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Abstract

The composition of the cobalt alloys contains only noncytotoxic elements (Cr, Si, and Mo) that ensure its biocompatibility, and consequently, the development and proliferation of cells at the implant/tissue interface. The cobalt alloy has an original composition with silicon addition and the proportion of the alloying elements was established so as to ensure a high biocompatibility and adequate physical-chemical characteristics for it to be used in various applications. Silicon is known to be a metal with a high biocompatibility; it can replace noble/non-noble metals in commercial alloys, thereby excluding the occurrence of any toxic corrosion products. We chose it as an alloying element because it confers good casting properties, has double role as hardener and oxidant, ensures an increase in the resistance to tear, and offers a proper fluidity in the liquid phase.

Keywords: cobalt, elaboration, microstructural characterization, tensile tests, electrochemical impedance spectroscopy

1. Introduction

This chapter aims to provide in-depth study and analysis of various synthesis methods, processing techniques, and characterization of cobalt that will lead to its increased application in the technology. The information provided is addressed to engineering professionals, medicine, manufacturers, and material scientists.

Our research is a cobalt-based alloy with an original composition that includes nontoxic and nonallergic Si as an alloy component, which endows the alloy with a high chemical resistance and a high biocompatibility. Our cobalt-based alloy is intended for medical applications.
Metallic dental alloys usually have very good durability, mechanical resistance, and biocompatibility characteristics. Dental alloys became more diverse in time, depending on the technology applied and the characteristics required for a specific type of dental prosthesis.

Cobalt-based alloys are frequently used to make the metallic framework of prostheses or to refurbish deteriorated ones due to their biocompatibility, their outstanding mechanical resistance, and their higher elastic modulus compared to other conventional alloys. The elastic modulus of titanium is inferior compared to that of cobalt-based alloys, its mechanical resistance is low, and the size of the prostheses made from it is larger.

The global concern to improve the classical technologies of execution both of the implants, and also the biomaterials from which are made, aims in the promotion of a new multifunctional implants, with best performances for a long time. About the materials for implants, the actual tendencies both in medical practice and also in research follow the utilization of materials with advanced biological and biomechanical characteristics, with advantages both in terms of biocompatibility with human tissue, and also the avoidance the risks of the infections or the rejection after implanting [1].

The classical alloys used such as biomaterials, the stainless steels, and titanium base alloys present disadvantages like elasticity modulus greater than biological materials (bone, conjunctive tissue), small corrosion resistance, or low biocompatibility with human tissues.

The most recent researches in medical domain show that titanium is a material with high biocompatibility, but his alloying with various metals to improve the mechanical characteristics is not always beneficial. It is the case of vanadium and nickel, which are classified as toxic elements, with carcinogen effects and aluminum, which are present in most of titanium commercial alloys, and which has shown a causal relationship with neurotoxicity [2].

The new type of implant is the zirconium and it presents numerous advantages compared to titanium; these affirmations have been sustained by dental medics. The zirconium implants are integrated better in soft tissues (in gingival), present high resistance, look like natural teeth, do not produce allergies, do not lead electrical current and heat, and are more easily accepted by human body, but the bigger disadvantage is about the price, his utilization is thus limited.

Cobalt-base alloys, like Vitalium, Vicalloy, “C” alloy, Wironit Extrahart, became the most used in manufacturing medical implants. The presence of chrome, silicon, and molybdenum has made the cobalt-base alloy to be considered the most healthy, safety, nontoxic, and nonallergic alloys, the fact demonstrated by laboratory analyses. These alloys present good cast properties, corrosion resistance, nonallergic properties, compatibility with human tissue, and high viability of cell, des-oxidation role.

Actually, researches have been developed in United States of America, European Union, Japan and China about the influence of the presence of cobalt alloying elements on the fibroblasts and osteoclasts cells from the appropriate tissue soft implants, more precisely at the interface implant/tissue [3]. The obtained results highlighted that alloying elements as nickel, aluminum, vanadium, and titanium are toxic, having a carcinogen character and a causal relationship with neurotoxicity and senile dementia, like Alzheimer.
2. Characterization of the cobalt alloys with silicon addition

The objective of the study was the elaboration of new performing alloys based on cobalt that consists in the identification of new composition, increasing the silicon content (99.99% purity) up to 10%.

Remelting was performed in electric arc furnace with an argon atmosphere that had been previously vacuumed at \(10^{-4}\) mbar [4]. Under the influence of the advanced vacuum in the chamber and in the crystallizer, a strong degassing occurs leading to a low gas content (nitrogen and hydrogen) in the final remelted alloy.

The furnace was used to remelt the alloy with its electric arc between the \(\Phi 6.5\) mm thoriated wolfram electrode and the metallic load. The crucible copper of the water-cooled electric arc remelting installation has cavities of various shapes (Figure 1) where the raw ingots were cast. To obtain a superior chemical and structural homogeneity, we remelted the alloy for seven times.

The technical characteristics of the installation are as follows [6]:

- water cooled 304 L stainless steel vacuum chamber with double walls;
- the crucible of the working chamber made of aluminum;
- loading is easy due to the articulated back of the bell;

Figure 1. Crucible design of VAR furnace [5].
visualization: the crucible and the electrode may be observed through the 4” (101.6 mm) window on the face of the furnace; behind there is a separate 1” (25.4 mm) window for lighting;

the visiting window is fit with an adjustable welding view-port to protect the eyes during melting;

the copper crucible has a series of cavities and is fixed to the water-cooled base of the furnace;

power supply cables to the electrode and the base of the furnace are water cooled;

the bell-shaped working chamber is mounted on a frame that encircles the welding device, to reduce the surface of the furnace;

a thoriated wolfram electrode (6.35 mm DIA. × 76.2 mm) is mounted centrally and may be moved radially so as to cover the entire surface of the crucible;

a protective sleeve is covering the electrode to prevent the electrocution hazard during functioning;

the advanced vacuuming system (0.013–0.0013 N/m²) consists of a preliminary vacuuming pump and a diffusion pump;

oxygen analyzer with a measuring domain of 0–10,000 ppm;

additional loading mechanism during melting;

release gauge at 13,780.2 N/m², fit to the working chamber to maintain a positive pressure inside, preventing gasses to enter the furnace.

For this type of furnace, the crucible in which the alloy is melted and produced is of high importance. The crucible of the furnace has oblong and circular cavities in which we obtained casting samples in standard test-piece sizes, necessary to characterize the properties of the alloys under research.

The total quantity of gas that can be exhausted during vacuum melting largely depends on the chosen raw materials, because at low pressures and even at an increase of the carbon content, the stable oxides may only partially get decomposed. Therefore, it is required that the materials intended to be melted contain minimal quantities of elements with a high affinity to oxygen. The metallic load from which to obtain biocompatible alloys of the CoCrMo system must be of very good quality, with a low content of phosphorus and sulfur, they must be degreased and properly prepared mechanically. During the first phase of the melting process, the maximum quantity of gas is released, 3–4 times more than that released during the refinement phase of the melting process. The degree of purity of the elements that compose the alloy is of over 99%.

The elements dosed in equimolecular proportions are introduced in an order dictated by the type of the cobalt-based alloy to be made, in the cavity on the crucible copper, from which one can subsequently make test pieces for various kinds of investigations.

Our experimental studies were performed on standard test pieces and focused on surface, chemical, and physical-structural characterization (cavity C4), mechanical and clinical study on the biocompatibility of the alloy to be patented (cavity S2).
2.1. Technological workflow

The technological workflow to produce the CoCrSiMo alloy involved the use of a remelting furnace presented in Figure 1 and it comprised the following operations:

- preparation of the raw materials (a CoCrMo pre-alloy and Si) by cutting to sizes adequate to the crucible and cleaning them in an ultrasound bath followed by degreasing with volatile organic solvents;
- raw material dosage by weighing, according to batch calculations;
- loading the raw materials into the crucible of the furnace;
- vacuuming the chamber, obtaining an inert controlled atmosphere (Ar) and pressure level inside the melting chamber;
- melting;
- gravitational casting;
- cooling and extraction of the solidified ingot from the crucible.

2.1.1. Raw materials

Designing a technology to obtain a cobalt-based alloy to be used in medical applications was based on our target to improve the quality of existing alloys, by using advanced analysis techniques that would confirm an improvement in certain properties. The vacuum arc remelting (VAR) furnace ensures the lack of contaminants in the alloy, and consequently, its quality is directly influenced by the purity of the raw materials used.

Considering the special destination of the alloy, it is absolutely necessary that raw materials with minimum impurities can be used, ones that would comply with the following quality requirements:

- prefabricated CoCrMo alloy with the following composition:

<table>
<thead>
<tr>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>65%</td>
<td>29%</td>
<td>5%</td>
<td>0.40%</td>
<td>0.35%</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

- 99.99% pure silicon.

2.1.2. Preparation of the raw materials

The preparation of the materials used to make our alloy consisted in cutting to pieces by electro-erosion. Electro-erosion is based on the erosive effects of electrical arcs in impulse, repeatedly applied between the material to be processed and an electrode, to remove the surplus material, and it allows cutting the metallic material into precise pieces (precise tolerance).
After processing by electro-erosion, the materials were chemically degreased, both to avoid contamination of the protective atmosphere inside the furnace and to avoid impurities in the resulted alloy.

2.1.3. The composition of the metallic load

To calculate the metallic load (dosage), one must take into account the theoretical degrees of assimilation of the elements in the melt mix and the possible losses by vaporization during the metallurgic process in vacuum or in argon-controlled atmosphere \[ \text{[4]}. \]

The losses are estimated based on data from relevant publications, on the degree of oxidation of the materials in the load, on the characteristic of those elements, on their position in the series of electrochemical potentials, on the characteristics of the melting device, and on the information from researches on the elaboration process.

The metallic load from which to obtain biocompatible alloys of the CoCrMo system must be of very good quality, with a low content of phosphorus and sulfur, they must be degreased and properly prepared (granulometrically).

The degree of purity of the elements that compose the alloy is of over 99%. The elements dosed in equimolecular proportions are introduced in an order dictated by the type of the cobalt-based alloy to be made, in the cavity on the water-cooled crucible copper.

The size of the batches was chosen so as to allow each sample to be processed after elaboration for various tests in regard to surface, physical, chemical, and structural characterization and for the clinical test of biocompatibility (cavity C4, Figure 1) and for mechanical properties (cavity S2, Figure 1).

2.1.4. The crucible loading

The losses by vaporization were low, because the raw materials we used did not contain impurities and elaboration was performed in a controlled atmosphere, in vacuum, and argon. The dosage of raw materials was done in progressive order according to specific weight; elaboration time was relatively short, which limited the evaporation losses to a minimum.

2.1.5. Achieving pressure levels

In order to make highly pure biocompatible alloys from the CoCrMo class, the working chamber was properly prepared by successive vacuuming operations and by argon purging for three times. Vacuuming was done by the preliminary vacuuming installations and the diffusion pumps that may ensure pressure levels of app. 3.5–4 × 10⁻⁴ mbar. For purging, we used 99.99% pure argon 5.3. Those operations ensure maximum 40–60 ppp oxygen content in the working chamber. The last stage in the process was argon purging the working chamber and establishing working pressure levels slightly above atmospheric pressure.

2.1.6. The melting of the metallic load

The process of making alloys from the CoCrMo class consists in melting materials under the action of an electric arc created between the thoriated wolfram electrode and the metallic
load. The electric arc is gradually conducted over the entire surface of the load, aiming an in-depth melting thereof. Adjustments in the power of the arc are done by manual controls.

The solidification of the obtained alloy occurs very fast, due to the intense water cooling of the crucible. Next, we remelted the samples seven times and returned them into the cavity from the crucible copper, so as to ensure a state of complete alloying and to improve the degree of chemical and thermal homogenization of the ingots. The entire elaboration process was performed by electric arc remelting in argon-controlled atmosphere.

The melting conditions in the installation were adapted to comply with the type of alloy to be obtained.

The thoriated wolfram electrode was moved during melting at a distance of approximately 6.35 mm from the electrode on the crucible copper and the electric arc covered the entire surface of the load so as to ensure a complete homogeneity.

After finishing melting and solidification, we obtained ingots with masses almost constantly matching the mass of the load we introduced into the VAR furnace.

2.1.7. Cooling the metallic test pieces

The alloy cooled almost instantly under the influence of the forced water cooling of the crucible copper (the crystallizer of the installation). The samples we obtained (ingots) had various shapes according to the shape of the cavity in the crucible copper. Those samples (test pieces) were analyzed to determine their chemical composition, their physical, chemical, and mechanical properties.

2.1.8. Extracting the metallic test pieces

After solidification, which occurred in the cavity from the crucible copper, the installation was kept for approximately 10 min in the argon-controlled atmosphere to avoid their oxidation during removal at high temperatures.

Afterwards, we removed the argon source from the installation and returned it to a regular atmosphere. The obtained samples were then weighted and marked to determine their properties.

2.1.9. Material balance

The samples obtained were classified according to their weight and during the remelting process, there were no weight losses.

The assimilation efficiency of the chemical alloying components depended on the following factors: the chemical efficiency of the elements in regard to oxygen, the specific mass of the alloying material, the degree of purity, chemical composition, etc.

The metallic load of the obtained cobalt-based alloy was calculated by the analytic method. The calculation of the load for the original alloy took into account, both the possible losses by vaporization and the theoretical degrees of assimilation of the elements in the mix.
2.2. Determination of chemical composition by optical emission spectrometry and EDX

The determination of chemical, structural, physicomechanical, and biocompatibility characteristics has been highlighted by experimental laboratory determinations performed on standard specimens specific to the tests. The methods of analysis that were used (optical and electron microscopy, structural analysis by X-ray diffraction, elasticity test, fractal analysis, hardness tests, corrosion resistance, and biocompatibility tests) are in compliance with the relevant technical standards and metallic alloy norms with applications in medicine [7].

The analyses are comparative with the same types of tests being carried out for both CoCrMo commercial alloy and CoCr alloy variants with different silicon additions.

The analysis were focused to characterize the CSi\(_k\) alloys (k = 4, 5, 6, and 7), which certify that we choose the appropriate technology, the efficiency of the arc melting furnace being very high (99.97%). The original alloy had a composition very close to the one we initially calculated, the losses registered being insignificant (Figure 2).

Using advanced laboratory equipment, analyses of new alloy variants give the assurance of a complete and highly scientific characterization, both from a chemical, structural, physicomechanical, and biological point of view. Major advances and spectacular advances in medical sciences have been due to ongoing efforts by research lab specialists in the field of biomaterials engineering to design and develop new alloys that can best substitute components of the human body, by applying modern reconstructive and repair techniques. The chemical composition, both for the CoCrMo commercial alloy and the developed variants, was achieved by optical emission spectrometry. The determined mass concentrations of elements of cobalt alloys are specified in Table 1.

By increasing the percentage of silicon, the alloying elements exhibited lower values, a significant change being to the main element, cobalt. If initially it was 62.10% in the CoCrMo commercial alloy, it reached 56.40% in CSi\(_7\) alloy.

2.3. Microstructural characterization of cobalt alloys

Macroscopic analysis is the first step of a surface structure analysis. This analysis requires a minimum of training and gives information on the nature of the alloy in the CoCrMo
system, the peculiarities of the casting structure, the character, and quality of subsequent machining, which confers the shape and final properties, the nature of the break, and its causes [8]. At the same time, the microscopic analysis allows the selection of the areas in the studied specimen, which must then be subjected to a detailed microscopic analysis. Microstructure of alloys used in medical applications is defined by crystallographic orientation, texture, morphology, distribution, size, and number of phases. A Vega Tescan LSH II scanning electron microscope was used to highlight the CoCrMo and CSiₖ alloys (k = 4, 5, 6, and 7) (Figure 3).

After completion of the elaboration process, the specimens required for structural analysis were processed by electro-erosion, and as methods of preparation we used polishing and revealing of the structure by chemical attack. The specimens of cobalt alloys subjected to microscopic analysis had a cubic shape with the side of 10 mm. The microstructure of metallic materials is a fine construction of the structure, which was highlighted using a metallographic chemical attack with the following composition: 5 ml of HNO₃, 200 ml of HCl, and 65 g of FeCl₃.

The SEM microstructures analyzed for commercial alloy and silicon alloy variants of 4, 5, 6, and 7% at the 500× BSE magnification power, show a dendritic structure specific to cobalt alloys cast with the existence of α and β phases, in varying proportions modifiable with increasing the percentage of silicon during casting processes.

From the point of view of the microstructural features, the alloyed with silicon alloy variants exhibit a polymorphic transformation (h.c.—c.f.c.) due to heating/cooling of the cobalt. The experimental research by electronic microscopy confirms the improvement of the properties of cobalt alloys by obtaining a uniform structure with fine eutectic dendritic separations.

### 2.4. Investigations by X-ray diffraction

X-ray diffraction is the process by which radiation, without wavelength to change, is transformed by interference with the crystal lattice into a large number of observable “reflections” with characteristic spatial directions (Figure 4).

### Table 1. Chemical composition of alloys in the CoCrMo system.

<table>
<thead>
<tr>
<th>Alloy element</th>
<th>CoCrMo</th>
<th>CSI₄</th>
<th>CSI₅</th>
<th>CSI₆</th>
<th>CSI₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>62.10</td>
<td>59.40</td>
<td>58.50</td>
<td>56.70</td>
<td>56.40</td>
</tr>
<tr>
<td>Cr</td>
<td>26.79</td>
<td>26.46</td>
<td>26.16</td>
<td>26.23</td>
<td>25.48</td>
</tr>
<tr>
<td>Mo</td>
<td>6.00</td>
<td>5.39</td>
<td>5.24</td>
<td>5.29</td>
<td>5.20</td>
</tr>
<tr>
<td>Ni</td>
<td>2.90</td>
<td>2.72</td>
<td>2.62</td>
<td>2.84</td>
<td>2.87</td>
</tr>
<tr>
<td>Si</td>
<td>0.78</td>
<td>4.64</td>
<td>6.06</td>
<td>7.40</td>
<td>8.45</td>
</tr>
<tr>
<td>Mn</td>
<td>0.42</td>
<td>0.38</td>
<td>0.43</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe</td>
<td>0.33</td>
<td>0.43</td>
<td>0.31</td>
<td>0.58</td>
<td>0.43</td>
</tr>
<tr>
<td>Others</td>
<td>0.68</td>
<td>0.58</td>
<td>0.68</td>
<td>0.57</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Indexing of the diffractogram reveals the following: nanocrystalline character and phase composition (major phase, minor phase) of the analyzed sample. Determination of the structural constituents is done by diffractograms in which the dependence between the diffraction radiation intensity and the double diffraction angle is represented.

The determination of the compositional phases was performed by qualitative analysis by X-ray diffraction, performed on the PanalyticalX’Pert PRO MPD X-ray diffractometer. The analysis range 2θ was between 20 and 1000, the step size being 0.0010, and the step time being 3 s/step. One channel proportional detector was used and the analysis being done in the Gonio mode. Cobalt alloy test specimens used for X-ray diffractometry have a 10 mm rectangular section and a 15 mm sample length. Indexing the diffractogram is the association...
between a peak-peak diffraction and a plane. Diffractometric X-ray analysis confirms the structural changes identified by microscopic analyses and made it possible to accurately determine the phases and structural constituents found in both the commercial alloy (Co Cr, Cr Mo, Cr Mo Si, Co Cr Mo ) as well as the elaborated and cast CSi alloys (k = 4, 5, 6, and 7).

2.5. Hardness determination of cobalt alloys

The hardness measurements were performed on a universal Wilson Wolpert machine, model 751 N, using a load force of 9807 N and a measurement time of 12 s. The Vickers method was chosen because this is a general method for determining the hardness of metallic materials.
and can be used without reservation in the case of cobalt-based experimental alloys [9]. For the accuracy of the results, three determinations were made for each alloy with certain measurement conditions. The hardness determination was performed on samples with two parallel planes, one of the surfaces being prepared by grinding on abrasive paper (Table 2).

The hardness measurements made on CoCrMo alloys provide information on mechanical strength, requiring or not the utility of thermal treatments. The silicon input added to the commercial alloy version of the CoCrMo system improved mechanical characteristics, especially hardness, by forming solid cobalt solutions and Cr$_3$Si and Mo$_3$Si chemical compounds, also favoring a fine grain structure. In CSi$_4$ and CSi$_5$ versions, the hardness increased (639.6 HV), sometimes making mechanical machining impossible, but in terms of corrosion resistance, they could have a major advantage. In this context, a possible processing with the help of a special instrument (extruder cutters) is envisaged.

2.6. Tensile tests

The tensile test of the standard specimens, made of cobalt alloys, was performed on the computer-assisted Instron 3382 test machine. The results obtained of the tensile tests were: elongation, modulus of elasticity, traction resistance, and elongation at break and they provide complete information on the mechanical properties analyzed. In order to be sure of the experimental results obtained, the research was carried out on specimens with specific dimensions to ISO 6892-1: 2009 (E) for both the tensile tests and the machine operating rules [10].

As a following of the tensile test, results have been obtained with respect to elongation, elastic modulus, traction resistance, and elongation at break. From the analysis of the mechanical characteristics variation, depending on the increase of the silicon intake, one can notice an obvious improvement of the properties of the alloys.

The specific elongation of cobalt alloys has close values (≈11%) for the CoCrMo commercial alloy and the CSi$_4$ and CSi$_5$ variants. This has also been confirmed by measured hardness values (up to 500 HV, alloys specific for medical applications). By alloying with 6 and 7% Si, CoxMoy and CrzCoxSi combinations (identified by qualitative X-ray diffraction analysis) that radically altered the mechanical properties of the alloys appeared (Figure 5).

According to experimental determinations, elongation decreases to below 1%. This is in direct correlation with both microstructural changes (interdendritic agglomerations) and mechanical

<table>
<thead>
<tr>
<th>Alloy</th>
<th>CoCrMo</th>
<th>CSi$_4$</th>
<th>CSi$_5$</th>
<th>CSi$_6$</th>
<th>CSi$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured punctual values</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>423</td>
<td>446</td>
<td>513</td>
<td>633</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>446</td>
<td>458</td>
<td>484</td>
<td>633</td>
<td>746</td>
<td></td>
</tr>
<tr>
<td>446</td>
<td>471</td>
<td>498</td>
<td>653</td>
<td>772</td>
<td></td>
</tr>
<tr>
<td>Average value</td>
<td>438.30</td>
<td>458.30</td>
<td>498.30</td>
<td>639.60</td>
<td>746.00</td>
</tr>
</tbody>
</table>

Table 2. Hardness of cobalt alloys.
strength, due to the excessive increase in hardness to values above 500 HV. The modulus of elasticity determined by tensile tests for the CoCrMo commercial alloy has values close to the experimental alloys CSi$_4$ and CSi$_5$ (the modulus of elasticity has values near to steels). The determined modulus of the elasticity modulus guarantees an improvement in the properties of the cobalt alloys providing good deformability. By alloying with silicon of 6 and 7%, the modulus of elasticity increases excessively, this gives the alloy some resistance to the plastic deformation processes.

On the basis of the measurement of the elongation test, it was found that the alloyed silicon alloys exhibited alternating values around the average value of the CoCrMo commercial alloy. From the macroscopic analysis of specimens subjected to tensile tests, both the control sample and variants in the CoCrMo system revealed a fragile fracture of the standard specimens.

2.7. Fractographic analysis

Cobalt alloy test specimens subjected to tensile testing were further investigated by fractal analysis. This analysis offers a complete characterization of mechanical properties, on how to behave in different mechanical actions (elasticity, fragility, breaking strength, creep, etc.) [11]. The examination by electronic microscopy (SEM) was performed according to: SR EN 1321: 2001. For the determination of the fractal analysis, an electronic microscope, Quanta Inspect S, FEI was used. The microscopic analysis was performed using the back scattered electrons (BSE) detector (2D image of the surface, better contrast of the different phases), the 1000× magnification order.

CoCrMo alloys subjected to fractal analysis were cleaned with propanol in an ultrasonic and warm-air bath (not chemically attacked). Measuring conditions: temperature: 24°C (reference temperature: 23 ± 5°C); humidity: 60%. Figure 6 shows the appearance of the breakage faces by means of a scanning electron microscope (1000×) for cobalt-based alloys.

The fractographic study is correlated with the results obtained in the traction tests and certifies that silicon-alloyed variants exhibit cleavage by break. In the case of fragile fracture, the cracks initiated in the breakage surface propagate sharp without a total deformation of the material, but only in micro-volumes located on the breaking surfaces of the type: Co$_x$Cr$_y$Mo$_z$ with cubic crystalline network, Cr$_x$Si with cubic crystalline network, and Cr$_y$Mo$_z$Si with cubic crystalline network (detected by diffractometric X-ray analysis).
The fragile break produces cuts in a plane approximately perpendicular to the stress plane and has a crystalline aspect (the rupture is initiated on grain boundaries with the aspect of cleavage planes). When the interphase adhesion of the metal matrix is insufficient, there are lamellar strips present on the cracked surfaces that attenuate the quick detachment of the blank space sub-microscopic.

2.8. Characterization by electrochemical impedance spectroscopy (EIS)

Using electrochemical impedance spectroscopy (EIS), information was obtained on the passivation process, which takes place in maintaining the CoCrMo commercial alloy and the new
CSiₖ (k = 4, 5, 6, and 7) in the solution. The advantage of this method (in alternative current) to other electrochemical methods (polarization methods—in DC) is that it can monitor some electrochemical changes over time, being a nondestructive method at the same time.

Electrochemical impedance spectroscopy is a stationary method capable of highlighting relaxation phenomena, whose relaxation times vary in different order of magnitude and allow mediation in the same experiment to achieve a high level of precision.

The CoCrMo alloys subjected to electrochemical characterization in simulated biological environments have a cubic shape with a 10 mm side.

The measurements were made at open-circuit potential, in fresh unpasteurized orange juice. The citric acid (unpasteurized fresh orange juice) was chosen to study electrochemical behavior because it is considered to be one of the five acids that try most often to enter our body, 5–9%. In high quantity, the fresh orange juice can affect the tooth enamel, thinning him, and generating thus the cavities appearance and unpleasant experiences associated to them [12].

The spectrums were recorded in the frequency domain of 10⁵–10⁻² Hz, at a potential in alternative current, with 10 mV amplitude, using a PARTSTAT 4000 potentiostat. Data processing was done with ZSimpWin software, version 3.22. ZSimpWin software uses a varied of electric circuits to correlate numeric the impedance data measured (Figure 7).

After each experiment, the impedance data was represented after Bode diagrams (impedance |Z| vs. frequency (f) and phase angle Φ (grade) vs. frequency (f)).

The dependence between phase angle and frequency indicates the fact that may exist one or more time constants, which can be used to determinate the elements values from equivalent circuit.

The advantage of Bode diagrams is that the dates are present for all frequencies measured and the impedance values can be represented on a high interval. It was obtained, after immersion

![Figure 7](http://dx.doi.org/10.5772/intechopen.70886)
for 750 s, in fresh unpasteurized orange juice; the impedance spectrums represented like Bode diagrams for four experimental samples from CSiₖ alloys (ₖ = 4, 5, 6, and 7). Bode diagrams for alloys from CoCrMo system were present in the Figure 7a and b.

In Bode representation for commercial alloy from CoCrMo and experimental alloys CSiₖ (ₖ = 4, 5, 6, and 7), present only one constant for relaxation time, indicated by a single maximum on variation curve for phase angle with frequency.

The electrochemical cell can be represented by a single equivalent circuit consisting of different combination of resistors, capacitors, and other circuit elements.

The correlation grade of equivalent circuit for obtained experimental data is expressed by χ² parameter, which is directly correlated with the relative error of measured current; to one χ² value of the order of 10⁻⁴, it corresponds to an error of measured value by 2%.

The interpretation of spectrum for all CoCrMo alloys was made by data modeling with an equivalent circuit. For simulation, it used ZSimpWin software. In this equivalent circuit, Rₛₒ𝑙 (R₁Q₁), Rₛₒ₁—solution resistance, Rₜ—resistance of passive layer (resistance to polarization), and Q₁—capacity of passive layer. In this case, to enlarge the scope of the model, in the place of ideal capacity of passive layer it introduced a constant phase element Q. The impedance of this constant phase element is equal with:

\[ Q = Z_{CPE} = \frac{1}{Y_o(j\omega)^n} \]  

where Q—adjustable parameter (F cm⁻² sⁿ⁻¹), Y₀—a constant, j—imaginary number (j² = -1), n—is related to the slope of the lg [Z] versus lg, f—frequency from Bode graphic, and ω is angular frequency.

When the value of n is equal with 1, the constant phase element describes an ideal capacitor (C).

For 0.5 < n < 1, the constant phase element describes a distribution of relaxation times in the frequency spaces and when n = 0.5, the constant phase element represents a Warburg impedance with diffusion character. When n = 0, the constant phase element describes a resistor.

The χ² coefficient values are included between 2 × 10⁻⁴ and 5 × 10⁻⁴, which confirm that the chosen equivalent circuit describes well the physic model, adjustment of experimental values being placed in 1–3% error limits. The resistance of solution not varied in the time of samples maintaining in these, the recorded differences for performed measurements varies in ±3 Ω cm² limits toward a medium value by 120 Ω cm².

The electric parameters of equivalent circuit for CoCrMo alloys maintained 750 s in fresh unpasteurized orange juice are shown in Table 3.

From the data present in Table 3, it is found that the resistance of passive layer increases once the increase of silicon content, for CSi₄, CSi₅ alloys, which means that, not catalyzes the oxidation process at superficial layer. For samples containing more than 5% Si, CSi₆ and CSi₇, the corrosion resistance decreases gradually.
The electrochemical impedance spectroscopy represented as Bode diagrams for four alloys, CSi\textsubscript{k} alloys (k = 4, 5, 6, and 7), and for the commercial alloy (CoCrMo) were obtained as a result of immersion 3000 s in fresh unpasteurized orange juice. The Bode diagrams for CoCrMo alloys are shown in Figure 8.

From the shape of Bode spectrometry to variants of silicon alloys, it is found that they exhibit similar electrochemical behavior after 3000 s immersion in fresh unpasteurized orange juice. The values of the electrical parameters of the equivalent circuit for the studied alloys maintained 3000 s in fresh unpasteurized orange juice are also presented in Table 3. In Figures 7 and 8, the experimental data are presented as individual points and the continuous line represents the theoretical spectra obtained from the simulation. Long contact between cobalt alloys and in fresh unpasteurized orange juice leads to superficial passivation of the alloys.

From the data presented in Table 3, it is found that the resistance of passive layer increases once the increase of silicon content for CSi\textsubscript{5} alloy, which means that it does not catalyzes the oxidation process at superficial layer. It has been noticed that silicon alloying of the CoCrMo alloys are obtained structures and properties that lead to the influence of corrosion resistance. The modification of properties can take to increased corrosion resistance of alloys in the CoCrMo system. The increase in the corrosion resistance of CSi\textsubscript{i} and CSi\textsubscript{y} alloys at a determined value of the alloying element is explained by the formation of complex structures of the type Co\textsubscript{0.94}Cr\textsubscript{0.06} with hexagonal crystalline network and Co\textsubscript{0.94}Cr\textsubscript{0.32}Mo\textsubscript{0.04} with cubic crystalline network identified with using the qualitative phase analysis by diffractometric X-ray investigations. These structures formed on the surface of the experimental alloys, CSi\textsubscript{i} and CSi\textsubscript{y}, high pellicle in layer.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>10\textsuperscript{4} R\textsubscript{i} (Ω cm\textsuperscript{2})</th>
<th>10\textsuperscript{6} Q\textsubscript{i} (S/cm\textsuperscript{2} s\textsuperscript{n})</th>
<th>n\textsubscript{i}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrMo</td>
<td>32</td>
<td>3.70</td>
<td>0.79</td>
</tr>
<tr>
<td>CSi\textsubscript{i}</td>
<td>164</td>
<td>2.40</td>
<td>0.82</td>
</tr>
<tr>
<td>CSi\textsubscript{y}</td>
<td>295</td>
<td>1.90</td>
<td>0.83</td>
</tr>
<tr>
<td>CSi\textsubscript{5}</td>
<td>56</td>
<td>3.20</td>
<td>0.80</td>
</tr>
<tr>
<td>CSi\textsubscript{7}</td>
<td>28</td>
<td>3.70</td>
<td>0.79</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>38</td>
<td>3.70</td>
<td>0.79</td>
</tr>
<tr>
<td>CSi\textsubscript{i}</td>
<td>211</td>
<td>2.30</td>
<td>0.82</td>
</tr>
<tr>
<td>CSi\textsubscript{y}</td>
<td>435</td>
<td>1.60</td>
<td>0.83</td>
</tr>
<tr>
<td>CSi\textsubscript{5}</td>
<td>64</td>
<td>3.20</td>
<td>0.80</td>
</tr>
<tr>
<td>CSi\textsubscript{7}</td>
<td>32</td>
<td>3.70</td>
<td>0.79</td>
</tr>
</tbody>
</table>

After 750 s immersion

After 3000 s immersion

Table 3. The electric parameters obtained by the adjustment of experimental data for CoCrMo- and CSi\textsubscript{i}-studied alloys in fresh unpasteurized orange juice at varied immersion times.

The electrochemical impedance spectroscopy represented as Bode diagrams for four alloys, CSi\textsubscript{k} alloys (k = 4, 5, 6, and 7), and for the commercial alloy (CoCrMo) were obtained as a result of immersion 3000 s in fresh unpasteurized orange juice. The Bode diagrams for CoCrMo alloys are shown in Figure 8.

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2.9. Characterization by linear polarization studies

The alloy measurements in the CoCrMo system have been performed in fresh unpasteurized orange juice. The linear polarization curves were indicating in the potential range: −0.8 to +1 V, using a rate of 1 mV/s.

Representation of linear polarization curves in coordinates: current density (j)/potential (E) (Figure 9a and b) allows to highlight corrosion potentials (E\textsubscript{cor}) as well as corrosion currents (j\textsubscript{cor}).

The main parameters of the corrosion process (E\textsubscript{cor} and j\textsubscript{cor}) are obtained by processing the linear polarization curves for four CSi\textsubscript{k} alloys (k = 4, 5, 6, and 7) and for the CoCrMo commercial alloy are centralized in Table 4. Corrosion potentials (E\textsubscript{cor}) show similar values for the original variants, compared to the value for the CoCrMo commercial alloy. The corrosion current (j\textsubscript{cor}) is the representative of the degree of damage to the material.

It is found that the density of the corrosion current, representative dimension of the level of degradation of the samples, is in the order of tens of μA/cm\textsuperscript{2} in all the studied cases. According to the experimental results, the value of the corrosion current decreases with the increase in the silicon content to CSi\textsubscript{5}, after which it increases by reaching a maximum value for the CSi\textsubscript{7} sample. This “positivity” of cobalt alloy surfaces immersed in fresh unpasteurized orange juice was attributed to the formation of passive layers, most likely oxides (Cr\textsubscript{2}O\textsubscript{3} and/or Mo\textsubscript{2}O\textsubscript{3}) that partially protect the surface of the alloys. The same tendency is observed in the case of the passive current density (j\textsubscript{pas}).

According to the Stern-Geary equation, the polarization resistance (R\textsubscript{1}) is proportional inversely to the density of the corrosion current (j\textsubscript{cor}) [13]:

\[ j_{\text{cor}} = \frac{B}{R_1} \]  

(2)

where B is the constant that depends on the nature of the material.
From the results obtained in the electrochemical impedance spectroscopy tests and those of the linear polarization, we find a good concordance, which is also confirmed by the Stern-Geary equation (Figure 10), more exactly the polarization resistance \( R_p \) is inversely proportional to the current density corrosion \( j_{cor} \).

2.10. The effect of corrosion on surface layer

In order to confirm the conclusions of the polarization studies and to understand the electrochemical corrosion mechanism of the CoCrMo commercial alloy and CSI\(_k\) \( (k = 4, 5, 6, \text{ and } 7) \), the surface microstructure was analyzed by scanning electron microscopy (SEM) with a Vega—Tescan LSH II microscopy.

For the identification of the corrosive effect on surface layer, SEM was used, equipped with back scattered electrons detector (BSE—2D image of surface, best contrast of various phases), at 2000× magnification.

Figure 11 shows the surface morphologies for the CoCrMo commercial alloy and the CSI\(_k\) \( (k = 4, 5, 6, \text{ and } 7) \) at the 2000× BSE magnification power, where the impedance spectrometry were recorded after 750 and 3000 s, respectively, immersing the samples in fresh unpasteurized orange juice.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( E_{cor} ) (mV)</th>
<th>( j_{cor} ) (( \mu \text{A/cm}^2 ))</th>
<th>( j_{pas} ) (( \mu \text{A/cm}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrMo</td>
<td>-245</td>
<td>735</td>
<td>39.1</td>
</tr>
<tr>
<td>CSI(_4)</td>
<td>-247</td>
<td>410</td>
<td>0.9</td>
</tr>
<tr>
<td>CSI(_5)</td>
<td>-217</td>
<td>290</td>
<td>0.9</td>
</tr>
<tr>
<td>CSI(_6)</td>
<td>-243</td>
<td>585</td>
<td>19.4</td>
</tr>
<tr>
<td>CSI(_7)</td>
<td>-257</td>
<td>770</td>
<td>39.6</td>
</tr>
</tbody>
</table>

Table 4. The main parameters of corrosion process for studied alloys in fresh orange juice, unpasteurized.
The electrochemical sequence used for corrosion resistance testing and analysis of its effects on cobalt alloy surface condition was: linear polarization at −0.8 to +1 V at 1 mV/s. The corrosion points on the alloy surface of 4, 5, and 6% have irregular shape, having different sizes can be observed in the 2000× BSE magnification power. At CSi7 alloy, the corrosion points have the large dimensions compared to the experimental alloys analyzed.

The SEM micrographs obtained for cobalt alloys indicate that the chemical attack (in fresh unpasteurized orange juice) occurs superficially, uniformly over the entire surface of the alloy, and only locally there are a series of superficial, very small corrosion points, which are randomly distributed on surface [14]. The behavior of the investigated alloys is consistent with the results of potentiodynamic measurements indicating low values for instantaneous corrosion rate (Table 4).

2.11. The clinical study on the biocompatibility of the obtained alloys

The central objective of this study was fulfilled by evaluating improvement of the properties of cobalt alloys, used in medical applications, which can resist longtime in human body, as well as knowledge development of new biocompatible structures [15]. If variants of alloys are not subjected to biological acceptance criteria by the animal body, they cannot be placed in the living organism, no matter how appropriate the properties of biomaterials are. The realization of alloy variants should also consider the possibility of the appearance of basic pathophysiological phenomena, which determine their long-term safety (thrombosis, inflammation, infection and/or induction, and neoplasm challenge) [16].

The CoCrMo commercial alloy implanted in subjacent area presents an adipose tissue with canalicular structures and large vessels, separated by membranes of conjunctive tissue with an increased fibroblast population or by islands of conjunctive tissue with similar cell aspect; associated, but and numerous high macrophages, with intracytoplasmic grains (Figure 12).

In subcutaneous tissue (Figure 12a) after 21 days, can observe a moderate inflammation with a broadcast distribution, rarely nodular, which presents perivascular and perineurals.
In subjacent area of implanted commercial alloy (Figure 12b), the skin presents normal aspect, with epidermis, without modifications, and a small diminution of the space occupied by dermis, in which are present numerous adipocytes, striated muscle tissue, but and a hypodermis characterized by the presence of a conjunctive tissue richly vascularized, with numerous active fibroblasts.

In lateral area (Figure 12c) of implanted commercial alloy (near pill), the skin has an easy papillomavirus epidermis, dermis is superficial and deep, collagenized intense and hialinizated. It can be observed in this area, near pill exist a hypodermis and muscular tissue normally striated.
CSi₄ alloy implanted in subjacent area (Figure 13a), presents a densification of conjunctive tissue with collagen fibers, parallel between them and numerous active fibroblasts, realizing a fibrous band, which delimits the implanted CSi₄ alloy. External to this band, it found a moderate inflammatory infiltrate, numerous macrophages with hemosiderin and numerous congested capillaries.

In superjacent area (Figure 13b) of CSi₄ implanted alloy, the skin presents a normal aspect.

At the CSi₄ alloy, it was not taken in lateral area, because the implanted material was surrounded by a compact film, described at subjacent area.

CSi₅ alloy implanted in subjacent area (Figure 14a) presents a conjunctive tissue with numerous adiposities and expended venules.

The superjacent area of CSi₅-implanted alloy (Figure 14b) presents skin with normal aspect, hypodermis with adiposities and muscular striated tissue.

![Figure 13. CSi₄ implanted alloy: (a) subjacent area and (b) superjacent area.](image1)

![Figure 14. CSi₅ implanted alloy: (a) subjacent area; (b) superjacent area; and (c) lateral area.](image2)
The skin area is with atrophic epidermis, taking place the diminution of skin axis, and dermis have relatively lax aspect.

The CSi₅ alloy implanted in lateral area (near pill) (Figure 14c), highlights a skin with atrophic epidermis. In hypodermis, it found collagenized and hialinized areas with numerous active fibroblasts. In this area, vascular elements appeared (capillary, arterioles, and venules) with reactive endothelium and numerous lymphocytes in lumen.

In comparison with the CSi₄ alloy, the CSi₅ alloy do not present a conjunctive tissue organized in delimit band of implanted material.

CSi₅ implanted in subjacent area of material (Figure 15a) presents a hypodermis with adipose tissue separated by bands and/or collagen islands with numerous fibroblasts. These are infiltrating chronic inflammatory, moderately represented big macrophages with grains.

In the case of CSi₄ alloy, it is found a densification of conjunctive tissue with collagen fibers, parallel between then and numerous active fibroblasts, realizing a fibrous band, which delimits the implanted material. The fibrous band obtained at CSi₅ alloy is thinner than that of CSi alloy.

In the superjacent area of CSi₅-implanted alloy, (Figure 15b) can be observed that the skin presents a normal aspect, a hypodermis with aspect similar with that described at subjacent area—densification of conjunctive tissue, under form of fibrous bands, like a wall-organized perimaterial implanted. In the case of this alloy, it is found that the lymphatic vessels are much expended.

In lateral area of CSi₆-implanted alloy (near pill) (Figure 15c), the skin presents normal aspect without modifications.

In subjacent area of CSi₆ alloy (Figure 16a) have infiltrate inflammatory by massive chronic type, arranged diffusive and/or nodular, perivascularar, and perinervous associating elements by acute type and macrophages.

In superjacent area of CSi₆-implanted alloy (Figure 16b), the skin presents a normal aspect, but not a normal hypodermis.

The CSi₆ alloy implanted in lateral (near pill) presents a densification of conjunctive tissue with collagen fibers, parallel between then, and numerous active fibroblasts (Figure 16c).

Due to active fibroblasts was made a fibrous band, which delimits implanted material, but is thinner than CSi₅ and CSi₄ original variants.

Figure 15. CSi₅ alloy implanted: (a) subjacent area; (b) superjacent area; and (c) lateral area.
The variants of alloys present aspect of biocompatibility detected by microscopic studies, conducted in same conditions like in the case of CoCrMo commercial alloy. The variants of alloys by CoCrMo system do not present major differences in comparison with commercial alloy. The modifications of tissue consist in appearance of one tissue by grain implanted peri-material, which can be interpreted like results of conjunctive organizing and repairing of a consecutive injury.

At variants of CSiₖ (k = 4, 5, 6, and 7), alloys exist supplementary, adjacent to implanted alloy, a densification of conjunctive tissue, which formed a delimited structure, type fibrous membrane, which is not significant for general state of tested biological organism, because the inflammation is low.

In the biocompatibility study, it is found that no locally histological modifications are recorded, generated by a possible toxicity of biomaterials, based on cobalt, meaning that these type of alloys can be used successfully in medical applications.

3. Conclusions

This scientific research presents the following advantages:

- The increases of chemical homogeneity grade in entire mass for cobalt-base alloy.
- The obtaining of dendrite, biphasic, and uniform structure, which offer an excellent machinability for final products.
- The CoCrMo alloy alloyed with Si, obtained by proposed method, present physical, mechanical, and osteo-integration properties superior than the CoCrMo and CoCr alloys, developed by direct alloying method.
- The ingots obtained by cast, from proposed used alloy, are exactly rigid and nondeformed, even at the small used cavities.
- The remelting installation does not require superheating for melting the alloy, infact it reduces the losses of alloying elements.

The important physical-mechanical characteristics like tensile strength, elasticity modulus, good hardness, and low density ensure the mechanical compatibility of alloy, which is necessary for integration in live tissue and the success for long time of implants.
Both European and National Standards, and also the law requirements from materials domain for medical implanted devices, imposed for biomaterials a high biological compatibility, this being a property influences the behavior of implant in human body directly.

Author details

Petrica Vizureanu*, Mirabela Georgiana Minciuna, Gianina Iovan and Simona Stoleriu

*Address all correspondence to: peviz2002@yahoo.com

1 “Gheorghe Asachi” Technical University Iasi, Iași, Romania

2 Faculty of Dental Medicine, University of Medicine and Pharmacy “Gr. T. Popa” Iași, Iași, Romania

References


