COMPARATIVE STUDY ON THE OBTAINING TECHNOLOGY INFLUENCE ON THE STRUCTURE AND PROPERTIES OF METAL CROWNS MADE OF Co-Cr-Mo ALLOY

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ABSTRACT

The aim of this paper is to highlight the influence of the dental prosthetic works obtaining technology on their structure and properties. Three metal skeletons of dental crowns made of Co-Cr-Mo alloy were developed by three different technologies: classical casting, milling and selective laser melting. Surface properties, μCT investigations, microstructure and mechanical test were used to comparatively investigate the obtained structures. At the same time, the experimental investigations carried out in this paper show that the technology of obtaining Co-Cr alloys can influence the structure and properties of materials. Within the limits of the presented study, it can be stated that the selective melting technology of Co-Cr-Mo alloys is preferred in dental restorations due to improved properties, longevity, but also good interaction with the oral environment.

Key words: Dental structures, obtaining technology, Co-Cr-Mo Alloy, properties, structure.

INTRODUCTION

In dentistry, prosthetics is used for oral rehabilitation treatments through fixed works (crowns, bridges) or mobile works (partial dentures, total dentures). The prosthetic works have the role of restoring the masticatory function of the dento-maxillary apparatus, the physiognomic function being ensured by ceramic or composite materials applied to the resistance structure [1]. In the dental field, the use of biomaterials has as main goal to improve oral health, the compatibility between functions, properties and structures of biological materials being necessary [2, 3]. Generally, the resistance structure of a dental prosthetic work is made of metallic materials. Metallic materials were and are considered materials of choice in the manufacture of prosthetic structures [4]. The metal materials most used in the manufacture of dental prosthetic structures are Co-Cr alloys [5]. In recent decades, digitized technologies have been used to manufacture metal prosthetic structures [6-8]. These technologies are based on computer-aided design (CAD/CAM) or additive manufacturing such as selective laser melting (SLM) [9]. One of the problems that arise in the manufacture of dental prosthetic works is related to the used manufacturing technology [10]. Co-Cr dental alloys are specially designed for introduction into the oral cavity, but from the raw material supplied by the manufacturer to the finished work, the alloy is processed, with the possibility of modifying its properties [11-14]. Research on the properties of Co-Cr alloys has shown that they have an advantage over noble alloys in terms of cost, have very good adhesion characteristics with ceramics, higher hardness and better corrosion resistance [15-18].

The metal-ceramic prosthetic works involve a complex laboratory technology with specialized equipment. The metal component must provide a precise and non-deformable structure allowing adhesion of the ceramic component. The metal-ceramic crowns are intended for the restoration of the front teeth, as well as those in the lateral area [19-21].

In some cases, the caps resemble a metal thimble or a thin-walled stem, while in other cases they resemble a crown with partially polished surfaces that will be covered with ceramic material. Metal caps, usually cast, are covered with three layers of porcelain: porcelain covered with metal, dental porcelain (gives color and shade to prosthetic restoration) and enameled porcelain (reconstructs the incisal edge of surrounding areas) [22]. The metal skeleton is obtained by different methods. The metal structure can be made of noble alloys, metal alloys such as Co-Cr or Ni-Cr, titanium-based alloys.

The main reason why this method of restoration is used is the ability to combine the mechanical strength offered by the metal structure and the aesthetic qualities of ceramic materials [23]. An important aspect in developing a dental prosthesis is related to the method of obtaining it. As previously mentioned, dental prosthetic works are obtained in the dental laboratory. The dominant method of metalworking was casting. Unfortunately, this technique has some drawbacks, one of which is the loss of material during its transition from liquid to solid phase. This aspect is very important and must be considered when preparing the part for casting. [24]

Co-Cr-based alloys are commonly used in dentistry due to their excellent corrosion resistance and good mechanical properties such as high rigidity [25]. However, Co-Cr alloys are difficult to treat and process due to too much hardness. In the case of casting, pores and other defects are present and visible in the structure of the cast element [26,27] Over time, new technologies for manufacturing dental prosthetic structures have been discovered and practiced [28,29]. This development came from the desire to obtain a durable prosthetic work with the best mechanical properties. In addition to aspects related to the characteristics of dentures, we also wanted to facilitate the work of dental technicians, even reaching 3D processing methods (Figure 1).

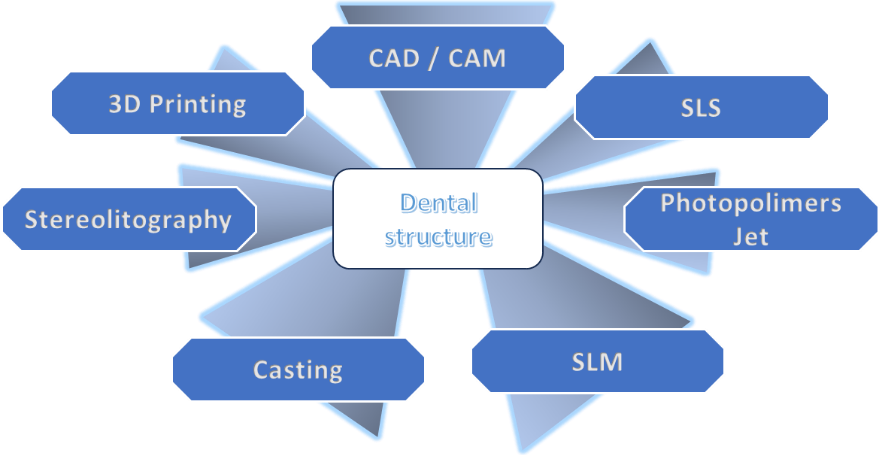

Figure 1. The main technologies for obtaining dental prosthetic structures used in dentistry

The purpose of this paper is to highlight the influence of the technology of obtaining dental prosthetic works on their structure and properties. Three metal skeletons of dental crowns made of Co-Cr-Mo alloy were developed during the work. The metal crowns were obtained using three different technologies: classical casting, milling and selective laser melting. At the same time, the experimental investigations carried out in this paper show that the technology of obtaining Co-Cr alloys can influence the structure and properties of materials. This statement raises a problem regarding the insertion of dental prosthetic works into the oral cavity in the form of resistance structures.

MATERIAL AND METHODS

The objective of the experimental research carried out within the present paper was to highlight the differences in properties of Co-Cr-based alloys obtained by three different technologies: classical casting, milling and selective laser melting. The comparative study looked at how the method of obtaining dental prosthetic structures influences their surface and microstructural properties. The materials used in the experimental program were represented by three experimental samples based on Co-Cr-Mo obtained by the methods listed above. The metal structures used as experimental samples were obtained in a dental laboratory. The The Co–Cr alloy was a commercial one (Heraenium® P-Kulzer GmbH, Hanau, Germany) with its chemical composition specified by the producer, as presented in Table 1.

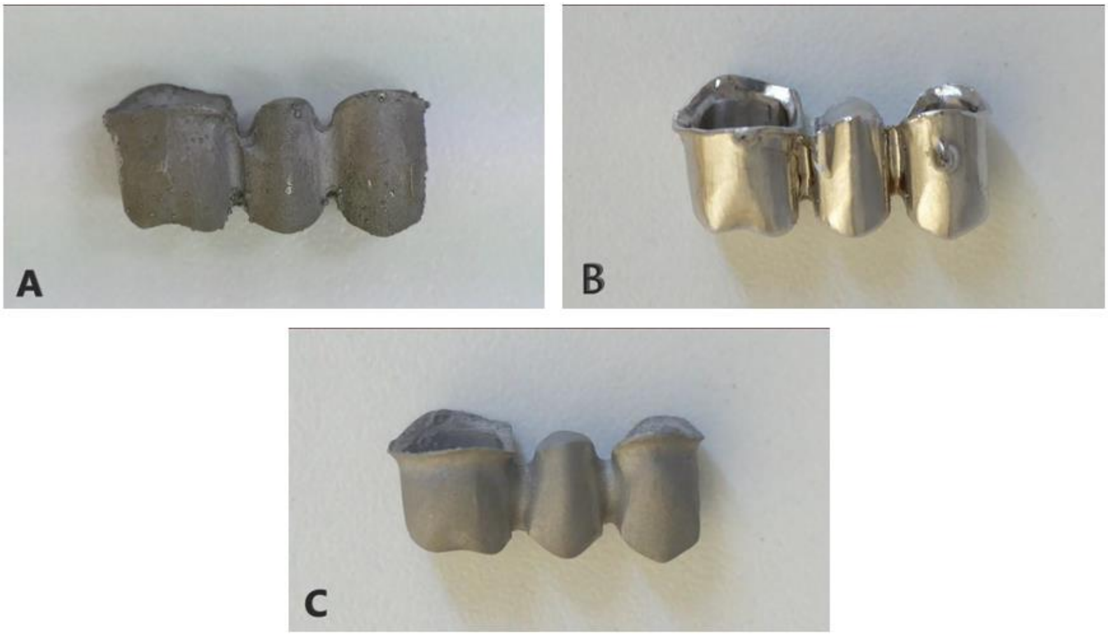

Figure 2. Appearance of experimental samples based on Co-Cr-Mo alloy obtained by: A. classical casting, B. milling, C. selective laser melting

Table 1. Chemical composition of the Co-Cr alloy used in the experimental procedure

Alloy	Element						
	Co	Cr	Mo	W	Mn	Si	N
Herenium	59.0	25.0	4.0	10.0	0.8	1.0	0.2

For the determination of surface properties, µCT investigations, stereomicroscopy investigations and Vickers microhardness test were used. For morphological and structural analysis, optical microscopy investigations were used.

The microCT analysis was performed using a Nikon MCT 225 CT scan. The pieces were positioned in a sponge, and the sponge was through in a p. This solution was chosen because the support into which the sample was inserted had to have a much lower density than the sample itself in order to easily remove the support in the analysis process and not to influence the sample surface. Because the experimental samples are made of Co-Cr metal alloy, it was chosen to use parameters with high values: Voltage – 165 kV; Intensity – 165 mA; Exposure time – 1s. To filter low-intensity rays, a 0.45 mm copper filter was used. High-intensity rays provide an image of the sample without reflections. Within the parameterization, the histogram values provided by the program were those that guided the values of the three parameters mentioned above. Thus, for the specified values, the minimum of the histogram was in the value of 2700, and the maximum in the value of 55000, this being, in theory, a perfect range. The track image has been corrected and visual errors have been eliminated. The acquisition is that the system divides a 360° rotation by 1440 projections, rotating the part. The procedure ends when all 1440 pictures have been taken. CT Pro.3D software was used for the reconstruction. A 16-bit format is used for maximum clarity. After the construction was completed, VG Studio Max 3:5 was used to analyse the scanned volume and porosities. To filter the results, 8 voxels were used as minimum pore value and maximum value 30 mm in diameter. In this way, both the largest and most small. The pores were included, a list is obtained containing all the pores included in that range, the total value of the combined pores, but also the percentage of pores in the matte surface.

To be analysed under an optical microscope, it was necessary for the experimental samples to go through several stages of preparation. The mechanical methods of preparing the surfaces of the experimental samples were as follows: Sectioning – The samples were cut to reduce the area to be embedded. Embedding – The parameters of the embedding process were: heating time 5 min, temperature 180°C, pressure 200 Pa. A red phenolic resin powder was used. Sanding and polishing – In order to be analysed under an optical microscope, the surfaces of experimental samples must have a "mirror" gloss.

To obtain this gloss, the experimental samples were first polished using metallographic silicon carbide (SiC) papers showing abrasive particles, then polished using diamond cloths and suspensions with particles up to 0.02 micrometers. The etching was made using Marble Reagent, a chemical attack for cobalt-based superalloys (10 g CuSO4, 50 mL HCl, 50 mL H2O) for 50-60 s with sample face up. A few drops of H2SO4 were added to the surface of the experimental samples during chemical attack to increase reagent reactivity.

The hardness tests were performed using a Vickers CV – 400 AAT micrometer (CV Instruments Europe BV). Since the samples were prepared in advance (they were embedded in cylindrical shape), this allowed the experimental samples to be placed on the support of the apparatus. The surface of the samples had to be flat, with a low roughness, allowing good observation in the measuring microscope. This was the main reason why the experimental samples went through the surface preparation processes presented above. The sample subjected to analysis was placed on the table of the device, the loading force was selected, the loading time, after which the load force was applied by pressing the START button. The parameters used in the experimental program for measuring Vickers microhardness were load force – 100gf; charging time – 20 s.

RESULTS AND DISCUSSIONS

The results of some experiments are presented as follows.

MicroCT: Following the attached images (Figure 3), but also analysing the values in the table 1, it can be concluded that the experimental sample obtained by classical casting has the largest volume of pores. The pore volume for the milled surface is smaller than the pore volume for the SLM surface, this being due to the mirror-gloss of the experimental sample obtained by milling.

Stereomicroscopy: As far as porous surfaces are concerned, it can be said that the milling method offers a glossy surface, without too many defects, compared to the surfaces of parts obtained by the other two technologies. In addition to surface images, measurements of experimental samples were made for comparative dimensional analysis (Figure 4).

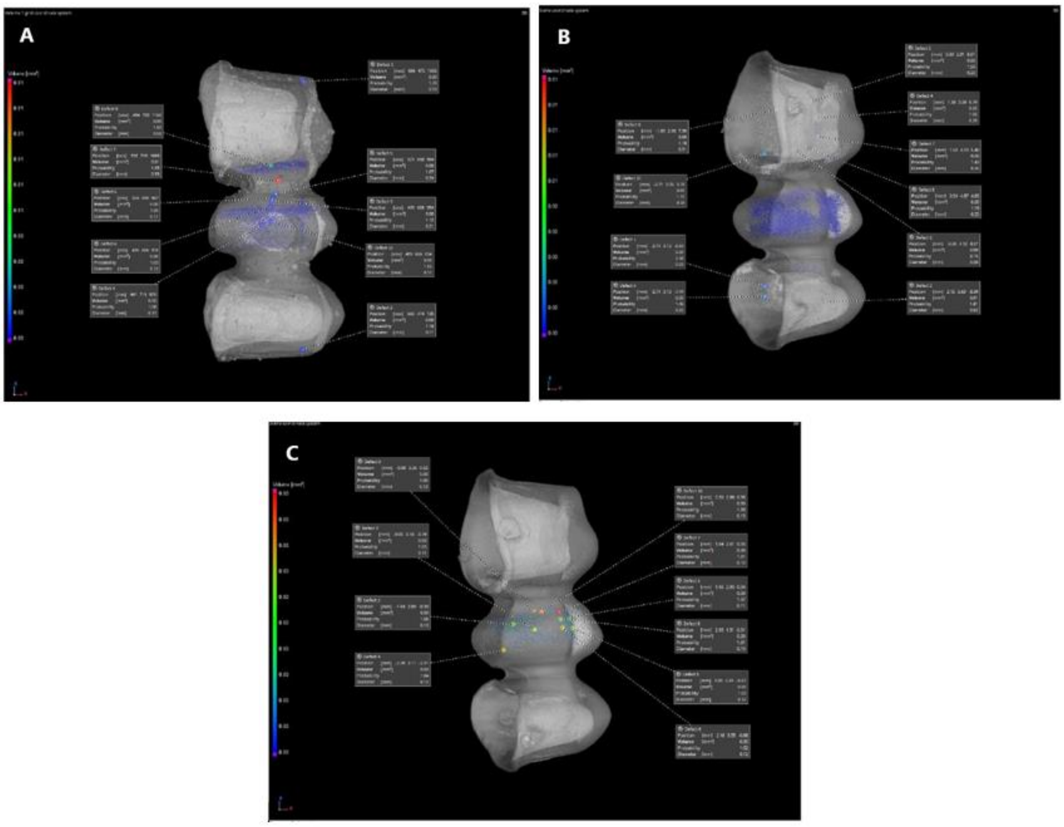

Figure 3. Total pore volume for the experimental sample obtained by: A. classical casting, B. milling, C. selective laser melting.

Table 2. Experimental results from porosity analyses performed on CT scans

Experimental sample	Total volume [mm^3]	Defects volume [mm^3]	Volume
Poured	612,27	0,39	
Milling	574,53	0,17	
SLM	567,25	0,28	

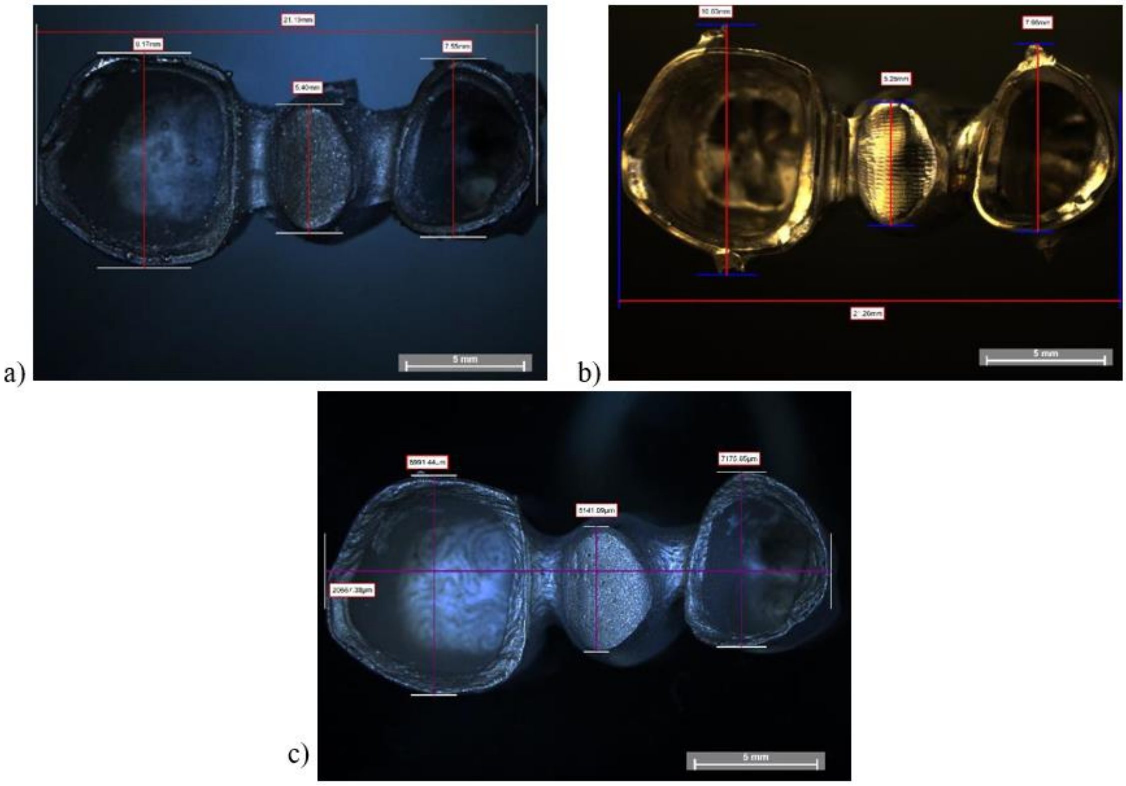

Figure 4. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c)selective laser melting – superior view

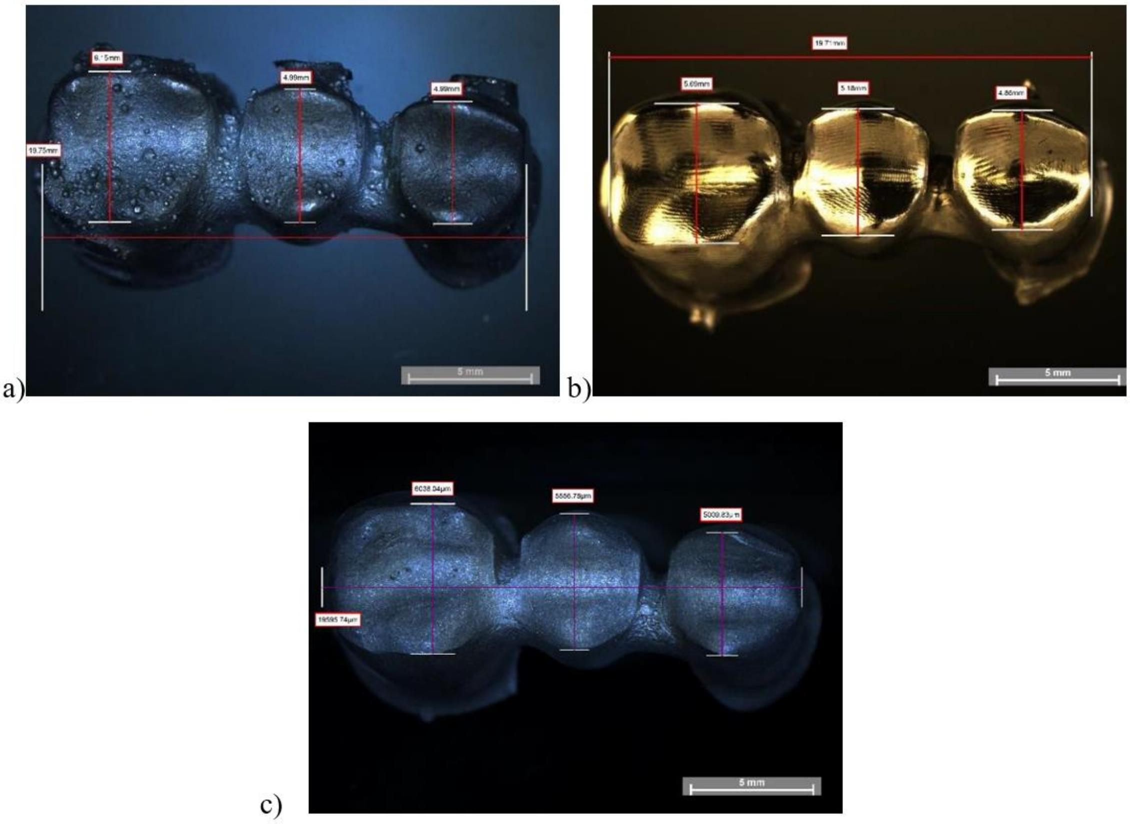

Figure 5. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c) selective laser melting – lower view

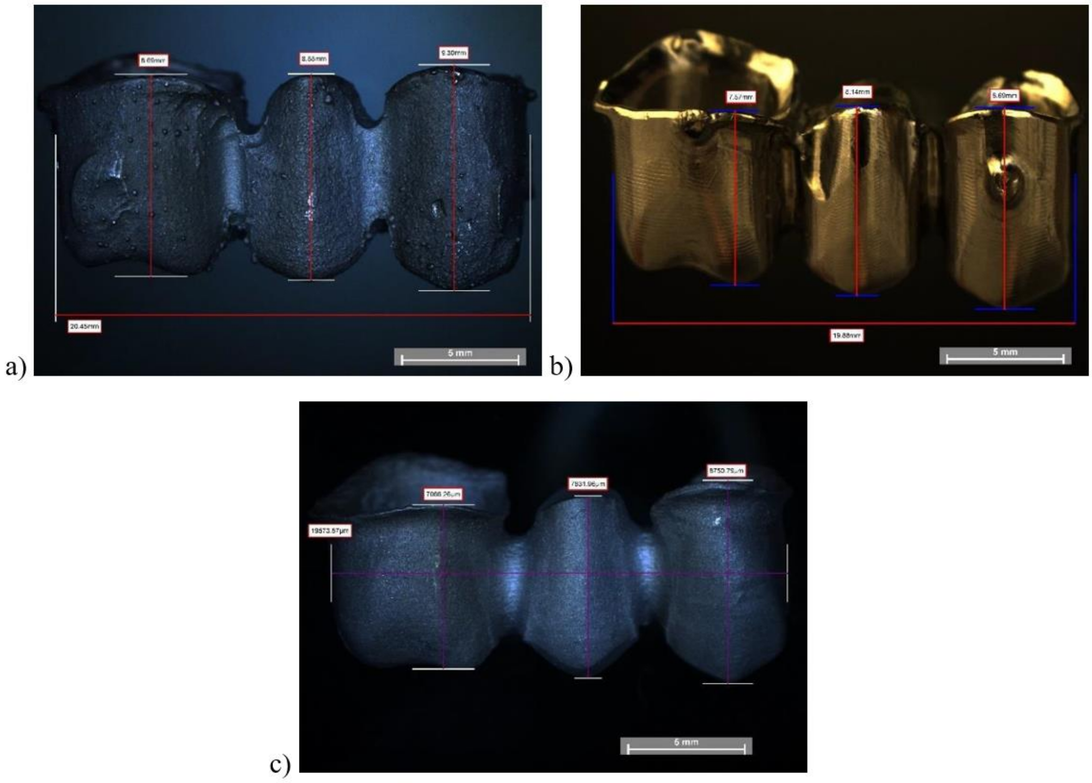

Figure 6. Macroscopic image representing the dimensional analysis of experimental samples obtained by: a) classical casting; b) milling; c)selective laser melting – side view

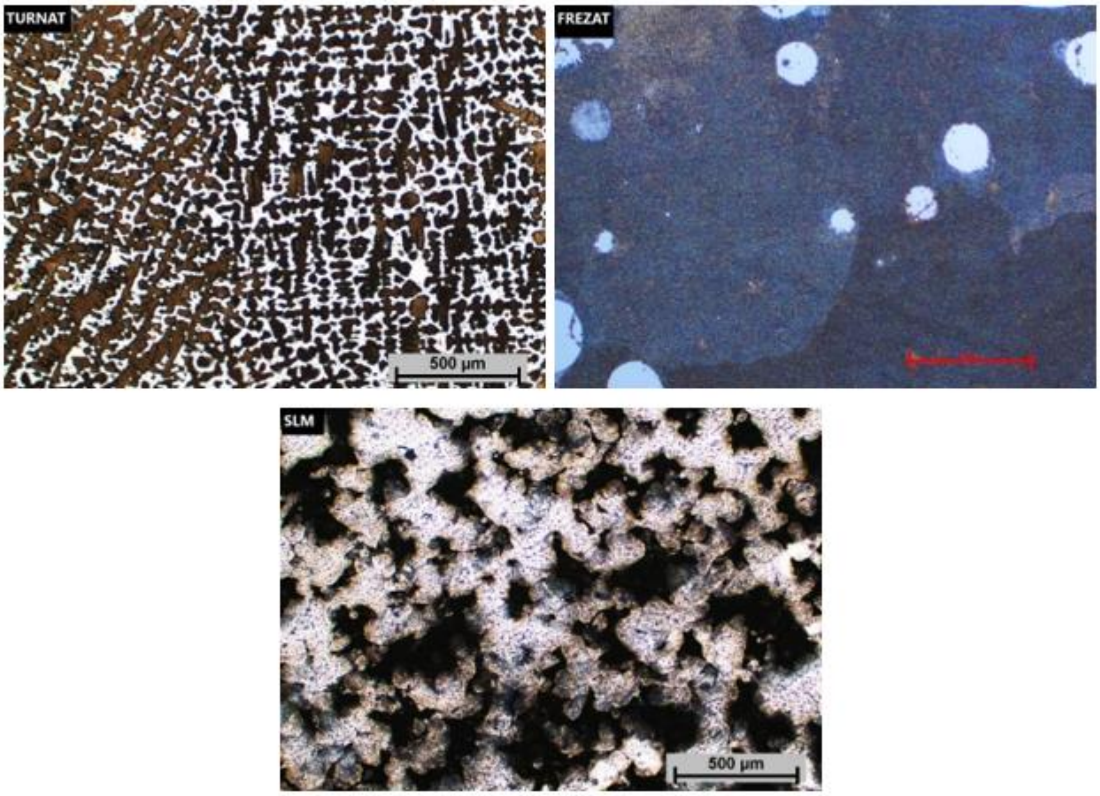

Figure 7. Optical microscopy images for experimental samples obtained by classical casting, milling and selective laser melting

Optical microscopy: The experimental samples obtained by laser milling and selective melting showed a microstructural homogeneity superior to those obtained by classical casting. This homogeneity can be explained by the complete, local melting and rapid cooling of the selective laser melting process.

The sample obtained by classical casting presents a dendritic microstructure with porosities and defects. Microstructural heterogeneity and the presence of large pores can generate stress, so that the bending strength of cast Co-Cr is low.

Milling technique improves alloy microstructure compared to casting, the samples being carried out under standardized industrial conditions. The microstructure of the experimental sample obtained by selective laser melting indicates the presence of dense structures with homogeneous granules, but with low porosities and defects. The homogeneous microstructure with lower internal porosity compared to the other two experimental samples may be a characteristic of corrosion resistance by decreasing the tendency of the material to corrosion in pitting. The rapid cooling rate during the selective laser melting process influenced transforming the γ phase into ε. A slightly higher phase peak was observed for ε the SLM experimental sample. This can be justified by the high laser power and the small distance between two sets of scanning line parameters. Selective laser melting technology showed superior microstructural homogeneity that positively affected hardness, as demonstrated in the following subchapter.

Hardness: After indenting the sample, the device automatically brings the measuring microscope lens above the trace left on the surface of the metallic material. The diagonals of the trace, d 1 and d2, were measured using the eyepiece. The diagonal of the trace was determined to be the arithmetic mean of the two diagonals, and the final value was displayed on the microhardmeter screen. For each experimental sample whose Vickers hardness was determined, 10 measurements were made. For hardness values, decimal places have been excluded. The arithmetic mean of the 10 measurements and the standard deviation were calculated (table 2).

Hardness values differ depending on the method of obtaining experimental samples. The sample obtained from cast Co-Cr alloy has the lowest hardness values, while the sample obtained from laser-melted Co-Cr alloy has the highest hardness values, representing even double the values of the casting.

The experimental sample obtained from milled Co-Cr alloy has hardness values much higher than those of the cast sample. At the same time, it also exhibits the largest standard deviation.

The difference in Vickers hardness values of the experimental samples is highlighted and can be visualised in figure 8.

A high hardness value indicates good resistivity and durability properties of the Co-Cr-based alloy. The high hardness favours the metal-ceramic interaction within the ceramic cladding of dental prosthetic works made of Co-Cr alloy. The superior resistance of the metal-oxide interaction and the reduction of the elimination of metal oxides in the oral cavity following the implantation of a prosthetic work made of Co-Cr alloy is ensured by a high hardness.

Analysing the graph illustrated in figure 8, it can be said that the Co-Cr alloy manufactured by selective laser melting meets the requirements of dental clinics, the dental prosthetic work being preferred by dentists due to the properties listed above.

Table 2. Vickers hardness values for experimental samples

Det. No.	CASTING	MILLING	SLM
1	213	424	434
2	201	479	446
3	181	418	426
4	194	484	493
5	208	469	424
6	211	273	499
7	212	318	506
8	192	370	499
9	178	325	440
10	219	337	453
Intercede	200,90	389,70	462,00
STD	14,13	75,46	33,30
Result	**200.9±14.13**	**389.7±75.46**	**462±33.3**

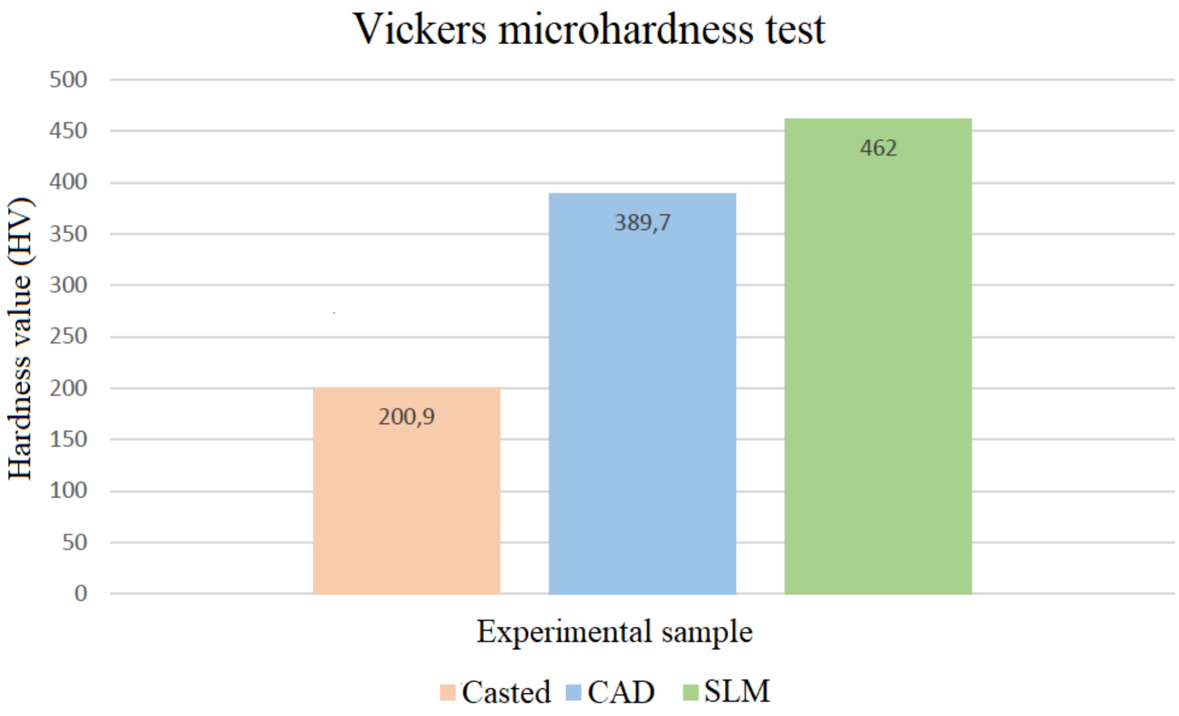

Figure 8. Graph of Vickers hardness measurements carried out within the experimental program

CONCLUSIONS

1. It is known that the improved surface and microstructural properties of Co-Cr-based dental alloys are closely related to the longevity of the prosthesis in the clinical scenario and depend largely on how they are manufactured.
2. Referring to macroscopic results, experimental samples obtained by milling and selective laser melting have surface properties superior to those obtained by classical casting, where the surface has cast defects and a large volume of pores.
3. From the perspective of dental rehabilitation, the characteristics used to manufacture metal structures based on Co-Cr alloy by selective laser melting, allow the realization of a microstructure with lower porosity, which leads to high mechanical and electrochemical properties necessary for the longevity of dentures.
4. In terms of microscopic results, the microstructure of the experimental sample obtained by selective laser melting is more homogeneous, with significantly lower porosities than the other two experimental samples. It was pointed out that, on the surface of alloys manufactured by selective laser melting method, the adhesion of ceramics to cladding is better than on the surface of cast structures. The main reason for the adhesion difference is the morphology of the casting structure caused by the large volume of pores.
5. The high hardness of the sample obtained by selective laser melting has a positive impact on the properties of the oxide film formed in the oral cavity. This improves the value of metal-ceramic resistance and results in a decrease in the release of metal ions through corrosion degradation, which is an imperative property for dental alloys, because the oral cavity is an aggressive environment for dental materials. This decrease is represented by the good corrosion resistance of Co-Cr-based alloys obtained by selective laser melting.
6. The fact that experimental samples obtained by classical casting have the lowest hardness value suggests that cast dental prosthetic works will not have good corrosion resistance, so they will not last over time.
7. Within the limits of the presented study, it can be stated that the selective melting technology of Co-Cr-Mo alloys is preferred in dental restorations due to improved properties, longevity, but also good interaction with the oral environment.
8. In future studies and research, the improvement of the surfaces of experimental samples based on dental alloy Co-Cr-Mo will be pursued in order to a good adhesion with plating ceramics in metal-ceramic prosthetic works.

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