Structural Behaviour of CoCrMoTi(Zr) Alloys for Dental Applications

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Currently, the prosthesis, both removable and fixed, are usually realized in Co-Cr-Mo alloys, which possess good corrosion resistance owing to the appropriate microstructure, but presents low machinability. Occasionally also allergic responses to the constituents of base metal alloys are observed. Most adverse tissue reactions attributed to the wearing of a base metal removable prosthesis, however, are manifestations of improper design or poor fit. Being the major component, cobalt imparts to the alloy its intrinsic corrosion resistance. Ti is one of the best biocompatible metals and is widely used as implant. In addition, the total weight of the prosthesis can be modified. The purpose of this paper is to develop new dental materials with superior mechanical performance and corrosion resistance as well as higher biocompatibility. The attention was focused on the possibility to obtain a new class of cobalt based alloy by Ti addition. Different composition of CoCrMo base system were obtained by RAV technology, alloying with 2- 5%wt. Ti. Different investigations were carried out for the microstructural identification of the constituents either by energy-dispersive X-ray spectroscopy, hardness values determination and mechanical characteristic behaviour. Finally a correlation between structure-mechanical properties due to scanning electronic microscopy was made.

Keywords: cobalt alloy, titanium alloying, mechanical behaviour, removable partial denture

The removable partial denture (RPD) prostheses from metallic alloys are very well appreciated in the international as well as in Romanian prosthetic dentistry [1-5]. They are applied especially to large segments of active population, with a medium income, for which it is foreseen to have long term prosthetic treatment. The RPD prostheses are made up from a number of materials that are physically or chemically combined [6]: a metallic component (cobalt based alloy, titanium alloy or platinum gold); an acrylic component (acrylic resin for saddles, for the self-polymerization and thermo-baro-polymerization acrylic base of the skeletal partial removable prosthesis); thermoplastic materials for injection. The metallic component of the skeletal prosthesis is a metallic cast part. The metallic saddles of the skeletal prosthesis are enhanced with acrylic resin, becoming the support for the artificial teeth which have an identical composition as those for total or partial acrylic prosthesis. The recent literature reveals the concerns of different research teams on the development of new biomaterials with high biocompatibility [7]. In order to increase the durability of removable partial prostheses, there are various current global trends: on one hand, the development of new dental alloys based on the CoCrMo system by alloying with different elements, and, on the other hand, the use of various coating techniques in order to increase the biocompatibility and to eliminate allergies. Analysing the development of dental alloys from various systems, it appears that the cobalt alloys market is well developed since over 60 years [8-12], endeavouring at alloying the CoCr base matrix with various elements [12, 13]. The presence of chromium provides a good corrosion resistance and the addition of small amounts of other elements such as iron, molybdenum and tungsten can confer strength properties at high temperatures. Increasing the molybdenum content, there is a considerable increase in the corrosion resistance, modifying also the solidification behaviour through the formation of intermetallic compounds like Co_3Mo and Co_7Mo_6 [13]. The removable partial denture prostheses made from Heraenium alloy contain about 50% cobalt, 25% chromium, 19% nickel and other small additions, which are normally found in cobalt base products. However, the molybdenum content of approximately 3.7% and the carbon content of about 0.2% are significantly lower than those of conventional cobalt-chromium alloys. In the case of fixed partial dental (FPD) prostheses, these contain approximately 53% up to 65% cobalt and approximately 27% up to 32% chromium [14-16]. The only problem with classic dental alloys, and also with CoCrMo alloys, is their extremely low ductility; however, this is not required to cast products. On the other hand, in the last few years titanium has become a metallic material which drew all the attention, due to the combination of outstanding properties: good corrosion behaviour, biocompatibility, low density and good physical and mechanical properties. Recent studies have stated the beneficial impact of titanium in cobalt alloys. Slokar, Malkovic[17] analysed for the first time, in 2004, the structure and properties of the CoCrTi alloys and stated that alloying with titanium may improve the mechanical behaviour and physical properties, recommending a minimum of 5% Ti. The same authors [18] have shown in 2006 the superior corrosion resistance of CoCrTi alloys and have determined that the value of punctiform corrosion potential is dependent upon the content of titanium, reaching out to the same conclusion for biomedical applications. It should be noted that T. Slokar, T. Matkovic and P. Matkovic [19] studied the CoCrTi system in titanium-based alloys, with Ti $\cong$ 55 $\div$ 85%, Cr $\cong$ 10 $\div$ 25% and Co $\cong$ 5 $\div$ 10%. These alloys belong to the group of b alloys, but the study does not indicate the applications to which such alloys can be used. Brazilian researchers [20] have studied the metal-ceramic bond on NiCr and CoCrTi alloys, identifying the superior behaviour of the alloy with Co $\cong$

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54%, Cr ≅ 15%, Mo ≅ 3% and Ti ≅ 10%, compared to the alloys without titanium. Nevertheless, literature indicates a negative behaviour of the CoCrTi alloy, identified by Brânzoi, Iordoc and Codescu [21], which highlights the superior corrosion resistance of the CoCrMo alloy in Hank solution. The purpose of this paper is to develop new dental materials with superior mechanical performance and corrosion resistance, as well as high biocompatibility.

Experimental part

Materials and methods

Experimental alloys were produced in a cold crucible melting furnace (Fives Celes), in argon. Then, they were cast directly into the ingot mold, in the same neutral atmosphere. The experimental samples were cut in cylinder pieces with dimensions of about Φ 20 x 50mm. Chemical compositions of the alloys were determined by using an optical spectrometer (Spectro Analytical Instruments GmbH & co. KG). The structures of the alloys were put in evidence through light microscopy (LM) and scanning electron microscopy (SEM) using a REICHERT optical microscope and a PHILIPS SEM microscope, respectively, after electrolytic attacks with reagent HCl + HNO_3 + H_2O_2, for 15 s. The phase composition of the alloys was investigated by X-Ray diffraction (DRON3 device). Mechanical characteristics were determined using an INSTRON 8801 apparatus.

Chemical composition

Chemical composition of the experimental alloys is shown in table 1. One may remark that the alloys have a titanium content in the range 2.5 ÷ 5. 0 wt. %. The first alloy has similar titanium and zirconium concentrations (about 2.5%), while the other two alloys have different titanium contents (4 and 5% wt, respectively). The metallic matrix contain approximately 61% cobalt, and different contents of molybdenum 4.5÷ 6% wt.

Structural characterization of the experimental alloys

Experimental cobalt alloys are part of the Co-Cr-Mo system to be joined to titanium as alloying element in different proportions. In accordance to ternary equilibrium phase diagram, the alloy is composed of a non-homogeneous solid solution, specific after casting, and also eutectic consisting in a mixture of solid solution and carbides. Titanium, due to its high affinity to carbon, is bound to carbon in the matrix base material, and the remaining unbound Ti is dissolved in solid solution.

Microstructural analysis performed on the experimental alloys with different proportions of titanium and zirconium is shown in figures 1 ÷ 3. Note that the alloys showed resistance to metallographic attack, performing numerous chemical attack tests with reagents recommended for this class of material, none of them giving the desired results.

The analysis was carried out using two regions, the central and marginal ones for each alloy, at different magnifications (x100, x200, x500) in order to determine the structural characteristics of the specific components. Detailed analysis of the microstructure, as evidenced by Reichert microscope, revealed that alloys with various proportions of titanium have similar structures, consisting of cobalt dendritic solid solution segregation, with numerous carbides in the presence of interdentritic eutectic. It is noted also the massive presence of carbides dispersed both in the matrix and the eutectic, while the central dendrites are fine, uniformly dispersed, with the minor axes of up to 10÷20 μm, the marginal parts of the axes of the dendrites can reach up to 100 μm (2.5% Ti alloy), 150÷200 μm (4% Ti alloy), and up to 200 μm (the alloy with 5% Ti). There are notable differences between the three alloys, as follows. For the 2.5% Ti alloy, dendrites are smaller and carbides are less developed (fig. 1); for the alloy with higher titanium content the segregation tendency is more pronounced and the dendrites are larger at the edges (figs. 2 and 3).

All the structural characteristics of the experimental cobalt alloys are in accordance to those observed by other researchers [17, 19, 22-29].

Table 1

CHEMICAL COMPOSITION OF THE EXPERIMENTAL COBALT ALLOYS

Alloy	Chemical Composition, wt. %							
	Cr	Mo	Si	Ti	Zr	C	other	Co
CoCrMoTiZr	26.5	4.5	1.0	2.5	2.5	0.33	2.0	Rest
CoCrMoTi4	26.5	6.0	1.0	4.0	-	0.34	1.5	Rest
CoCrMoTi5	28.0	4.5	1.0	5.0	-	0.33	0.5	Rest

Results and discussions

The SEM micrographs are shown in figure 4. This analysis allows a more careful and thorough observation of the new structures of the experimental alloys. SEM analysis clearly reveals defined, contoured rounded and dark carbides present especially in the eutectic mechanical mixture. The images evidenced the dominant presence of particles from the eutectic (fig. 4 b, d). Figure 4f highlights both complex carbides of titanium and molybdenum in eutectic and simple titanium carbides, as contoured shapes. The abundance of these particles is due to higher concentrations of titanium content.

XRD spectra of the investigated cobalt alloys are shown in figure 5. This analysis complements the analysis performed by metallographic optical microscopy or scanning electron microscopy, specifying the nature of the phases present in the alloy. Due to their preparation, the experimental casted alloys do not exhibit classical XRD spectra. The spectra present several transitional areas, which can indicate a homogenous structure of the alloys. This is common for removable partial dentures that do not

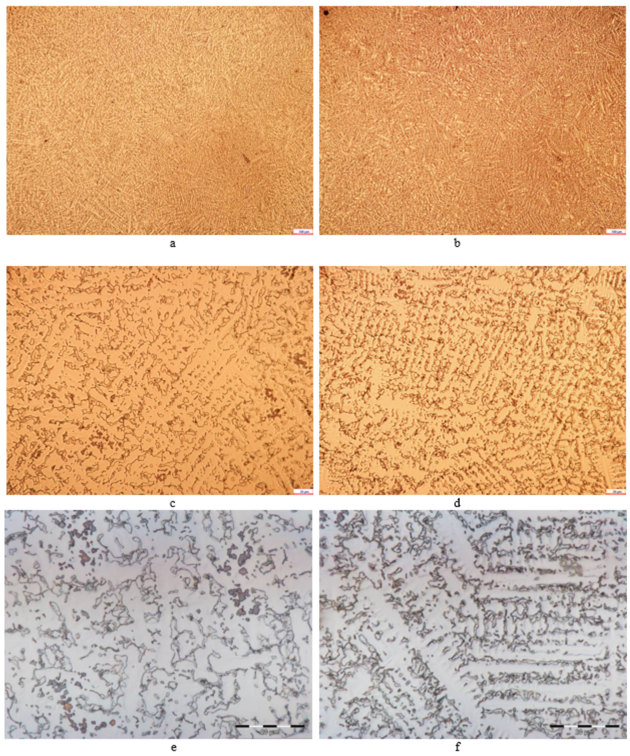


Fig. 1. Structural aspect of the CoCrMoTiZr alloy (Electrolytic attack HCl+HNO_3+H_2O_2): a, c, e- central field; b, d, f- edge zone

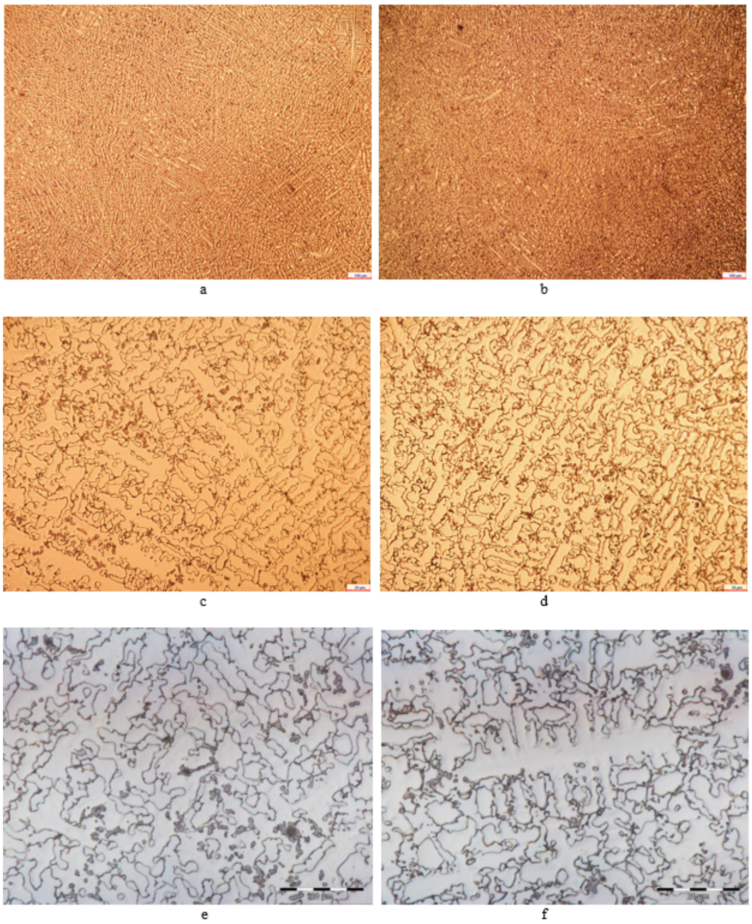


Fig. 2. Structural aspect of the CoCrMoTi4alloy (Electrolytic attack $HCl+HNO_3+H_2O_2$): a, c, - central field; b, d, f- edge zone

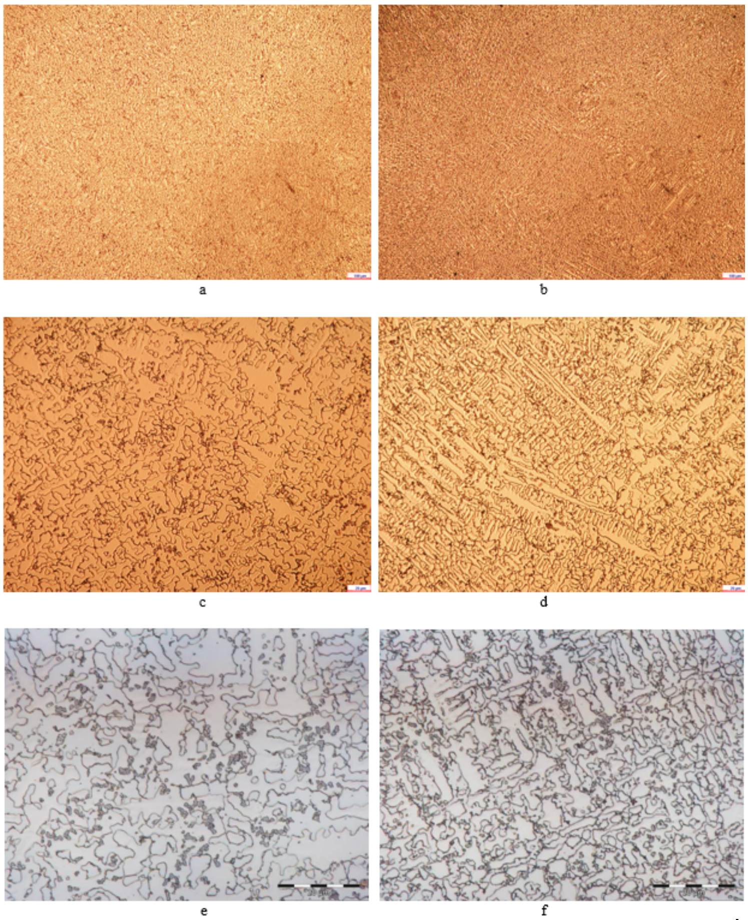


Fig. 3.Structural aspect of the CoCrMoTi5alloy (Electrolytic attack $HCl+HNO_3+H_2O_2$): a, c, e- central field; b, d, f- edge zone

involve other forms of heat treatment and plastic deformation. It is noted that the alloys are composed of cobalt chromium solid solution - with BCC crystalline structures, and simple or complex carbides. So, in the 2.5%Ti alloy one may find chromium carbides type $Cr_{23}C_{3;}$ and other types of carbides could not be defined due to low content of zirconium or titanium. In alloy with 4%Ti, one may find also chromium carbides type $Cr_{23}C_3$ and in alloy with 5%Ti one may find both Cr_7C_3 and TiC_8. The explanation of the presence of TiC_8 consists in high titanium content and its high affinity to carbon.

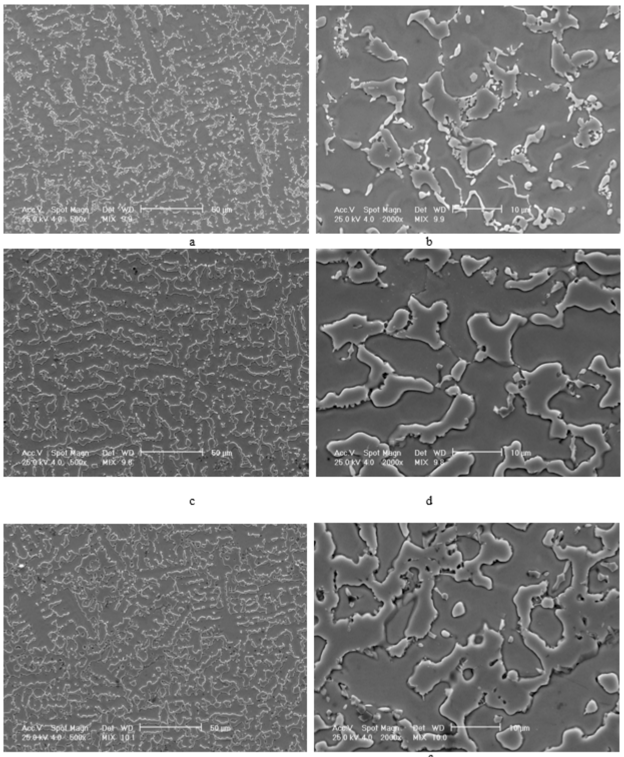


Fig. 4. SEM images of the cobalt alloys (electrolytic attack $HCl+HNO_3+H_2O_2$): a, b- CoCrMoTiZr alloy, c, d- CoCrMoTi4 alloy, e, f- CoCrMoTi5 alloy

The results are similar with outcomes from other scientific papers [26, 30, 31], in which there were investigated alloys with the same Ti content but different concentrations of the alloying elements.

Mechanical characteristics

An important factor in assessing sustainability of the partial removable dentures is the mechanical behaviour. Mechanical characteristics measured by different mechanical tests are fundamental in assessing the materials selection. The characteristics measured by tensile test are strength, yield strength, elongation and necking. Bending test characterizes the behaviour of the material to an applied load perpendicular on the longitudinal axis of the specimen. The bending test allows to determine the modulus of elasticity, which is related to the moment of inertia of the specimen. Complex study conducted in this study aimed to reveal the mechanical behaviour of experimental cobalt alloys in cast state. The partial removable dentures resulted by casting often present many technological discontinuities, defects of compactness which may cause their rapid failure. Although commercial dental alloys have well defined brand prescriptions, labelled on each package provided by the dental offices, they finally have different mechanical characteristics than brand technical requirements. Mechanical behaviour of the cobalt alloys after tensile and bending tests is shown in figure 6 and Figure 7. The values of the mechanical characteristics of the experimental alloys after both tests are shown in table 2. Careful analysis of the mechanical behaviour highlights the fact that these alloys have no elongation, with fracture without prior plastic deformation. As shown in figure 6, one may remark that the strain at break is extremely small as 0.12%, which may lead to the conclusion that these alloys do not have the limit of the flow. Though mechanical strength values are slightly different for the three alloys, theCoCrMoTi5 alloy exhibits the highest strength, followed by the alloy CoCrMoTiZr and CoCrMoTi4. Regarding the bending behaviour, the compression experiments were made up to the maximum load of the mechanical testing device.

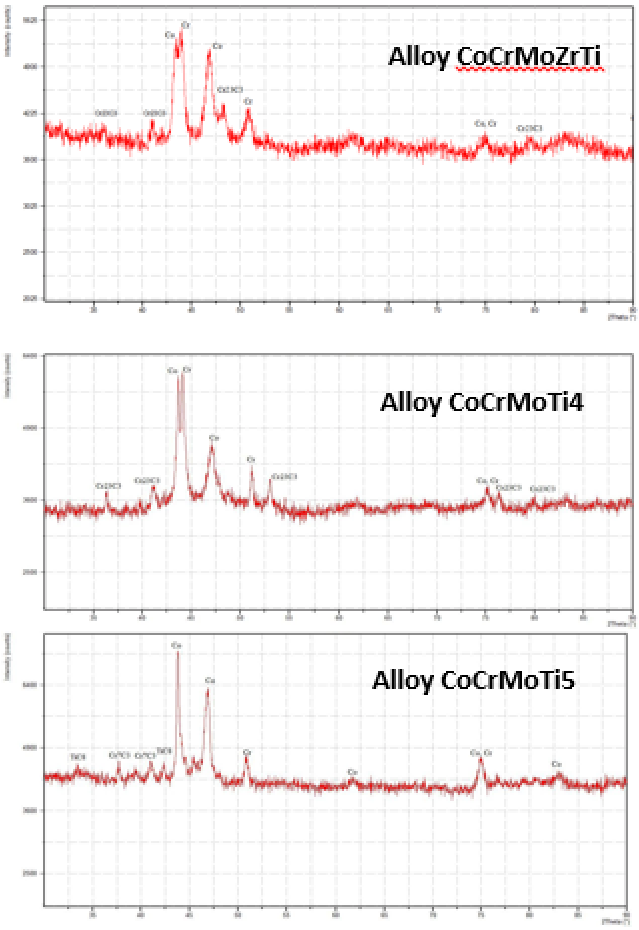


Fig. 5X-Ray diffraction patterns of the cobalt alloys

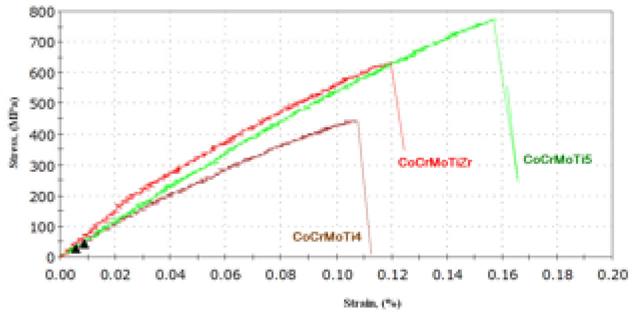


Fig. 6. Stress vs. Strain curves of cobalt alloys at tensile test

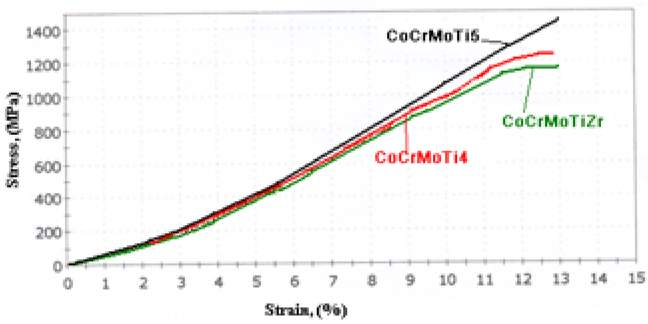


Fig. 7. Stress vs. Strain curves of cobalt alloys at bending test

Mechanical behaviour of the cobalt alloys after tensile and bending tests is shown in figure 6 and figure 7. The values of the mechanical characteristics of the experimental alloys after both tests are shown in table 2. Careful analysis of the mechanical behaviour highlights the fact that these alloys have no elongation, with fracture without prior plastic deformation. As shown in figure 6, one may remark that the strain at break is extremely small as 0.12%, which may lead to the conclusion that these alloys do not have the limit of the flow. Though mechanical strength values are slightly different for the three alloys,

Table 2
MECHANICAL CHARCTERISTIC VALUES OF THE COBALT ALLOYS

alloy	Young modulus of elasticity (MPa)		Fracture strength, σ_m, (MPa)		Fracture elongation (%)
	Tensile test	Bending test	Tensile test	Bending test	Tensile test
CoCrMoTiZr	177113.53	12578.33	625	-	0.120
CoCrMoTi4	202411.87	12998.25	440	-	0.145
CoCrMoTi5	192382.44	13573.09	760	-	0.158

Table 3
MICROHARDNESS VALUES OF THE COBALT ALLOYS

Alloy	State	Field 1		Field 2		Field 3		Average	
		Solid solution	Eutectic mixture	Solid solution	Eutectic mixture	Solid solution	Eutectic mixture	Solid solution	Eutectic mixture
CoCrMoTiZr	*cast*	461	650	498	623	486	678	482	650
CoCrMoTi4	*cast*	497	661	503	658	512	695	504	671
CoCrMoTi5	*cast*	516	791	528	1074	577	585	540	816

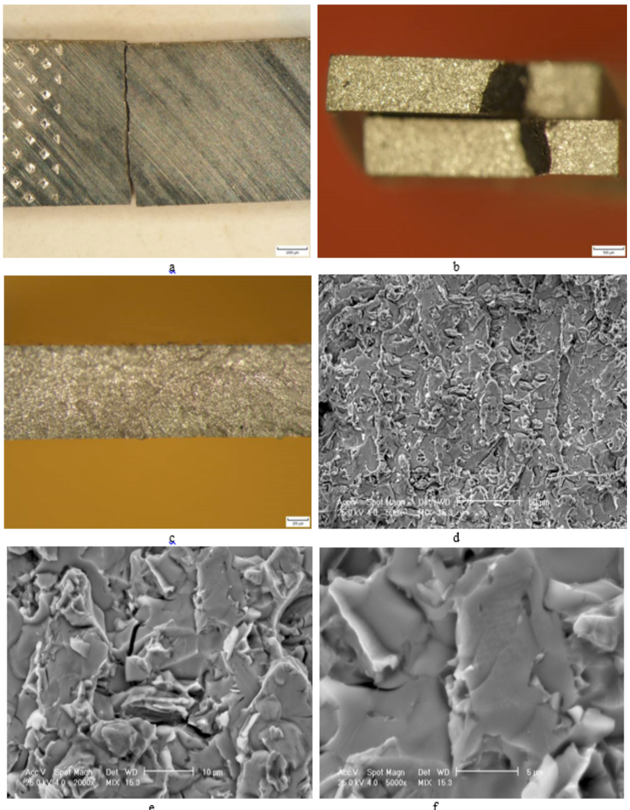


Fig. 8. Fractographic aspects of CoCrMoTiZr surfaces after tensile test: a, b, c- stereomicroscope images; d, e, f- cross sectional SEM images

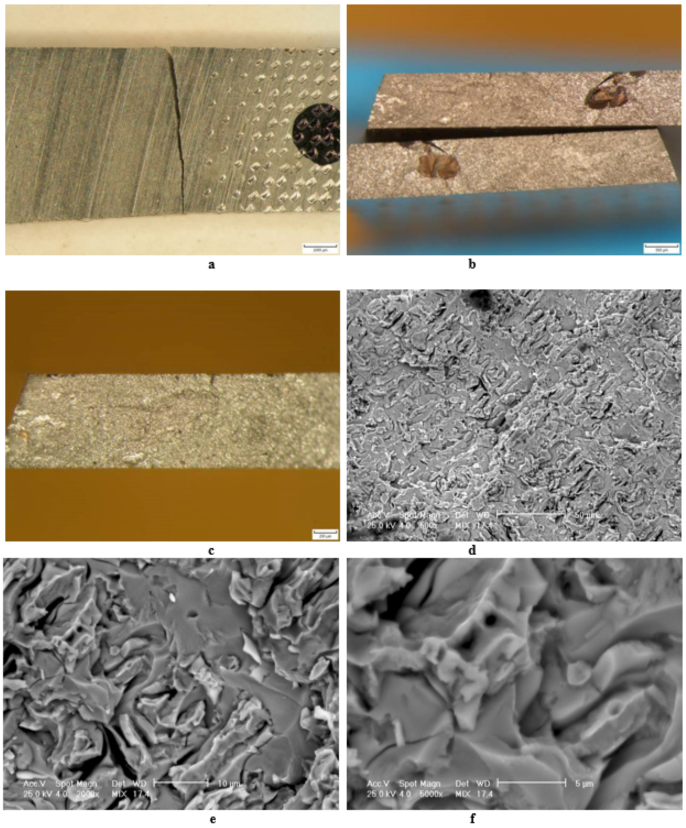
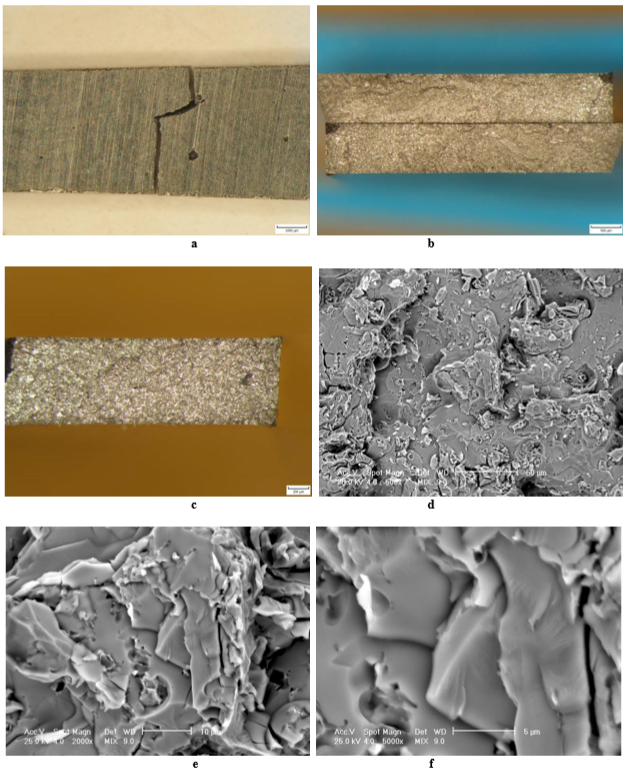


Fig. 10.Fractographic aspects of CoCrMoTi5 surfaces after tensile test: a, b, c- stereomicroscope images; d, e, f- cross sectional SEM images



theCoCrMoTi5 alloy exhibits the highest strength, followed by the alloy CoCrMoTiZr and CoCrMoTi4. Regarding the bending behaviour, the compression experiments were made up to the maximum load of the mechanical testing device. Thus, up to 13% strain, compressive load values were very high, e.g. about 1150 MPa for the alloy CoCrMoTiZr, about 1230 MPa for the CoCrMoTi4 and about 1410 MPa for CoCrMoTi5, without cracks in materials. Consequently, the mechanical test device used could not allow to determine the tensile strength values of the experimental alloys subjected to compression.

Fractographic aspects of the fracture surfaces after tensile tests are specific to brittle cleavage breakdown without stretching before breaking. Analyses carried out using both stereo and scanning electron microscope (figs. 8-10) showed brittle fracture character. The fracture surfaces consist in a cleavage aspect with cut-plane shape put in evidence by scanning electron microscopy. All alloys present similar aspects of the fracture zone, revealing the brittle nature of the fracture, with cleavage fracture zones with intergranular cracks and numerous interdendritic

Fig. 9.Fractographic aspects of CoCrMoTi4 surfaces after tensile test: a, b, c- stereomicroscope images; d, e, f- cross sectional SEM images

secondary cracks, which, by coalescence, allowed and facilitated the movement of fracture front propagation.

The fractography put in evidence in this paper is in accordance with the structural aspects observed by other researchers [32-34]. The microhardness values of the experimental alloys are given in table 3, from which one can highlight the fact that the alloys have different values of the microhardness in solid solution and in eutectic areas. The highest average microhardness, in both solid solution and eutectic mixture, was found for the alloy with the highest titanium content (CoCrMoTi5), followed by CoCrMoTi4 and CoCrMoTiZr.

Conclusions

The experiments of different cobalt alloys with titanium in the range of 2.5- 5 wt. % revealed the following conclusions.

Structural analysis revealed the appearance of a solid solution with specific dendritic segregation cast structures, present in all alloys. The increase in titanium content determined change of the fine eutectic size and also expansion of the eutectic carbides volume. At the same time, for the same carbon content, 0.3 – 0.4%, increasing the titanium content leads to the formation of heavy precipitation and dissolution of titanium in both the matrix and the eutectic. Detailed analysis of the microstructure as evidenced by optical microscopy showed that alloys with various proportions of titanium have similar structures consisting of dendritic segregation of the solid solution of cobalt, with a number of carbides in the presence of the interdendritic eutectic. It is noted also the massive presence of carbides, dispersed both in the matrix and the eutectic. The central dendrites are fine, uniformly dispersed, with the minor axes of up to 10÷20 mm, while the marginal parts of the axes of the dendrites can reach up to 100 mm (2.5% Ti alloy), 150÷200 μm (4% Ti alloy), and up to 200 μm (5% Ti alloy).

Mechanical behaviour of the experimental cobalt alloys was determined by both tensile and bending test. The highest values of the modulus of elasticity and fracture strength were for 5%Ti alloy, followed by the alloy with 2.5%Ti+2.5%Zr and 4%Ti alloy. The same hierarchy was established for the bending tests. Being in cast state, the elongation of the alloys was very low, in the range of 0.12÷ 0.158%.

The fractography made on mechanically tested sample revealed the brittle behaviour of all alloys in cast state. The fracture surfaces showed a cleavage aspect, with intergranular interdendritic cracks, which were developed by coalescence.

Acknowledgements: The work has been funded by MANUNET Project entitled: Development of a new generation of cobalt alloys modified with titanium for dental applications with acronim DENTICO, 2012-2013 and the POSDRU project /159/1.5S/132397, entitled "Excellence in research by doctoral and postdoctoral scholarships".

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Manuscript received: 29.09.2015