- A summary of the advantages and disadvantages of using metal-ceramic systems, presented below, was obtained.

8.3. Future research directions

Metal-ceramic restorations were and are considered a good option for repairing damaged teeth, due to the fact that they have good mechanical properties, satisfactory aesthetic qualities and acceptable interaction with dental tissues.

As a future research direction, the possibilities of technology transfer to dental offices of technologies for obtaining and processing alloys developed in this doctoral thesis will be evaluated.

One of the main challenges of these metal-ceramic systems used in dentistry is to achieve strong and reliable adhesion between the two materials. Ceramics have a fragile nature, which makes it difficult to bond perfectly to the metal material used as a backing, especially under conditions of continuous occlusal loading. Chemicals such as silane coupling agents and hydrogen fluoride have been examined for ceramic surface treatment to improve adhesion, but with limited success. Various factors can affect the strength and reliability of adhesion in metal-ceramic dental systems, including surface preparation, primers or adhesives used, bonding mechanisms, material compatibility, thermal mismatch between metals and ceramics, and clinical conditions such as saliva contamination or oral hygiene. Also, the mismatch of the coefficient of thermal expansion and the presence of an oxide layer on the surface of the metal can compromise the strength of adhesion of the ceramic material to the metal support. In the future, various solutions for modifying the surface of the prosthetic support made of metallic materials from the category of Co-Cr alloys will be studied, in order to improve adhesion.

Functional testing and evaluation of dental restorations is a challenge, and a future direction will be the development of functional testing systems for metal-ceramic dental prosthetic restorations.

Capitalization of research results

Articles (4):

1. Dawod N, Miculescu M, Antoniac IV, Miculescu F, Agop-Forna D, *Metal-Ceramic Compatibility in Dental Restorations According to the Metallic Component Manufacturing Procedure*, Materials 16(16):5556, 2023.

2. Dawod N, Stoia D, Focșăneanu S, Antoniac A, Robu A, Dura H, Cârstoc D, Dragomir B, *Shear Stress Analysis by Finite Elements of a Metal-Ceramic Dental Bridge on a CoCr Alloy Support*, U.P.B. Sci. Bull., Series B, 85(3), 2023.

3. Dawod N, Florescu A, Antoniac IV, Stoia DI, Hancu V, Biclesanu FC, *The FEA Study of the Biomecanic Behavior of Canine Reconstructed with Composite Resin,* Rev. Chim.; 70(7):2456-2462, 2019.

4. Dawod N, Antoniac A, Antoniac I, Miculescu M, Robu A, Ungureanu E, Agop-Forna D, Cârstoc I, Dura H, Dragomir BR, *Corrosion behavior and microstructural analysis of some Co-*

Cr alloys used for metal–ceramic restorations in dentistry, U.P.B. Sci. Bull., Series B, 85(4), 2023.

Brevete (2)

1. Brevet RO134131B1 din 29.09.2023 (BOPI nr.9/2023)

Co-Cr dental alloy with corrosion resistance and high biocompatibility

Antoniac Vasile Iulian; Rau Julietta; Semenescu Augustin; ***Dawod Nazem***; Geantă Victoraş; Voiculescu Ionelia; Mateş Ileana Mariana; Șolea Marina Roxana

2. Brevet RO134132B1 din 29.09.2023 (BOPI nr.9/2023)

Ruthenium-alloyed Co-Cr alloy for metal-ceramic dentures

Antoniac Vasile Iulian; Rau Julietta; Semenescu Augustin; ***Dawod Nazem***; Geantă Victoraş; Voiculescu Ionelia; Mateş Ileana Mariana; Șolea Marina Roxana

Participation in international conferences (1):

Nazem Dawod, Iulian Antoniac, Marian Miculescu, Aurora Antoniac, Alina Robu, Elena Ungureanu, *Influence of alloying with precious metals on the microstructure and corrosion resistance of the Co-Cr dental alloy,* International Conference on Biomaterials and Regenerative Medicine, Iulie 19 - 21 Sibiu, 2023, ROMANIA

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LIST OF FIGURES

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