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COMPARATIVE ANALYSIS OF DIFFERENT DENTAL IMPLANTS – PART I: THE VARIATION OF CHEMICAL COMPOSITION AND MICROSTRUCTURE

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Abstract: Medical alloys are used in the medical field to create devices and implants due to their specific properties, such as biocompatibility, corrosion resistance, and suitable mechanical properties. The use of these alloys in modern medicine has revolutionized many procedures and treatments, enabling the creation of more durable and compatible implants with the human body. The choice of a specific type of alloy depends on the specific application and the necessary properties to ensure the long-term success of the implant or medical device. In this paper, possible detrimental effects caused by chemical and microstructural inhomogeneities of implants were studied. Three types of dental alloys often used in practice were investigated, namely: NiCrMoSiVCuFe, NiCrMoSiFeAlMgZn and CuAlNiFeMgZnSi. By correlation of SEM microscopy with the EDS data regarding the elemental compositions it results that there is a chemical inhomogeneity at the level of the investigated samples and structural inhomogeneity at the micron scale. These obtained data represent an essential step in understanding and improving implant performance and their impact on durability.

Keywords: biomedical alloys, dental implants, chemical composition, SEM

1. INTRODUCTION

Medical alloys are used in the medical field to create devices and implants due to their specific properties, such as biocompatibility, corrosion resistance, and suitable mechanical properties. The use of these alloys in modern medicine has revolutionized many procedures and treatments, enabling the creation of more durable and compatible implants with the human body. The choice of a specific type of alloy depends on the specific application and the necessary properties to ensure the long-term success of the implant or medical device [1–2].

The alloy containing cobalt, chromium, and molybdenum is mainly used for orthopedic implants, hip and knee prostheses due to its durability and excellent wear resistance. The nickel–titanium alloy, known for its shape memory properties and super–elasticity, is used in stents, guide wires, and other medical devices that require flexibility and the ability to return to the original shape. Al–Mg–Si alloys are used in temporary applications such as support rods or orthopedic fixation plates [3]. These alloys have low density and good mechanical properties but are not intended for permanent implants due to long-term biocompatibility issues [1, 2, 3].

Zinc alloys can include small amounts of aluminum and magnesium to adjust the resorption rate and mechanical properties. Zinc is being investigated for use in resorbable implants due to its biocompatibility and ability to be absorbed by the body. Dental alloys based on Ni–Cr–Mo (nickel, chromium, molybdenum) are frequently used in dentistry due to their excellent mechanical properties, corrosion resistance, and biocompatibility [5]. These alloys are often used to make crowns, bridges, and other dental structures due to their combination of hardness, flexibility, and dimensional stability [4–6]. Nickel contributes to the hardness and strength of the alloys, making them durable and wear resistant. Nickel also allows for precise adjustment and adaptation of dental devices. Chromium forms a protective oxide layer on the surface of the alloy, preventing corrosion and maintaining the structural integrity of the dental device in the oral environment. Chromium contributes to the alloy's biocompatibility, reducing the risk of allergic reactions and irritations. Molybdenum improves corrosion resistance, increases the hardness of the alloy, and adds dimensional stability, maintaining the shape and function of dental devices in the long term [5, 6].

The main advantage of dental alloys based on Ni–Cr–Mo is their excellent corrosion resistance. Chromium and molybdenum form a protective oxide layer on the surface of the alloy, preventing corrosion in the often acidic and moist oral environment. Hardness and mechanical strength are major

advantages, with nickel and molybdenum giving the alloys superior hardness and mechanical strength, allowing them to withstand masticatory forces and daily wear [7, 8]. Dimensional stability is another advantage, as Ni–Cr–Mo alloys maintain the shape and size of dental devices over the long term, ensuring a precise and durable fit. Biocompatibility is an essential advantage, with chromium and molybdenum contributing to the alloys' biocompatibility, reducing the risk of allergic reactions and irritations in patients. Additives such as tantalum and titanium can further improve biocompatibility [9–10].

Processing versatility is an advantage that allows easy processing and precise casting into complex shapes, facilitating the manufacture of detailed and customized dental devices. Compared to other high-performance alloys, Ni–Cr–Mo alloys are relatively affordable, offering good value for money for dental applications. High-temperature resistance allows the alloy to maintain its mechanical properties and corrosion resistance even at high temperatures, which is beneficial in manufacturing processes and clinical use [11].

Ni–Cr–Mo dental alloys are versatile and can be used to manufacture dental crowns and bridges. Ni–Cr–Mo alloys are used for making crowns and bridges due to their wear resistance and masticatory forces. They can also be used as bases for dental prostheses. These alloys are ideal for the bases of dental prostheses, offering long-term stability and durability. Ni–Cr–Mo alloys can be used in the manufacture of dental implants due to their biocompatibility and corrosion resistance. Orthodontic wires and other orthodontic devices can be made from Ni–Cr–Mo alloys due to their flexibility and hardness. Ni–Cr–Mo alloys are used in the manufacture of complex dental restorations, such as inlays and superstructures for implants [8, 9, 10, 14].

Ni–Cr–Mo dental alloys offer numerous advantages, including excellent corrosion resistance, superior hardness and mechanical strength, dimensional stability, and biocompatibility. Their versatility in use allows these alloys to be applied in a wide range of dental devices, from crowns and bridges to implants and orthodontic devices. These characteristics make Ni–Cr–Mo alloys a top choice in dentistry for manufacturing durable and efficient dental devices [9].

Cu–Al–Ni medical alloys are shape memory alloys (SMAs) with interesting applications in the medical field due to their unique properties. These alloys can return to a predetermined shape when heated above a certain transition temperature [6, 7, 11]. This phenomenon is known as the shape memory effect and is exploited in various medical applications. The main advantages of Cu–Al–Ni alloys are shape memory, super-elasticity, corrosion resistance, and biocompatibility. These alloys can be deformed at low temperatures and then return to their original shape when heated. The ability to withstand large deformations and return to the original shape without permanent deformation. Important in biological environments where contact with body fluids can damage materials [6, 7, 12]. They are relatively biocompatible, making them suitable for implants and other medical devices. Medical applications of Cu–Al–Ni alloys include cardiovascular stents, orthodontic wires, orthopedic implants, and minimally invasive devices. SMAs are used to make stents that can be introduced into blood vessels in a compact form and then expanded at body temperature to keep the vessels open. The shape memory properties and super-elasticity are used to create wires that apply a constant force to the teeth to correct alignment. They are used to fix fractured bones and stabilize joints. Used in procedures that require instruments that can be inserted in a compact form and then expanded or shaped in situ [6, 7, 13].

Cu–Al–Ni shape memory alloys offer innovative and effective solutions in the medical field, with the potential to significantly improve treatments and minimally invasive interventions. Continuing research in this field is crucial to expand the use and optimize the performance of these materials [3, 14].

Dissociation of medical alloys, also known as biodegradation or biocorrosion, is a crucial process that involves the degradation of metallic materials used in implants due to interaction with the biological environment of the human body. This process can occur for various reasons, including chemical and electrochemical reactions, mechanical stress, and friction. The results of this process may include the release of metal ions, particles, and corrosion products into the surrounding tissues, which can affect the durability of the implant and the patient's health [14].

Dissociation of medical alloys refers to the processes by which the component materials of an alloy can separate or react in the human body environment, thus affecting their integrity and performance. It is a phenomenon of great importance in the field of biomaterials because it can influence the biocompatibility, durability, and safety of implanted medical devices. Causes and mechanisms of dissociation of medical alloys can include electrochemical or galvanic corrosion, pitting and crevice corrosion, mechanical wear (friction and abrasion, mechanical fatigue), and chemical degradation (reactions with body fluids, oxidation). In the body environment, metallic alloys are exposed to body fluids, which are ion conductors and can induce electrochemical reactions. This can lead to metal corrosion, especially in areas where the passive oxide layer is compromised. When two different metals are in direct contact in the human body, galvanic reactions can occur. One of the metals may act as an anode and the other as a cathode, accelerating the corrosion of the anodic metal. Pitting and crevice corrosion is a localized form of corrosion that occurs in areas where oxygen is limited, such as in cracks or under biological deposits. This can lead to rapid perforation of the material. Mechanical contact between alloys or between the alloy and body tissues can cause wear and dissociation of materials. This is common in artificial joints or other orthopedic implants [12, 13, 14]. Cyclic stress and repeated loads can cause microscopic cracks and ultimately dissociation of alloys. Alloys can react with the chemical components of body fluids, such as proteins, enzymes, and ions. For example, chloride ions in sweat or body fluids can accelerate the corrosion process. Prolonged exposure to oxygen can cause oxidation of metallic surfaces, which can affect material integrity. Effects of dissociation on biocompatibility can include the release of metal ions (toxicity, inflammation, and immune reactions) and the formation of corrosion products (biodegradability, structural integrity). Dissociation of alloys can release metal ions into the surrounding tissues, which can be toxic. For example, nickel ions can cause allergic or inflammatory reactions. Released metal ions can cause inflammatory and immune reactions, affecting implant integration and causing discomfort or pain for the patient. Some corrosion products may be biodegradable and can be absorbed or excreted by the body, but others may form solid deposits that can cause local inflammation. The formation of corrosion products can affect the structural integrity of the implant, leading to weakening or fracture [12, 13, 14].

2. MATERIALS AND METHODS

The main objective is to highlight possible detrimental effects caused by chemical and microstructural inhomogeneities of implants. Possible effects can include electrochemical corrosion due to different potentials of adjacent phases relative to the implanted environment, pitting corrosion at phase interfaces that can generate particle disaggregation and emission of elements and oxides in the implanted area, or toxic ionic dissolution. Conducting a study on medical prostheses to correlate the obtained data with dissociation phenomena and their impact on durability is an essential step in understanding and improving implant performance. For this study, the following aspects were considered: identifying types of prostheses (detailed recording of the characteristics of each prosthesis, including patient history and duration of implant use) and materials used, and analyzing dissociation phenomena. Three types of prostheses were analyzed. The composition of the prostheses, the history, and the number of years of the implant are presented in Table 1.

Table 1. Representative data for the analyzed samples

Sample code	Alloy type	History	Operating life [years]
Sample 1a, b	NiCrMoSiVCuFe	It comes from a 65-year-old patient	15
Sample 2	NiCrMoSiFeAlMgZn	It comes from a 47-year-old patient	11
Sample 3	CuAlNiFeMgZnSi	It comes from a 69-year-old patient	21

The metallographic preparation of samples for microstructural analysis was an essential and complex process involving a series of rigorous steps to obtain precise and relevant results. The aim of this procedure was to create representative samples that maintained the integrity of the original material structures. Choosing a representative portion of the base material was crucial to ensure that the analysis accurately reflected the structure of the entire material. The samples were cut with a precise cutting device (metallographic cutting machine OG-1), which minimized deformation and excessive heating, thus avoiding microstructural alteration. The samples were cut longitudinally and then embedded in

epoxy resin for fixation and to facilitate subsequent handling. The embedding was done hot, and the mounted samples were left to fully polymerize to obtain a solid and stable base. After polymerization, the embedded samples were ground using coarse grit abrasive paper to remove the uneven surface and achieve the necessary flatness. Fine grit abrasive paper was used in successive steps to further refine the sample surfaces. The samples were polished with aluminum oxide suspensions to obtain a surface as smooth as possible, free from visible scratches. The final polishing was done with a fine colloidal silica suspension, resulting in mirror-like surfaces, essential for clear microstructural observations. The samples were carefully cleaned to remove any traces of abrasive or polishing material that could interfere with the analysis.

Sample 1 was cut longitudinally and embedded for analysis, resulting in two samples, namely 1a and 2a. Sample 2 and Sample 3 were embedded without being cut in section.

The investigated samples have complex geometries that were initially obtained by casting alloys in molds and subsequent processing by manual grinding.

The microstructural analysis was performed using the EBSD technique, using a TESCAN VEGA II—XMU scanning electron microscope (SEM) provided with a BRUKER eFlash1000 EBSD detector, and also through this device the chemical compositions of the studied alloys were determined.

3. RESULTS AND DISCUSSION

The samples presented in Figure 1 were investigated by scanning electron microscopy (SEM) and chemically analyzed by point EDS spectrometry. Three representative positions were selected, i.e. in the center, inner edge, and outer edge. Table 1 shows the chemical compositions of sample 1.1a in atomic percentages and mass percentages of the detected elements.

Table 2. The result of the EDS analyzes performed on the Sample 1.a

Element [%]	[At. %]			[Wt. %]		
	Inner edge	Center	Outer edge	Inner edge	Center	Outer edge
Ni	61.36	61.39	61.37	56.16	56.53	55.85
Cr	28.57	28.54	28.54	23.16	23.29	23.01
Mo	3.97	4.04	3.96	5.93	6.08	5.90
Si	4.96	4.85	4.99	2.17	2.14	2.17
V	0.38	0.38	0.37	0.33	0.33	0.31
Cu	0.21	0.19	0.20	0.23	0.26	0.22
Fe	0.29	0.35	0.4	0.38	0.17	0.17

As it results from Table 1, Sample 1.a is made of Ni base alloy (56 wt. %) with high content of Cr (23 wt. %) and significant contents of Mo (6 wt. %) and Si (2 wt. %). The contents of V, Cu and Fe are minor. In principle, the dental alloy of this type must have a homogeneous elemental composition to give a uniform behavior of the implant. Unfortunately, the EDS studies reveal a significant chemical inhomogeneity of the investigated implants, as shown in Figure 2 where it is shown the graphical variations of the element's chemical composition. The chemical inhomogeneity of the implant is also confirmed by the SEM images related to the EDS microanalyses, which reveal a nodular microstructure with inclusions of variable shapes (vermicular, nodular, fibrous) of micron size.



Figura 1. The overall picture of the investigated samples

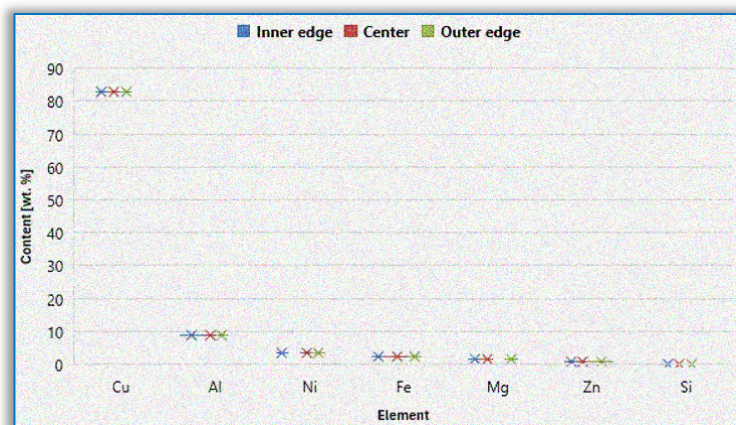


Figure 2. The variation of the chemical composition in the three analysis points for Sample 1.a

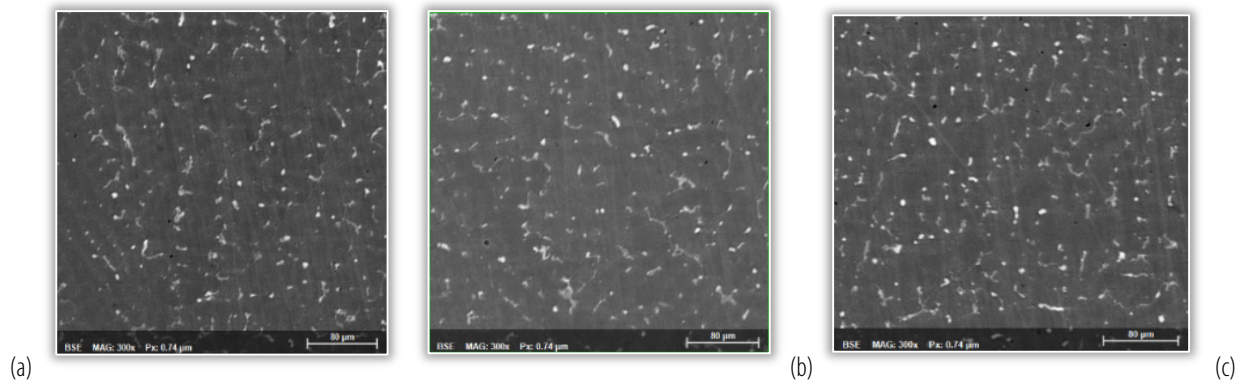


Figure 3. SEM images of Sample 1.a: a) Inner edge b) Center c) Outer edge

Table 3. The result of the EDS analyzes performed on the Sample 1.b

Element [%]	[At. %]			[Wt. %]		
	Inner edge	Center	Outer edge	Inner edge	Center	Outer edge
Ni	61.47	61.35	61.33	56.09	56.25	56.14
Cr	28.67	28.75	28.64	23.17	23.35	23.22
Mo	4.24	4.24	4.29	6.31	6.36	6.43
Si	4.90	4.91	5.01	2.13	2.15	2.19
V	0.33	0.33	0.33	0.26	0.26	0.26
Cu	0.26	0.36	0.24	0.25	0.26	0.24
Fe	0.12	0.13	0.12	0.10	0.12	0.10

The data presented in Table 3 attests to the fact that sample 1b is compatible with sample 1a from the point of view of the elemental composition, but has slightly different compositions, i.e. Ni base alloy (56 wt. %) with a similar content of Cr (23 wt. %) and slightly different contents of Mo (6.5 wt. %) and Si (2.2 wt. %). The contents of V, Cu and Fe are minor and are similar to sample 1.a. The EDS investigations also show in this case a significant chemical inhomogeneity of the investigated implants, as can be seen from Figure 4 where is shown the graphical variations of the elements chemical composition are shown in Figure 4.

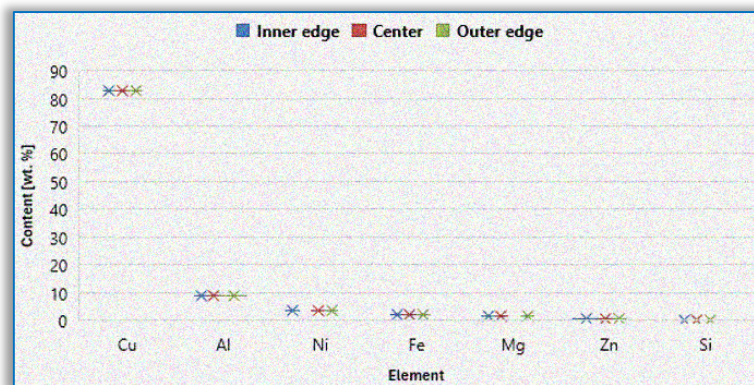


Figure 4. The variation of the chemical composition in the three analysis points for Sample 1.b

The microstructure of sample 1.b revealed by the SEM images (Figure 5) differs in texture i.e. it shows periodic microstructural bands and an aligned "linear array" type distribution of what appear to be predominantly vermicular compounds or inclusions. And in this case, SEM investigations are combined with EDS analysis in the sense of attesting a chemical and microstructural inhomogeneity that can have detrimental consequences on the behavior of the implant in the oral cavity.

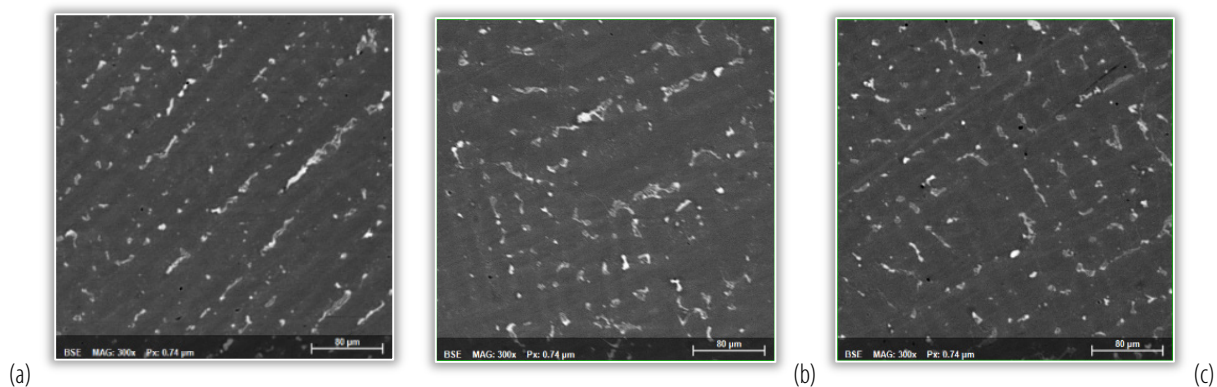


Figure 5. SEM images of Sample 1.b: a) Inner edge b) Center c) Outer edge

Table 4. The result of the EDS analyzes performed on the Sample 2

Element [%]	[At. %]			[Wt. %]		
	Inner edge	Center	Outer edge	Inner edge	Center	Outer edge
Ni	61.28	61.12	61.17	56.28	55.64	56.04
Cr	28.60	28.78	28.69	23.27	23.21	23.28
Mo	4.38	4.40	4.40	6.58	6.54	6.58
Si	3.47	3.48	3.51	1.52	1.51	1.53
Fe	1.40	1.41	1.41	1.23	1.21	1.22
Al	0.38	0.38	0.38	0.16	0.15	0.16
Mg	0.40	0.43	0.44	0.17	0.16	0.16
Zn	0.0011	0.003	0.0009	0.0017	0.003	0.0016

Sample 2 is considered to belong to the class of dental alloys NiCrMoSiFeAlMgZn. As it results from Table 4, Sample 2 is made of a Ni-based alloy (≈ 56 wt. %) with a content of Cr (23 wt. %) and Mo (≈ 6.6 wt. %) similar to the alloy from which Sample 1 was made, but with lower contents of minor alloying elements, respectively Si (≈ 1.5 wt. %), Fe (≈ 1.2 wt. %), Al (≈ 0.2 wt. %), Mg (≈ 0.2 wt. %) and Zn (≈ 0.002 wt. %). And in this case, the EDS investigations show that the sample is affected by a significant chemical inhomogeneity, as can be seen from Figure 6 where is shown the graphical variations of the elements chemical composition.

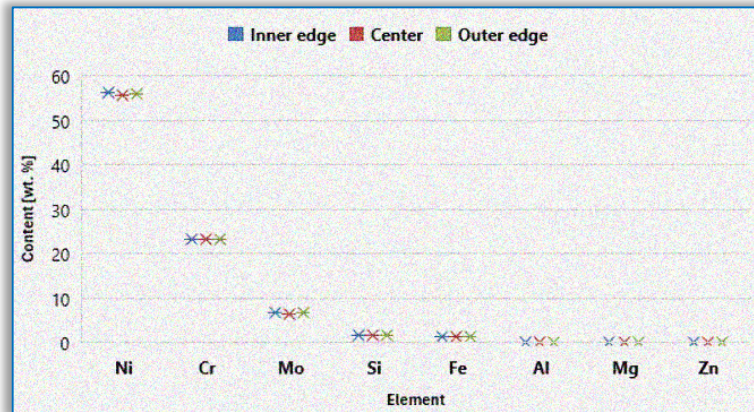


Figure 6. The variation of the chemical composition in the three analysis points for Sample 2

The microstructures of Sample 2 (Figure 7) show a cellular aspect in which the grid of cells is marked by inclusions or compounds that suggest their distribution at the edges of the grains. The microstructural cells have an apparent diameter of about $30 \mu\text{m}$. And in this case there are reasonable suspicions that the chemical inhomogeneity combined with the microstructural inhomogeneity can lead to detrimental effects regarding the reduction of the life time of the implant.

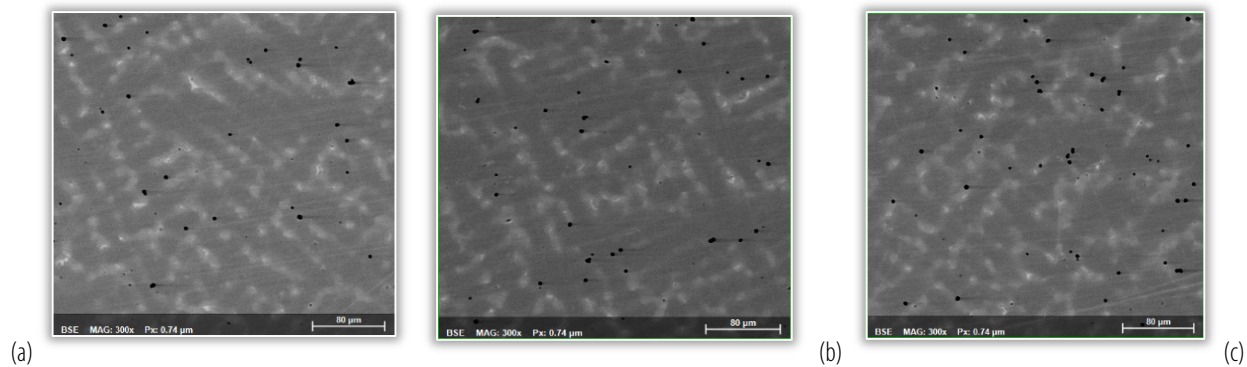


Figure 7. SEM images of Sample 2: a) Inner edge b) Center c) Outer edge

Table 5. The result of the EDS analyzes performed on the Sample 3

Element [%]	[At. %]			[Wt. %]		
	Inner edge	Center	Outer edge	Inner edge	Center	Outer edge
Cu	73.34	73.12	73.08	82.91	82.75	82.74
Al	18.37	18.53	18.59	8.82	8.90	8.94
Ni	3.38	3.42	3.45	3.53	3.58	3.60
Fe	2.22	2.26	2.26	2.20	2.25	2.25
Mg	1.62	1.58	1.55	1.58	1.55	1.51
Zn	0.64	0.65	0.63	0.75	0.76	0.73
Si	0.43	0.44	0.45	0.22	0.22	0.22

As it results from Table 5, Sample 1 is made of Cu base alloy (≈ 83 wt. %) with moderate content of Al (≈ 9 wt. %) and significant contents of Ni (≈ 3.6 wt. %), Fe (≈ 2.2 wt. %), Mg (≈ 1.6 wt. %), Zn (≈ 0.8 wt. %) and Si (≈ 0.2 wt. %). This type of dental alloy has a hyper-entropic alloy character that involves a complex

solidification with aspects of dendritic kinematics. The EDS investigations carried out in 3 representative points reveal chemical inhomogeneity in this case as shown in Figure 8.

As expected, the SEM images reveal complex, intricate microstructures that arise in the type of solidification with inhomogeneous germination that generates dendritic growths. Dendritic growth implies segregation of elements at the level of the melt and implicitly chemical inhomogeneity superimposed on microstructural inhomogeneity at the micrometric scale, as can be clearly seen in Figure 9.

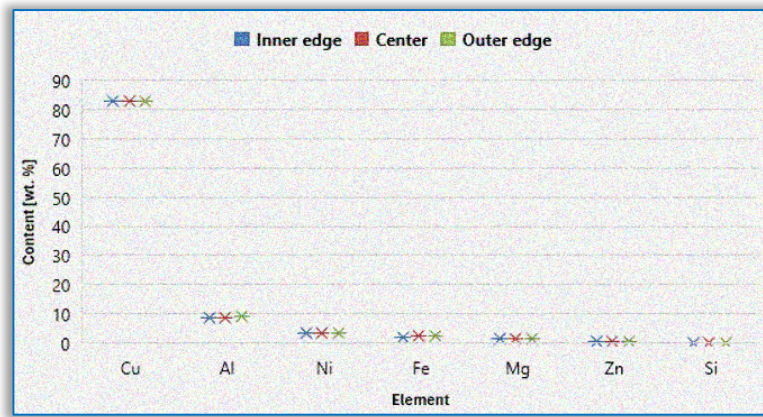


Figure 8. The variation of the chemical composition in the three analysis points for Sample 3

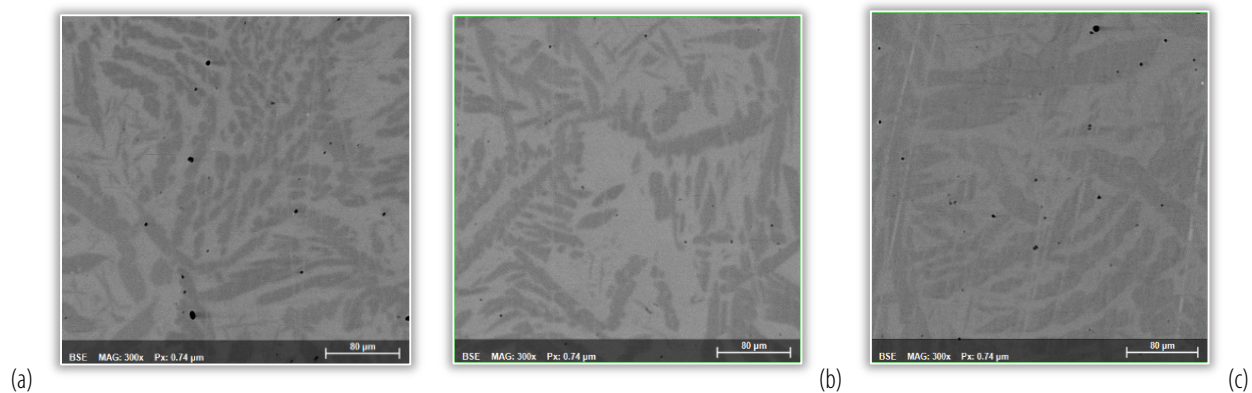


Figure 9. SEM images of Sample 3: a) Inner edge b) Center c) Outer edge

4. CONCLUSIONS

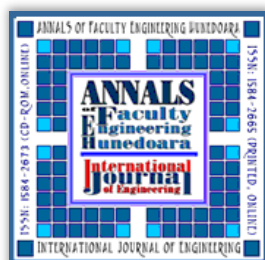
The results of the SEM and EDS investigations on the explants are important because the sampling is an action with deontological implications, respectively this type of investigation is not abundant in the specialized literature. From the optical analysis of the microstructures revealed by SEM microscopy and by correlation with the EDS data regarding the elemental compositions of NiCrMoSiVCuFe, NiCrMoSiFeAlMgZn and CuAlNiFeMgZnSi alloys, it results that there is a chemical inhomogeneity at the level of the investigated samples which correlates with the structural inhomogeneity at the micron scale. Chemical and microstructural inhomogeneities can have detrimental effects on the behavior of prostheses in the implanted environment that can lead to patient discomfort and shorten the life time of the implant.

Aspects revealed in this paper must be analyzed more deeply both from the point of view of biomaterial science and the interaction at the implant–tissue interface seen through the lens of the clinical dentist. In this sense, detailed investigations will be carried out using other techniques such as FTIR, XRF and electrochemical tests to investigate the bioelectrical behavior of these types of implants.

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