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Surface Characterization of New Biomaterials

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Abstract: This paper presents the characterization of new alloys CoCrMoSi6, CoCrMoSi7, CoCrMoSi10, in terms of hardness determinations, fractographic analysis and surface analysis. The original version of the alloy was obtained by casting process in a vacuum arc furnace. Experimental results obtained from this study confirms that by increasing content of silicon, the mechanical properties are superior and the positive results obtained at surface studies favoring the formation of compounds, that lead to the reduction of alloying grade for α solid solution and the plasticity of the alloys.

1. Introduction

The worldwide researches aiming to improve the traditional manufacture technologies of both implants and of the biomaterials of which they are made has the final goal to promote a new generation of multifunctional implants with long-term performances. In regard to the implant material, the current trends in both medical practice and in researches focus on the use of materials with enhanced biologic and biomechanical characteristics, which provide advantages both in regard to biocompatibility with the human tissue and in avoiding the risk of infection or rejection after implanting.

The CoCrMo alloys were highlights by their advantageous properties. In composition of these alloys it is found non-noble metals, which improve the properties by increase the resistance and protect the alloys from oxidation, by passivation [7].

Due to low cost of alloying elements, the obtaining techniques less demanding, but also the advantageous properties, it can specify that CoCrMo alloys have a large utilization, being followed by titanium alloys [3,4,15].

The opportunity of experimental researches is the result of numerous observations, which highlights that the general properties and surface properties (roughness, fractografy) of alloys affect the quality of implants [4].

The experimental researches, present in this study, have like principal objective to improve the properties of cobalt alloys, used in medical applications [1,10,11]. To fulfill this objective, were elaborated new variants of biomaterials, which have a long lifetime, as well as replacement of current materials based on stainless steels and titanium alloys.

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2. Material and methods

2.1. Obtaining technologies of new alloys by CoCrMo system

The establish of utilizations domain of CoCrMo alloys is based on knowledge of their physical, chemical, biological, technological properties, as well as their mutual influences between these.

On base the CoCrMo commercial alloy, with known properties, was obtained new alloys, by CoCrMo system, with improved properties, by addition of silicon [9,11].

The materials used (CoCrMo commercial alloy and silicon), for production of these alloys are with advanced purity and was properly selected, in the terms of chemical composition and grain size, in the order to be placed in alveoli made on cooper plate, cooled with water, by installation.

Alloy	Chemical composition [%]					
	Со	Cr	Mo	С	Si	Mn
"C" commercial alloy	65	29	5	0.4	0.35	0.25

Table 1. Medium contents of elements by CoCrMo commercial alloy.

In table 2 are present the characteristics of CoCrMo commercial alloy, according to quality certificate from producer.

Melting domain	1330-1400°C	
Hardness	402 HV	
Tensile strength (R _m)	760N/mm ²	
Density	8.26 g/cm ³	
Modulus of elasticity	219000 MPa	
Elongation	3%	

Table 2. Characteristics of CoCrMo commercial alloy, according technical sheet of product.

To improve the properties of alloys by CoCrMo system is adding silicon, in varied content, in the elaboration time.

The increase of silicon content, for the alloys of CoCrMo system, determines the properties improvement by: hardness increase, realization of micro-crystalline structure and low values of roughness after cast process [2,13,14].

Silicon content added	Resulted alloy	Notation	Origin
	CoCrMo		commercial
6%	CoCrMoSi6	CSi6	
7%	CoCrMoSi7	CSi7	original
10%	CoCrMoSi10	CSi10	

Table 3. New alloys obtained after cast process.

To highlight the properties improvement, realized by content modification of silicon, was considered that the important laboratory investigations, for characterization of new alloys by CoCrMo

system, are: electronic microscopy, structural analysis by X-ray diffraction, hardness tests, fractographic analysis and roughness determinations [5,8,12].

2.2. Micro-structural characterization of cobalt based alloys

For identification of structure, phases and constituents, it is used a SEM, with BSE detector, at 500X magnitude.



Figure 1. Microstructure of investigated alloys at 500X BSE magnitude.

SEM microstructure for commercial alloy and original variants allied with silicon in 6, 7 and 10% contents, at 500X BSE magnitude, present a dendrite structure, specific to cobalt based alloys, in cast state, with existence of α and β phases, in varied proportions, modified once with the increase of silicon content, in the time of elaboration and cast processes.

2.3. Fractographic analysis

This analysis offer, with help of SEM, a complete characterization of mechanical properties, about the behavior at different mechanical actions (elasticity, fragility, tensile strength, creep).



Figure 2. The aspect of surface for a sample made by CoCrMo commercial alloy.

In the figure 2, it can observe the aspect of breaking plans, with SEM, for CoCrMo commercial alloy. The aspect of surface for a sample made by CoCrMo commercial alloy, present a mixed breaking ductile-fragile, with micro-cracks and hard compounds.



Figure 3. The aspect of surface for a sample made from CSi6 original variant of alloy.

In the figure 3 CSi6 original variant of alloy, present a break by cleavage (fragile) with cracks, slides and nests of hard compounds.



Figure 4. The aspect of surface for a sample made by CSi7 original variant of alloy.

In the figure 4 CSi7 original variant of alloy present a break by cleavage and cracks developed around the nests of hard compounds.





In the figure 5 CSi10 original variant presents a break by semi-cleavage, oriented on dendrite formations and highlights many micro-cracks.

2.4. Investigations using X-ray diffraction

The establishing of compositional phases was made by quantitative analysis, with X-ray diffraction, using X-ray difractometer, model Panalytical X'Pert PRO MPD.

It is used an X-ray fascicule, characteristic CuKa, monochrome with Ni filter. The 20 analysis domain is between 20...1000, step time is 3 second/step and step value is 0.0010.



Figure 6. X-ray diffractograms obtained for new alloys by CoCrMo system.

Table 4. Phases identified at alloys by CoCrMo system.				
Alloy	Phase	2θ angle		
CoCrMo	Co with cubic crystalline network	44.19°		
	Cr _{0,7} Mo _{0,3} with cubic crystalline network	43.56°		
	MoSi ₂ crystallized in tetragonal network	44.48°		
CSi6	Co with cubic crystalline network	43.91°		
	Co ₂ Mo ₃ crystallized in tetragonal network	44.59°		
	Cr _{17,4} Co ₂₉ Si _{11,6} with cubic crystalline network	44.10°		
CSi7	Co with cubic crystalline network	44.10°		
	Cr ₂₉ Co _{17,4} Si _{11,6} with cubic crystalline network	44.10°		
CSi10	Cr _{8.7} Co _{14.5} Si _{5.8} with cubic crystalline network	44.10°		
	Cr _{0.3} Mo _{0.7} with cubic crystalline network	41.39°		

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2.5. Surface analysis of alloys by CoCrMo systems

It was made roughness measurements, on samples whose surfaces are finished by polishing and it was use a specialize apparatus, type Tester, Mitutoyo SJ-301 mark. The average values of parameters specific to roughness for CoCrMo commercial alloy and CSiK (K = 6, 7, 10) original variants, are present in table 6. In the table 5 is present the investigation realized on surface quality, have like principal objective the highlighting of roughness variations, corresponding to samples of CoCrMo and CsiK (K = 6, 7, 10) alloys.

Table 5. The average values of all parameters specific to roughness.				
	Average value measured for R_z , R_a , $R_q[\mu m]$			
Alloys	R _z	R _a	R_q	
CoCrMo	0.63	0.09	0.24	
Csi6	0.24	0.03	0.04	
CSi7	0.53	0.08	0.10	
CSi10	1.17	0.19	0.25	

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After the study of roughness, the alloy which presents the lowest values (high quality) is CSi6 original variant alloy.

2.6. Hardness determinations of cobalt based alloys

To obtain the optimal result was made three determinations for each alloy, with same measurement conditions. Hardness measurements was made on Wilson Wolpert universal hardnessmeter, model 751N, using a press force by 9.807 N and a measurement time by 12 seconds. Hardness measurements made on new alloys by CoCrMo system, offer information about mechanical resistance, imposed or not the utility of heat treatments.

Table 6. Hardness of cobalt based alloys.				
Alloys	CoCrMo	CSi6	CSi7	CSi10
Method	HV			
	423	633	720	800
Punctual measured value	446	633	746	832
	446	653	772	772
Medium value	438.3	639.6	746.0	801.3

3. Conclusions and discussions

By increase the silicon content (6, 7 and 10%), decrease the contents of cobalt, molybdenum and chrome, which are found on samples surface.

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For cobalt alloys, the structure become homogenous and all the alloying element are found finely dispersed in structure.

The fractografic analyses were highlight the fact that new alloys by CoCrMo system, present a linear behavior until break, being part by fragile materials category. In the case of fragile break, micro-cracks initiated in breaking surface suddenly propagates, without a global deformation of materials, but only in micro-volumes localized on breaking surface, like: $Co_xCr_yMo_z$ with cubic crystalline network, CrSi with cubic crystalline network and Cr_yMo_zSi with cubic crystalline network. The fragile breaks produce sections in a plan approximately perpendicular on request plan and have a crystalline aspect (the break is initiated on grain limits with appearance of cleavage plans). The phase's composition of structure, as well as the characteristics of elemental cell for each identified phases were established by X-ray diffraction, but the principal objective was determination of compositional phases, microstructure and micro-composition of commercial alloy and for new alloys by CoCrMo system.

The values obtained at surface analysis confirm the fact that CSi6 alloy is the most indicate to be use in medical applications, because present a high corrosion resistance. Roughness with values slightly upward is specific to CSi10 alloy and implied a probability by high absorption, but and physical – chemical interactions of elements by biologic liquid with surface materials, more powerful.

The hardness tests have demonstrated that the silicon addition at the commercial variant of alloy by CoCrMo system, improve the mechanical characteristics, by formation of solid solution and chemical compounds like Cr_3Si and Mo_3Si , favoring also a structure with fine grains. After 60%Si, the hardness increase very much (639.6 HV), sometimes making impossible the mechanical processing. In this context, it is considered a possible processing, with a special device (super-hard mills).

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