



# Investigation on Cobalt based alloy modified by Titanium for dental applications

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## ABSTRACT

**Purpose:** The main goal of this study is to develop and obtain some competitive products, with high added value. In particular, the attention will be focused on the possibility to obtain a new class of Cobalt based alloy by Ti addition.

**Design/methodology/approach:** Modification of the composition by Ti addition can increase the corrosion resistance, processing and at the same time can improve the alloy biocompatibility.

**Findings:** Addition of these elements has a positive effect on the alloy hardness. Up to 6% of Ti or combining Ti and Zr as alloying elements there are no significant differences as hardness concerns. As corrosion resistance in a simulated oral cavity environment concerns, no significant release of metal ions was observed, the pH value and the weight loss fulfil the conditions required by the Standard ISO 10271/2011. However, the best behaviour was obtained employing CoCrMoTi6 alloy.

**Research limitations/implications:** Based on the up to date achieved outcomes, it appears that a quite homogeneous and good mechanical properties have been obtained modifying the original alloy with 6% of Ti. The future research work will be oriented to get additional and detailed data on the biocompatibility of the alloy.

**Practical implications:** The central issue is the valid transfer to dentistry application.

**Originality/value:** The aim of the paper is to obtain a new class of Co based alloy by the modification of the original chemical composition.

**Keywords:** Cobalt based alloy; Ti addition; Microstructure; Mechanical properties; Corrosion resistance

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## MATERIALS

## 1. Introduction

Medical implants are typically produced using metallic materials, like austenitic stainless steel, cobalt-chromium alloys and titanium and its alloys.

The most popular materials, thanks to their relatively low fabrication cost, are related to the stainless steel. However, these materials are tending to localized attack in long-term applications when they are in contact with aggressive biological environment [1]. The ions, coming from F, Cr, Ni and/or Mo, can be accumulated in the tissues close to the implant or they can be transported to other parts of the human body and can have different dangerous effects [2,3,4]. Several studies have revealed that the ions released owing to different mechanism including corrosion, mechanically accelerated electrochemical processes, i.e. stress corrosion, corrosion fatigue and fretting corrosion, depends on the corrosion resistance of the alloys [5,6,7] and result to be governed by corrosion rate of the metals and by the solubility of the primary developed corrosion product [8,9].

Metallic biomaterials are constantly employed as orthopaedic and dental implant material, thanks to their excellent mechanical properties, as their strength, hardness and toughness which complement to an adequate corrosion resistance and good biocompatibility. Excellent tribological properties and good wear resistance confer to Co-Cr a particular attention. Additionally, Ti-based alloys are considered very attractive materials for implant production [10, 11] due to their good properties, i.e. high biocompatibility, good strength-to-weight ratio and also for the excellent corrosion resistance in many environment.

The first commercially employed Co-based alloy has been originated from Co-Cr-W and Co-Cr-Mo ternary alloys and firstly has been investigated by Elwood Haynes at the beginning of the 20th century. Co-CrMo casting alloy, known as Vitallium, has been developed in the 1930s for dental prosthetics and it is considered as highly biocompatible alloy and free of Be and Ni. Vitallium 2000 has been proposed to maintain the prominent strength of Vitallium and at the same time presents an improved working behaviours. Another well-recognized and world-wide used alloy for more the 30 years is related to the Wironit, while Heraenium alloys are clinically evaluated, biocompatible and corrosion-resistant Co-Cr metal/ceramic alloy which represents an inexpensive option for reliable, high quality dental restorations (crowns and bridges). Such alloys do not contain Be, Cd and Ni and guarantee good processing properties combined with good corrosion resistance.

For vascular implants Co-Cr-Mo-Ni-Fe and Ni-Ti-based alloys are the most employed metallic materials [12]. In particular, Ni-Ti alloy, which has superelasticity, and Co-Cr-Mo-Ni-Fe alloys with excellent elasticity, mechanical strength, ductility and cold workability have received much more attention as materials for stents and stent grafts production [13,14]. Ni can amplifies the ductile properties of the Cr-Co metallic alloy and can stabilize the faced centred cubic structure which is favoured due to its better tenacity of the Co-matrix, but at the same time this element is a potent allergen component and can cause higher hypersensitivity reaction compared to other metallic or ceramic materials used in such application. Inflammatory responses, associated to Ni-Cr alloy restoration subside when the alloys is removed and replaced with Ni-free materials [13,14].

The influence of the surface finishing condition of the Ni-based dental casting alloys has been also widely investigated [15-19] and it has been found to be a critical factor.

For removable partial dentures the most employed alloys are belong to the Co-Cr system and consist of about 50% Co, 25% Cr, 19% Ni with minor other elements. For the fixed partial dentures the composition usually contains about 53% to 65% Co and about 27% to 32% Cr. Chromium-type casting alloys are lighter than their gold alloy equivalents and they are particularly employed for the construction of large and bulky maxillary removable devices [20-22].

Cr is a key element from corrosion resistance point of view and gives to the alloy intrinsic corrosion resistance. This behaviour is related to the ability of this metal to develop a passive chromium oxide ( $\text{Cr}_2\text{O}_3$ ) layer. Cr and Mo act as solid solution strengthening elements and can modify the alloys thermal coefficient of expansion.

Introduction of different alloying elements in order to modify one or more properties has been considered as a suitable alternative solution for the development of new metallic alloys. At the same time some difficulties related to the toxicity, allergenic properties of the alloys can be avoided.

Addition of small amounts of other elements i.e. Fe, Mo, or W can give enhanced properties at high temperature, in addition to superior abrasion resistance.

Strengthening of alloys can be obtained by a combination of solid solution hardening or carbide precipitation hardening following to the addition of Cr, Mo, W, Ni or C to the pure metal matrix. Cr and Ti has a high tendency to the carbide formation increasing in this way the alloy strength and also the wear resistance [23].

The corrosion resistance of the Co-Cr-Mo dental alloy depends on the levels of Cr and Mo. Lower level of these elements considerably decreases the corrosion resistance of the alloy. As Cr and Mo content increases the alloys hardness raises and as a results a reduced workability has been obtained. The biocompatibility of dental alloys is primarily related to their corrosion behaviour [7]. When the corrosion resistance of the alloy is low, high amount of elements will be released in the organism and the risk of unwanted reactions in the oral tissues may be increased. These unwanted reactions include unpleasant tastes, irritation, allergy or other reaction [7].

According to some studies [24,25] fatigue resistance and the biocompatibility of the metallic implants result to be influenced by the corrosion resistance of the alloy.

The aim of this study is to obtain a new class of Co based alloy by the modification of the original chemical composition:

- by addition of different amount of Ti (6 and 4% respectively), labelled as CoCrMoTi6 and CoCrMoTi4;
- by the simultaneous addition of Ti (2.5%) and Zr (2.5%), labelled as CoCrMoTi2.5Zr2.5.

The properties of the obtained alloys have been monitored and compared to those obtained with the reference material, actually employed in dentistry. The aim is to find an optimal composition to be proposed for further dental application.

## 2. Experimental procedures

Cold crucible levitation melting procedure has been chosen for the alloys synthesis. Three types of alloys have been produced,

modifying the Co-Cr based alloy composition by addition of different amount of Ti or Zr and modifying the Mo content. The chemical composition of the prepared alloys has been reported in Table 1. As reference material Wirobond®280 (Co60.2, Cr25, Mo4.8, W6.2, Ga2.9) has been used.

Samples has been prepared by conventional cutting and polishing procedures. The characterization has been performed using traditional methods.

X-ray technique (X-ray, PANanalytical tool with Cu  $k_{\alpha}$  wavelength of 1.5418 Å) has been employed for phase identification.

The microstructure evolution has been monitored by Optical Microscope (OM, MeF4 Reichart-Jung) and by Scanning Electron Microscopy (SEM, Leo 1450VP) equipped with Energy-Dispersive X-ray Spectrometry (EDS, Oxford microprobe). As concern the mechanical properties, microhardness measurements have been performed on the polished samples using a Volpert DU01 tester. A force of 5 N has been applied for 15 s for each measurement and a minimum of 15 indentations were performed on each samples.

To determine the corrosion behaviour of the metallic alloys the procedures indicated in the Standard ISO 10271/2011 has been considered. Static immersion test has been carried out at 37°C ( $\pm$  1°C) and pH = 2.2-2.4 in accordance with the standard, using samples with 10 cm<sup>2</sup> area. The immersion has been realised in acid solution simulating the oral cavity environment (7.5 ml lactic acid, 5.85 g NaCl, 300 ml H<sub>2</sub>O di grade 2 purity, and 700 ml H<sub>2</sub>O). The solution/exposure surface ratio has been maintained at 1 ml/cm<sup>2</sup> as indicated in the standard method. The samples have been monitored after the permanence in the acid solution for 28 days, even if the norms indicate only 7 days. Comparison has been realised using an acid solution maintained in the same condition without any metallic alloy inside.

### 3. Results and discussion

Fig. 1 shows the microstructure of the alloys in as-cast state following etching with HCl+HNO<sub>3</sub>+H<sub>2</sub>O<sub>2</sub> solution for 1 min. The modified alloys reveal a non-homogeneous microstructure.

A typical dendritic solidification features has been obtained in all cases and consist mainly of two characteristic phases: a light one corresponds to the dendritic phases, while the dark one is related to the interdendritic eutectic phases. A more homogeneous microstructure and a special orientation of the dendrites has been observed in the case of the reference alloy, Wirobond®280 (Fig. 1), while in the case of the alloy containing Zr a more ramified dendritic structure has been developed (Fig. 4).

For all modified alloys (Figs. 2-4) the average size of the dendrites, with a casual disposition, corresponds to about 10  $\mu$ m.

It can be observed from the figures that a decrease of Ti content does not affect significantly the secondary dendrite arm spacing values of the alloys (it remains in the range of 10-30  $\mu$ m for all cases). In the modified alloys, the presence of carbides (dark points on the graphs Figs. 2-4) has been detected. Moving from the alloy with the highest content of Ti to the lowest one a different type of carbide has been detected as main constituent.

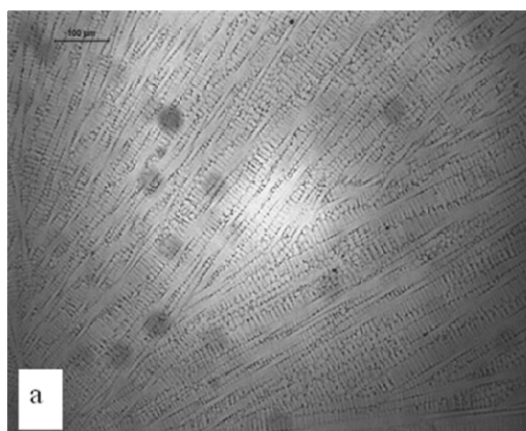


Fig. 1. Optical micrograph of the as-cast Wirobond®280 alloy

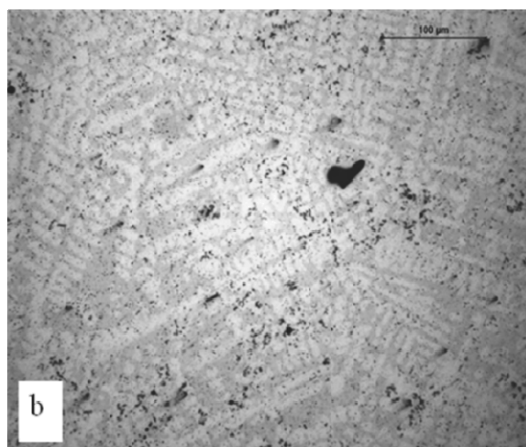


Fig. 2. Optical micrograph of the as-cast CoCrMoTi6 alloys

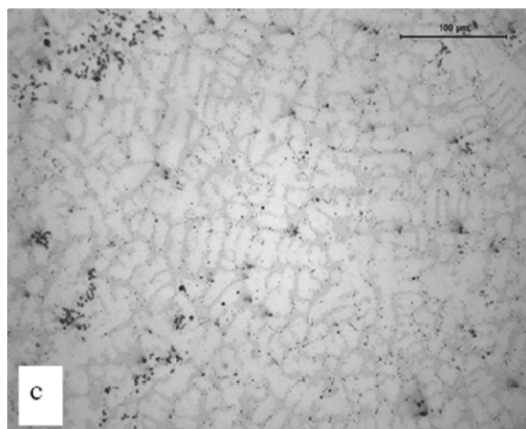


Fig. 3. Optical micrograph of the as-cast CoCrMoTi4 alloy

The chemical composition of these carbides has been identified by EDS and the results have been confirmed by X-ray diffraction analysis.



Table 1.

Chemical composition (wt %) of the prepared alloys

| No | Alloys           | Cr   | Mo   | Ti   | Zr  | C     | Si    | Mn   | P      | S      | Ni    | Co      |
|----|------------------|------|------|------|-----|-------|-------|------|--------|--------|-------|---------|
| 1. | CoCrMoTi6        | 27.9 | 5.84 | 5.93 | -   | 0.276 | 1.800 | 0.64 | 0.0006 | 0.0011 | 0.098 | balance |
| 2. | CoCrMoTi4        | 26.5 | 6    | 4    | -   | 0.356 | 0.510 | 0.67 | 0.0010 | 0.0068 | 0.109 | balance |
| 3. | CoCrMoTi2.5Zr2.5 | 26.5 | 4.5  | 2.5  | 2.5 | 0.336 | 0.074 | 1.17 | 0.0006 | 0.0019 | 0.080 | balance |

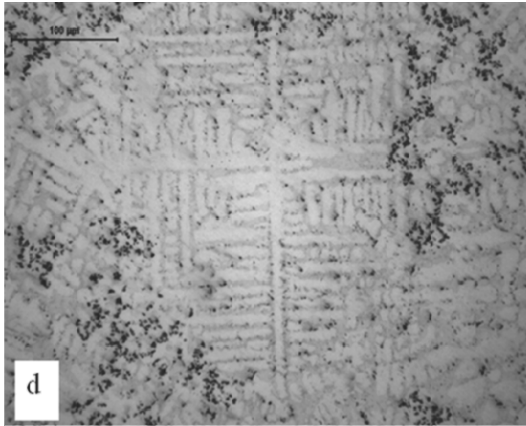


Fig. 4. Optical micrograph of the as-cast CoCrMoTi2.5Zr2.5 alloy

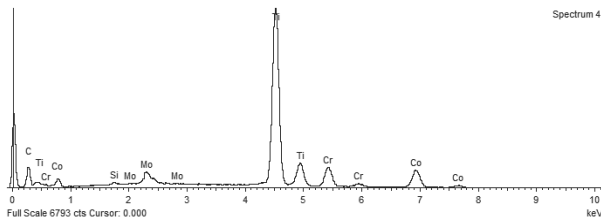
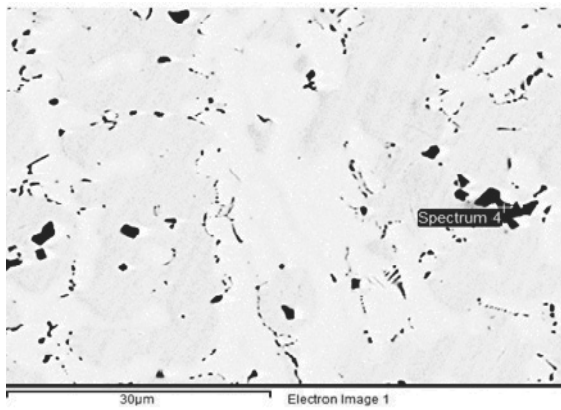


Fig. 5. SEM-EDS results showing the composition of the CoCrMoTi6 alloy

As expected in the case of the alloy with the highest (6%) content of Ti, the carbides are prevalently made of Ti (Fig. 5) with a minor content of other carbides (Cr, Mo). By X-ray analysis the presence of the main constituents (Co, Cr), the hexagonal  $TiC_8$  and an orthorhombic  $Cr_7C_3$  (Fig.5) has been detected.

As the Ti content decrease (to 4%), the  $TiC$  content decreases and increase the presence of Cr and Mo carbides (Fig. 6).

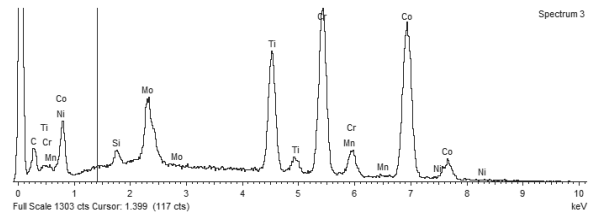
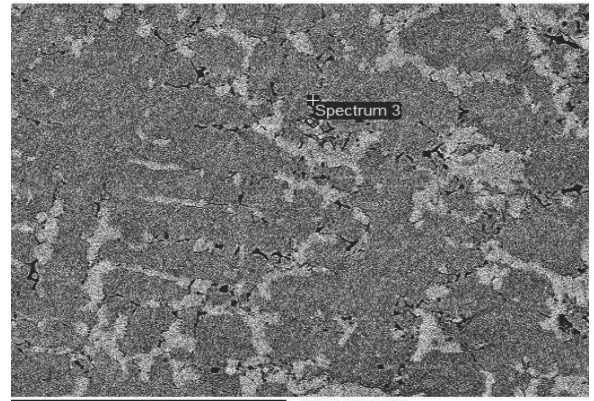


Fig. 6. SEM-EDS results showing the composition of the CoCrMoTi4 alloy

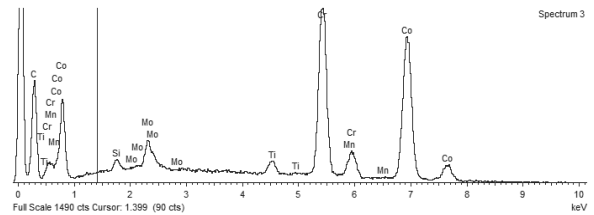
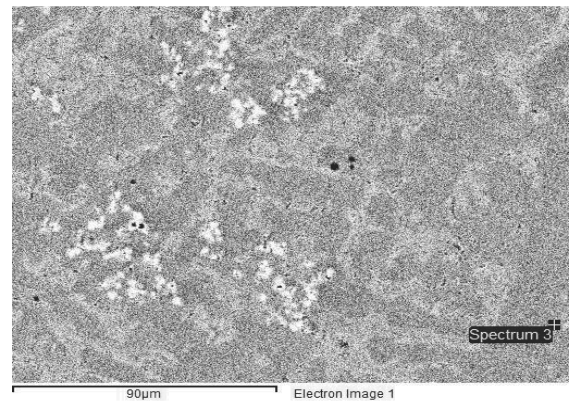


Fig. 7. SEM-EDS results showing the composition of the CoCrMoTi2.5Zr2.5 alloy

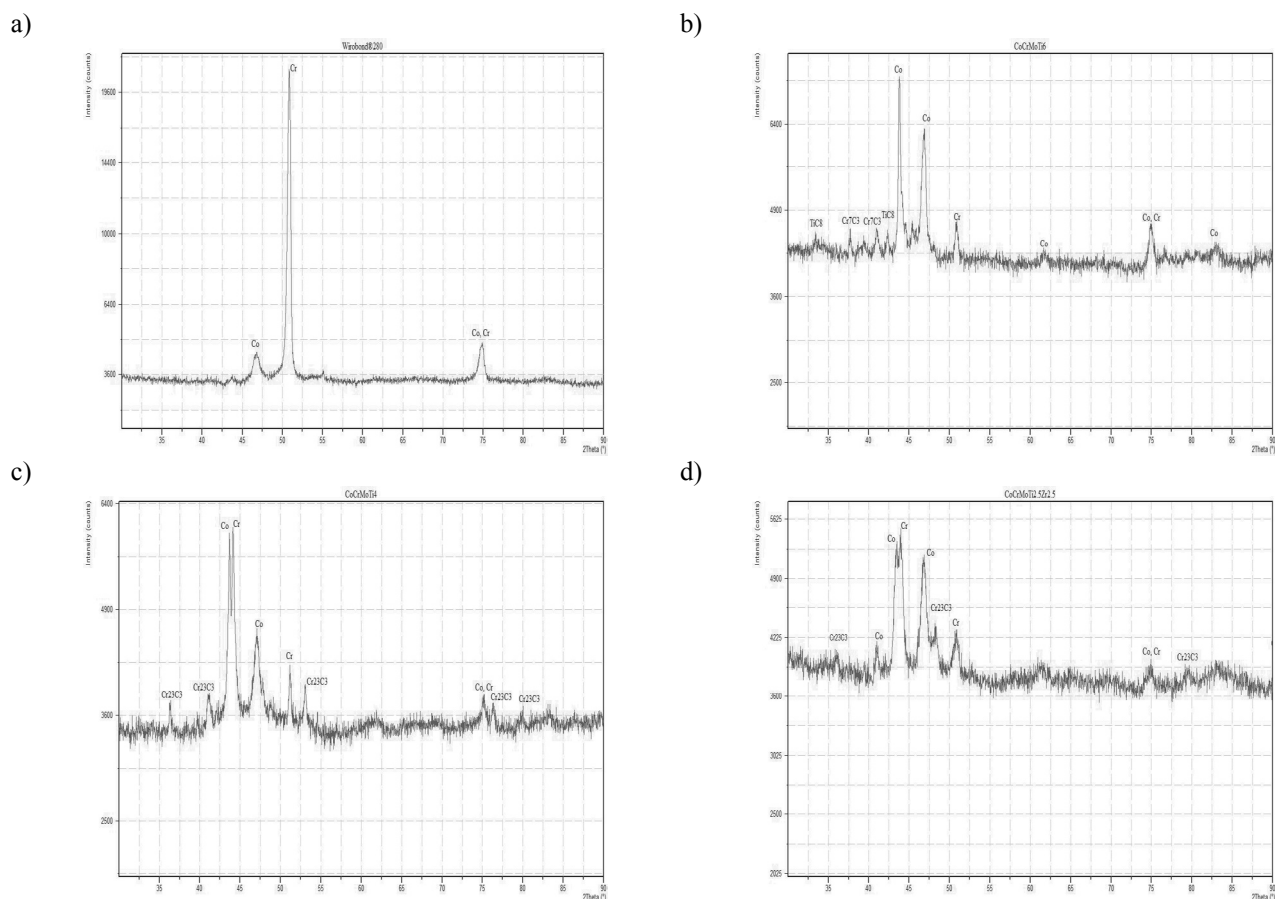


Fig. 8. X-Ray diffraction patterns for the reference: a) Wirobond®280, b) CoCrMoTi6, c) CoCrMoTi4 and d) CoCrMoTi2.5Zr2.5 alloys

The appearance of a cubic  $\text{Cr}_{23}\text{C}_3$  crystalline phases has been detected by X-ray analysis (Fig. 8) as major carbide compounds. The amount of MoC is very low and the peak due to this compound does not become visible in the X-ray spectra. The main composition of the carbides remain the same by adding 2.5% Ti and 2.5% of Zr (Figs. 7 and 8). In this last case the presence of some agglomeration of a hexagonal Zr rich (about 14 weight % as reveals by EDS analysis) phases has been detected (bright white areas in Fig. 4).

The porosity of the alloys has been investigated by optical microscopy, using an image analyser. As expected for the reference alloy, Wirobond®280, no porosity has been detected and for the modified alloys the porosity content is very slow (lower than 0.1 % in all cases).

As mechanical behaviour concerns, the differences following the modification of the alloy with Ti, as a brilliant candidate for carbide formation, microhardness measurements have been carried out.

The carbide development confers to the alloy excellent hardness and, therefore, wear and corrosion resistances. Microhardness measurements have been performed with a standard Vickers pyramidal indenter (square-based diamond pyramid of face angle  $136^\circ$ ) starting from the edge of the samples toward the centre with a step of 1 mm. This way, with a defined

condition, allows to obtain information about the evolution of the hardness when the indenter is in contact with different regions and components (which could be hard particles) in the matrix. Fig. 9 reports the obtained results. As expected, all modified alloys show higher hardness and an increase of hardness of about 40% has been achieved. In addition in these cases a lower standard deviation has been reached indicating that the data points tend to be close to the mean value.

The highest standard deviation obtained for the reference alloy can be a sign that the data points are spread out over a large range of values and the measurement can be considered less reliable. The lowest standard deviation is obtained in the case of the alloy with 6% of Ti, with no negative effect on the workability of the alloy, important features in the case of future application. The imprints realized with optical microscopy did not reveal any dangerous effect on the samples surface such as lateral cracks to be formed during the indentation load action.

As corrosion resistance regards, the samples have been surface-finished and then ultrasonically cleaned to remove any impurities and to avoid any contamination. The bottles used for the test have been disinfected. Each samples have been placed separately in the bottle and one bottle has been monitored containing only the solution.

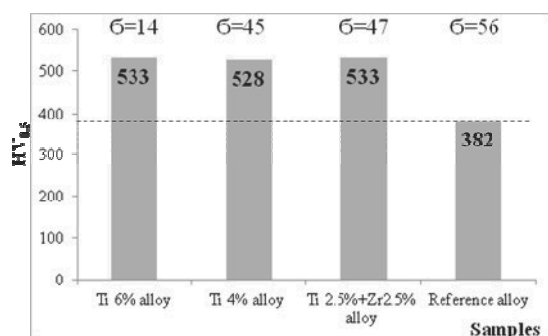


Fig. 9. Average of the Vickers hardness for the considered alloys

The pH of the solution has been measured at the pre-set time intervals. Table 2 summarizes the results. During one week all tested materials maintain the initial pH value. The quantity of metal ions released from CoCrMo6Ti4 and CoCrMo5Ti2.5Zr2.5 alloys results to be much higher than those released from the reference and CoCrMo6Ti6 alloys, but they are however negligible even after 28 days.

The dissolution of the passive film developed on the surface of the alloy has a very low rate. Consequently this layer results to be able to protect the alloy in such conditions, which simulates very well the oral cavity environment. Consequently, the release of Ni, is lower than 0.1% within the week, and this is below the threshold level in the Standard.

Table 2. Concentration of the hydrogen ions in the solution with and without metallic alloys

| pH                 | Initial condition | After 7 days | After 14 days | After 21 days | After 28 days |
|--------------------|-------------------|--------------|---------------|---------------|---------------|
| CoCrMoTi6          | 2.33              | 2.33         | 2.33          | 2.33          | 2.33          |
| CoCrMoTi4          | 2.33              | 2.32         | 2.32          | 2.32          | 2.31          |
| CoCrMoTi2.5Zr2.5   | 2.33              | 2.32         | 2.32          | 2.32          | 2.30          |
| Reference alloy    | 2.33              | 2.33         | 2.33          | 2.31          | 2.30          |
| Reference solution | 2.33              | 2.33         | 2.33          | 2.33          | 2.33          |

The corrosion test has been completed and verified with weight loss measurement. After a regular time, the weights of the samples have been measured. As pointed out also by the previous test, the CoCrMoTi6 alloy does not present any weight alteration after 28 days. The other modified alloys and the reference one reveal some minor changes as illustrated in Table 3.

Table 3. Weight loss measurement results solution with and without metallic alloys

| $\Delta$ Weight % | After 1 day | After 7 days | After 14 days | After 21 days | After 28 days |
|-------------------|-------------|--------------|---------------|---------------|---------------|
| CoCrMoTi6         | 0           | 0            | 0             | 0             | 0             |
| CoCrMoTi4         | 0           | 0.00         | 0.01          | 0.01          | 0.01          |
| CoCrMoTi2.5Zr2.5  | 0.02        | 0.05         | 0.05          | 0.05          | 0.07          |
| Reference alloy   | 0           | 0.06         | 0.07          | 0.07          | 0.07          |

The result obtained indicate that the alloys maintain the condition requested from the Standard (according to the Standard used for the test the deviation for the initial state could be only 1%). From corrosion resistance point of view, the alloys fulfil all the required Standard conditions.

## 4. Conclusions

The aim of this study was to develop a new class of Cobalt based alloy by Ti and Zr addition. The obtained modified alloys were characterized from microstructural, mechanical and corrosion resistance points of view.

Addition of these elements has a positive effect on the alloy hardness. Up to 6% of Ti or combining Ti and Zr as alloying elements there are no significant differences as hardness concerns. Due to the growth of some carbides the amplification of the hardness was obtained. As standard deviation regards, the lowest value was obtained in the case of alloying with 6% of Ti, indicating that the results obtained are more reliable.

Using a higher amount of Ti the hardness will be further improved, but at the same time a negative effect has been observed on the workability, being this characteristic important when the alloy will be further processed to be employed. The simultaneous addition of Ti and Zr leads to the formation of extended Zr covered areas which interrupt the homogeneity of the structure.

As corrosion resistance in a simulated oral cavity environment concerns, no significant release of metal ions was observed; the pH value and the weight loss fulfil the conditions required by the Standard ISO 10271/2011. However, the best behaviour was obtained employing CoCrMoTi6 alloy. The future research work will be oriented to get additional and detailed data on the biocompatibility of the alloy.

On the basis of this investigation one can claim that CoCrMo6Ti6 alloy is a good candidate as a material for dental application.

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