

Structural characterization and properties analysis of CoCrMoSi Alloys

M. G. MINCIUNĂ^{a,b}, P. VIZUREANU^{a,b*}, D. C. ACHIȚEI^{a,b}, A. V. SANDU^{a,b,d}, A. BERBECARU^c, I. G. SANDU^{a,d}
^aFaculty of Materials Science and Engineering, „Gheorghe Asachi” Technical University from Iași, Blvd. D. Mangeron 41, Iasi, 700050, Romania

^bCenter of Excellence Geopolymer & Green Technology, Universiti Malaysia Perlis

^cFaculty of Materials Science and Engineering, Politehnica University Bucharest, 313 Splaiul Independentei, 060042, Bucharest, Romania

^dRomanian Inventors Forum, Str. Sf. Petru Movilă, nr. 3, Bl.L11, Sc. A, Et. III, Ap. 3, 700089, Iasi, Romania

This experimental research in the field was lead by numerous observations, which have revealed that the general properties and surface characteristics of metal implants made of CoCrMoSi alloys, affects directly, and in some cases, can even control the dynamics of the tissue interface. Using the Xray Diffraction the phases of the microstructure was identified. The study concluded that the elaborated alloys can be succesifully used as scheletal prothesis due to their good hardness (500/800HV) and roughness properties ($R_a = 0.2...0.38\mu\text{m}$).

(Received May 12, 2014; accepted February 10, 2016)

Keywords: CoCrMoSi5, CoCrMoSi10, Alloys implants, Tissue interface, Hardness, X-ray diffraction, Spectrometry

1. Introduction

Metals and alloys have many applications in dental therapy, being used in the manufacturing process of artificial substitutes for missing teeth. Amalgam alloy was first made, used as a filling material, subsequently recorded by the first attempts to pour gold (1904) and stainless steel (1912), later in 1932 Co-Cr alloy was obtained [1-6].

Nowadays, increase in the number of implantation procedures is expected. After more than a hundred years when various metals such as: gold, silver, copper, zinc, chrom, nickel, iron and carbon steels, aluminum, magnesium etc. have been tested for such procedures leading to the conclusion that some of these are very

reactive in the body for long term and other are too expensive. Metallic alloys used in our century [7-9] are typically derived from three materials systems: stainless steels, which include 316 and 316 L [10], cobalt-chromium based alloys [11-15] and titanium alloys [16-20]. In all cases the stability of alloy is due to a passive oxide stratum formed spontaneously on the surface of alloy.

Currently, in the global market for dental alloys are available over 3,000 brands of materials. When choosing the material the following main aspects must be taken into consideration: physical, chemical, mechanical, technological characteristics and biocompatibility [21-27] (Table 1).

Table 1. Characteristics required for choosing dental alloys

Physical	Chemical	Mechanical	Technology	Biological
solidification temperature, melting point; fluidity; density; coefficient of linear expansion; metallic luster; insipid; silvery-white; odorless.	corrosion resistance; resistance to oxidation; chemical stability; chemical inertness.	hardness; tensile strength; elongation; torsional stiffness; compressive strength; Poisson's ratio; resistance to wear; modulus of elasticity.	moulding; ductility; surface quality; machinability by cutting; aesthetic aspects; weldability; the ability to be bonded; bonding.	biocompatibility; biostability; cytotoxicity bioinert; bioactivity.

Due to superior mechanical properties, high biocompatibility and low cost, non-noble alloys were used more and more, now almost completely replacing the noble ones [28-34].

Taking into account that due to the lower price of stainless steel and CoCrMo alloy compared to titanium, such alloys are the choice in many implant cases, the

present paper is focused on microstructural properties and surface characteristics investigation on CoCrMoSi alloys.

2. Materials and methods

The alloy was made using arc remelting facility, MRF vacuum ABJ 900, followed by remelting it for 7 times, in order to refine and homogenize the structure. The advantages of this furnace are: very high temperatures are reached in a few seconds, the obtained alloys have a uniform composition due to the strong stirring effect of the melting electric arc, the potential of mixing the components with different melting temperatures. During the melting and casting operations a vacuum atmosphere or inert gas can be made, to prevent reaction with oxygen or nitrogen in the furnace atmosphere [21, 25].

Development of CoCrMoSi10 and CoCrMoSi5 alloy was performed by the semi-melting method which is used on cobalt alloys. We have chosen this method for remelting in an electric arc furnace, under vacuum, because it is considered a melting process of high-purity for metals and alloys.

Commercial alloy, CoCrMo alloys belonging to the class of non-noble alloys, were introduced in the form of "bars", to which 5 % and 10 % silicon was added, with a purity of 99.99 %, there were melted by the heat of the electric arc, and remelted for 7 times, in order to achieve a good homogeneity (fig. 1).

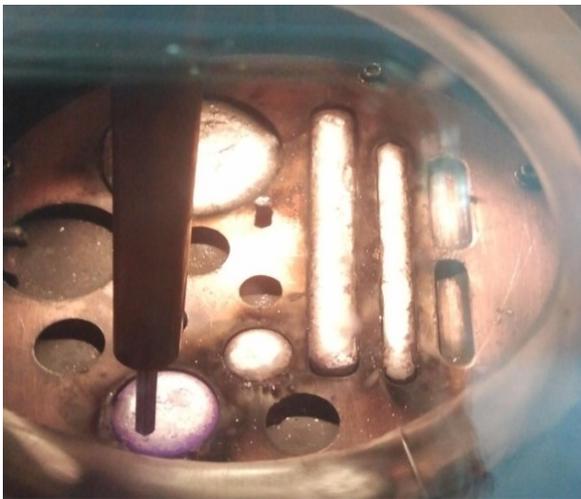


Fig. 1. Experimental alloy melting.

For the CoCrMoSi5 alloy we used 72.030 g of commercial alloy C and we added 3.790g silicon (purity 99.9%), obtaining 75.820 g of alloy. For obtaining 35.470g of CoCrMoSi10 alloy we used 33,700 g of commercial alloy and added 1.770 g of silicon. In table 2 is presented the composition of the commercial alloy.

Table 2. The average Concentrations (% weight) of commercial CoCrMo

Sample number	Elements					
	Co	Cr	Mo	C	Si	Mn
Commercial alloy CoCrMo	65	29	5	0.4	0.35	0.25

The mechanical characteristics of the commercial CoCrMo alloys are:

- yield strength $R_{p0.2}$ to 560 N/mm²,
- breaking strength R_m - 760 N/mm²,
- elongation, A - 3%,
- modulus of elasticity, E - 219000 N/mm²,
- hardness, HB - 380, the density - 8.26 g/cm³
- melting range - 1330 to 1400°C.

Chemical composition of cobalt-based samples was determined by optical emission spectrometry in the Laboratory of Optical Emission Spectrochemical tests and X-ray fluorescence, using a spark SPECTROMAXx device. The new SPECTRO Plasma Generator excitation system with specially selected CCDs emission spectrometer with a new "read-out" performance, innovative and unique optical ICAL logic system, SPECTROMAXx provides analytical possibilities previously only achieved with the conventional photomultiplier.

Characterization of the Co-Cr-Mo alloys was performed by XRD, X'Pert PRO MPD, PANalytical device, at the center of Metallurgical Research and Expertise Eco ECOMET. Monochromatic X -ray beam leaves the anode, is narrower apertures and then faces the object being examined. 2θ ranged from 20-1000, the step size is 0.0010 and the time step is 3 seconds. The analysed surface was a square section of 10 mm, respectively 15 mm.

In order to **determine the hardness** of the alloy an Universal Hardness Testers Wilson Wolpert, 751N model was used, which measures the hardness of the metal material, HB, HRC, HV.

On the finished surfaces, roughness measurements were made. For this, we use specialized equipment Mitutoyo SJ -301. Three measurements of the roughness were done, corresponding to the different parts of it.

The roughness has a strong influence on surface adhesion of living tissue. An implant that has a smooth surface may have a reduced contact area with living tissue and finally a poor linking of implant, this was practically demonstrated by numerous clinical experiments. Increasing the implant surface roughness, the living tissue adhesion is increased, concluding that the bonding strength is higher due to a bigger specific surface area of the implant in the tissue -implant contact.

3. Results and discussions

By conventional production of CoCrMoSi5 and CoCrMoSi10 alloys in an electric arc furnace, under vacuum, we present their composition in table 3.

Table 3. The average concentrations (% weight) of the alloys.

Sample	Elements									
	Co	Cr	Mo	Ni	Si	Mn	Fe	W	S	P
CoCrMoSi5	59,07	26,16	5,24	2,62	6,06	0,42	0,3	0,11	0,007	0,012
CoCrMoSi10	55,8	25,48	5,2	2,8	9,8	0,38	0,43	0,09	0,01	0,008

The samples were processed by cutting to convenient size and chemically etched to remove the oxide traces.

The analysis on chemical composition revealed that the key elements identified in cobalt alloys are Co, Cr, Mo and respectively Si, in different concentrations. The initial alloy had a concentration of 0.35% Si, and was raised at 6.06% for CoCrMoSi5, and 9.8% for CoCrMoSi10.

Due to its short analysis and accuracy of the method, optical emission spectrometry is one of the most effective methods of analysis in development control metal alloys. Adjusting the experimental data lies within an error from 1-2%.

Using XRD device we characterised the obtained alloys. Determination of structural constituents by diffraction is dependent to the diffracted radiation intensity and double diffraction angle.

Fig. 2 shows the diffraction pattern obtained from the sample CoCrMoSi5.

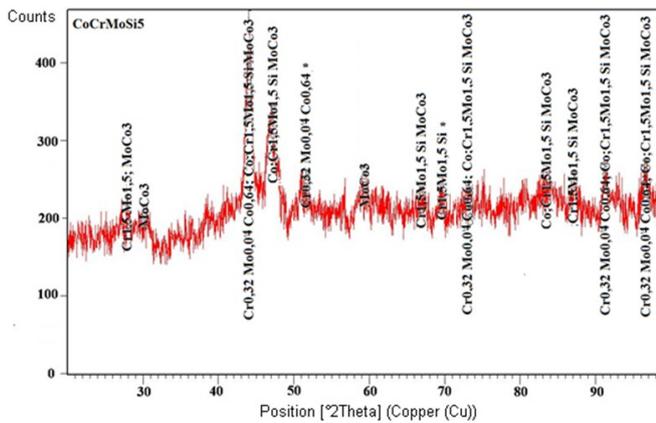


Fig. 2. XRD pattern for CoCrMoSi5 sample

Indexing diffractometry is the association of maximum - diffraction peak and a plan. Indexing diffractogram reveals that are present the following phases: $Co_{0.64}Cr_{0.32}Mo_{0.04}$ with cubic crystal lattice, a main peak at $2\theta = 43.634^\circ$ and $Cr_{1.5}Mo_{1.5}Si$ angle with cubic crystal lattice, the main peak being at 2θ angle = 42.522° , Co_3Mo with hexagonal crystal lattice, having the main maximum at $2\theta = 46.465^\circ$ angle and Co with hexagonal crystal lattice, and the main maximum at the $2\theta = 47.215^\circ$ angle.

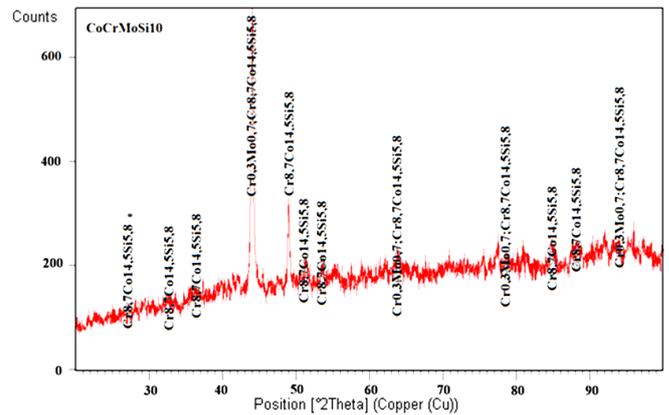


Fig. 3. XRD pattern for CoCrMoSi10 sample.

The analysis reveals that the following phases are present: $Cr_{8.7}Co_{14.5}Si_{5.8}$ with cubic crystal lattice, having the main peak at $2\theta = 44.101^\circ$ and $Cr_{0.3}Mo_{0.7}$ angle with cubic crystal lattice, having the main peak at $2\theta = 41.385^\circ$ angle.

Hardness measurements were performed on Wilson Wolpert microhardness device, model 751N with standard measure of hardness HV 0.2 using a force measuring 9807 N and a measurement time of 12 seconds. Were conducted a total of 3 measurements for each alloy, with the following measuring conditions: temperature $28^\circ C$ (reference temperature: $23 \pm 5^\circ C$) and humidity of 62 %.

Table 4. Hardness of the alloys

Alloy	CoCrMoSi5		CoCrMoSi10	
	HV	HRC	HV	HRC
Point values measured	513	50	800	63,9
	484	48	832	64,9
	498	49	772	63
The mean value	498,3	49	801,3	63,9

Hardness is the mechanical property which is inversely proportional to the workability of the alloy. Vickers hardness of enamel is 320 HV and the noble alloys, depending on composition and heat treatment is between 180 and 300HV. Non-noble alloys hardness is much higher than of the enamel (about 500HV).

From table 4 it is obvious that for CoCrMoSi5 alloy the hardness is in the reference range (498.3 units), instead CoCrMoSi10 alloy which has a higher hardness, reaches a value of 801.3 units. The fact that the alloy CoCrMoSi10

has increased its hardness could be a major advantage as it will be able to provide great resistance to abrasion, wear and compressive strength, far beyond that of conventional alloys used in medical applications.

The average value of maximum height of the roughness profile (Rz) for CoCrMoSi10 and CoCrMoSi5 alloy varies in a small range (between about 1.76 μm and 1.94 μm). These occur due to ripped particles which caused scratches. From this analysis it can be seen a variation of the average peak height depending on the material CoCrMoSi5 > CoCrMoSi10 (Fig. 4).

The amount of surface roughness will vary in a smaller range depending on the material of the dental alloy. This shows that less pronounced irregularities have occurred after the processing. These changes have resulted in variations in the uniformity of surface roughness, Ra (arithmetic mean surface roughness).

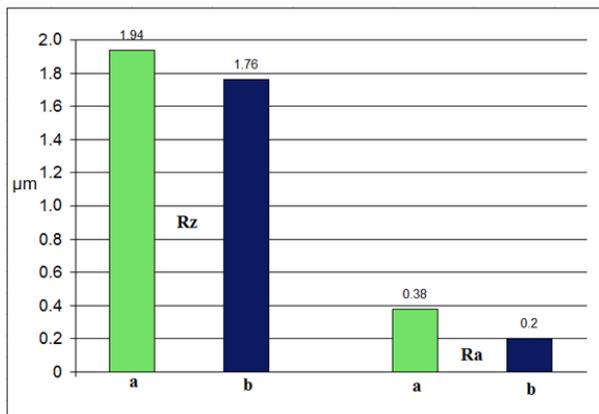


Fig. 4. The Rz and Ra of the alloys: a - CoCrMoSi5; b - CoCrMoSi10

From a scientific analysis of averages, it can be noticed a value decrease depending on the material roughness: CoCrMoSi5 > CoCrMoSi10 (Figure 4). Taking into account the average values of the maximum height this can prove the mechanical strength of the material, the wear occurring at a smaller depth.

Phasic composition of the cell unit structure and the characteristics of each phase, were identified by XRD.

The Non-noble alloys have a hardness much higher than that of enamel (about 500HV).

The presented data shows that the CoCrMoSi5 alloy has a hardness of 498.3 units which corresponds the reference range.

The fact that the alloy CoCrMoSi10 has a much higher hardness could be a major advantage being able to provide great resistance to abrasion, wear and compressive strength far beyond that of conventional alloys used in medical applications.

From the obtained roughness values, we can confirm that the CoCrMoSi10 alloy surface is uniform (0.2 micrometres) and the CoCrMoSi5 alloy presents values slightly increased. Taking into account the average values of the maximum height this can prove the mechanical strength of the material, the wear occurring at a smaller depth.

4. Conclusions

Microstructural examination by X-ray diffraction allowed us to explain the correlation of the structure and the effects on the performance of the alloys and the alloying elements, mainly silicon, and their thermal processing parameters on reaction conditions similar to those actually encountered in medical applications.

The value of surface roughness varied in a small range, depending on the alloy composition used in medical applications. This shows that less pronounced irregularities occur after the training process.

The new elaborated alloys can be used successfully in skeletal prostheses, due to enhanced characteristics and low cost.

Acknowledgement

“This work is supported by the Sectoral Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390/“

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*Corresponding Author: peviz2002@yahoo.com