Effect of Si on the Microstructure and Mechanical Properties of Biomedical CoCrMo Alloy

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The paper presents a comparative study about the modifications of microstructure and mechanical properties, for 2 alloys for Co-Cr-Mo system alloys. The structural modification are evidenced by complex microscopic analysis made on a metallographic microscope and an electronic microscope coupled with EDX detector, but also by X-ray diffraction analysis, determining the inter-metallic compounds and phases specific to cast state of analyzed alloys. In terms of mechanical properties, the standard samples from analyzed alloys was subject to tensile test and hardness measurements. The obtained values both for CoCrMoSi1Mn1 alloy, and for allied alloys with 5%Si (CoCrMoSi5Mn1), are subject to standard limits of metallic alloys, with medical applications.

Keywords: CoCrMo alloys, microstructures, tensile test, hardness measurements, X-ray diffraction, castability

Since to beginning of Co-base alloys development some of them found the place in medical field due to their inertness in human body, and their adequate properties for structural medical applications [1-3]. First use of Co-base alloys in medical field was in dentistry as cast removable partial denture frameworks [1]. Along the time, the medical applications of the Co-base alloys were diversified, but only few Co-base alloys being dedicated for such applications especially from Co-Cr-Mo and Co-Cr-W systems [1, 4]. Recently, both Co-Cr-W-Si and Co-Cr-Mo-Si alloys gained the attention of researchers [5-9]. In Co-base alloys, elemental silicon additions stabilize hcp phase, having a similar effect with the chromium, molybdenum, and tungsten [1], change microstructure of as-cast and heat treated Co-Cr-Mo alloys [5, 10], impart good casting properties and increase ductility for nickel-containing alloys [6, 11], and modify shear bond strength between porcelain and Co-Cr metallic substrate for metal-ceramic dental restorations [6, 12].

In the CoCrMo alloys, the face-centered cubic (FCC) and the hexagonal closed packed (HCP) crystalline structures co-exist. Typically, the FCC phase metastable is predominant at room temperature, but the FCC→HCP transformation could be isothermally or strain-induced [8-10]. The other main feature of the Co-based alloys is the presence of carbon which forms carbides whose distribution and size is influenced by the manufacturing process [13, 14]. The main factors that affect the wear resistance of CoCrMo alloys are the carbon content, the homogeneous distribution of the carbides and the presence of the phase with HCP crystal structure [15-22].

The purpose of this study is to evaluate the effect of high Si content on microstructure and mechanical properties of CoCrMo alloys used in medical applications.

Experimental part
Materials and methods
Small ingots (about 130 g, 17 x 9 mm² cross-section area and 120 mm length) were obtained from a “C” trade mark Co base dental alloy (Vasscut Kohaszati Kft., Hungary, nominal chemical composition 65 %wt. Co, 29 %wt. Cr, 5 %wt. Mo, 0.35 %wt. Si, 0.25 %wt. Mn, 0.40 %wt. C) by its remelting and alloying with Si and Mn (commercial purity) using a vacuum arc melting furnace (MRF model ABJ 900). The ingots experimentally obtained were remelted three times in order to homogenize chemically the alloys. The chemical compositions were measured using an optical emission spectrometer (SPECTROMAXx), and the chemical compositions and symbols used for the both alloys in this work are shown in table 1.

Table 1

<table>
<thead>
<tr>
<th>Symbol alloy</th>
<th>Chemical compositions, [wt. %]</th>
</tr>
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<tbody>
<tr>
<td>CoCrMoSi1Mn1</td>
<td>nominal</td>
</tr>
<tr>
<td>Type</td>
<td>Co</td>
</tr>
<tr>
<td>measured</td>
<td>64.65</td>
</tr>
<tr>
<td>CoCrMoSi5Mn1</td>
<td>intended</td>
</tr>
<tr>
<td>Type</td>
<td>Co</td>
</tr>
<tr>
<td>measured</td>
<td>61.65</td>
</tr>
</tbody>
</table>

Structural characterization
The microstructural samples were obtained by machining from initial ingots. Subsequently, the samples were prepared by grinding and polishing with emery papers (grit from 180 up to 2000) followed by mirror polishing.
with alumina suspension (from 0.800 μm up to 0.020 mm). To put in evidence the morphology of metallographic constituents, the samples were etched with a dedicated etchant: 5 mL of HNO₃, 200 mL of HCl and 65 g FeCl₃.

Microstructural analysis was performed using a Zeiss inverted metallographic microscope (D1m AxioObserver) with dedicated software for image acquisition and analysis (Omniment). Also, a scanning electron microscope (VegaTescan LMH II) equipped with an X-ray detector EDAX (Quantax, Bruker) was used for microstructure and chemical composition analysis.

**Diffraction**

The phase analysis of investigated alloys was performed using an X'Pert PRO MRD diffractometer (PAN’Analytical, Netherlands) with high-intensity CuKα irradiation (λ = 1.5406 Å). The preparation of samples used for XRD analysis was performed as in the case of samples used for the microscopy (excepting chemical etching).

**Mechanical tests**

Tensile tests were conducted on a universal testing machine Instron 3382 European Standard ISO 6892-1:2009, IXTM Series Bluehill software [24, 25]. The ingots were cut by electro-erosion machining at the dimensions of test plate samples. The sample dimensions for tensile test are present in figure 1. Four samples were prepared and tensile tested from each alloy [26-28].

Hardness measurements were performed on a Wilson Wolpert universal hardness tester, type 751N, using a force measuring 9.81 N and a load time of 12 s. It was conducted a total of 3 measurements for each alloy [29].

**Results and discussions**

**Microstructure analysis**

In figure 2 is shown XRD patterns and its details, and in figures 4 and 5 optical and SEM micrographs of experimental alloys.

The analysis of the XRD patterns obtained for CoCrMoSi1Mn1 and CoCrMoSi5Mn1 alloys showed that the both alloys contain γ phase (fcc), M₆C carbides, and π (s)/η phases. The π (M₆X-type carbide with a β-Mn structure) and η (M₆C-M₁₂C-type carbide) phases were identified by Alfirano et al. [10] in Co-Cr-Mo-Si-Mn alloys which contained 0.98 %wt. Si, 1.02 %wt. Mn and 0.26 % C. More peaks could be assigned to M₆C carbide for alloys with higher Si content, this statement being an argument to sustain that the increasing Si content the formation of M₂₃C₆ carbide is favored.

In figure 1 it is shown the optical microstructure of the two alloys. Major differences are observed: the sizes of γ (fcc) dendrites decreased and morphology was changed, in case of CoCrMoSi5Mn1 alloy, the interdendritic zones are more large that means a great quantity of eutectic and carbides, finding sustained by XRD patterns.

**Table 2**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Microstructural zone</th>
<th>Chemical composition, [% mass]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>CoCrMoSi1Mn1</td>
<td>dendrite</td>
<td>68.71</td>
</tr>
<tr>
<td></td>
<td>interdendritic</td>
<td>62.51</td>
</tr>
<tr>
<td>CoCrMoSi5Mn1</td>
<td>dendrite</td>
<td>65.49</td>
</tr>
<tr>
<td></td>
<td>interdendritic</td>
<td>44.90</td>
</tr>
</tbody>
</table>

**Fig. 2.** XRD patterns of investigated CoCrMoSi alloys: a) general patterns; b) detail

**Fig. 3.** Optical micrographs: a) CoCrMoSi1Mn1; b) CoCrMoSi5Mn1

The results of SEM/EDS analysis are found in table 2 and figure 4.

Regardless of chemical compositions, the contents of Cr, Mo, Si, and C are increased in interdendritic zones, and are decreased in dendritic zones; conversely, higher contents of Co and Mn are in the dendritic zones than in the interdendritic zones (table 2). Henriques et al. [12] investigated the Co-Cr-Mo alloys containing 2.2 % wt. Si, and they found that interdendritic regions of as-cast alloy contain three phases with different chemical compositions, but all have a higher content of Cr, Mo and Si in comparison with dendritic regions.

Figure 4a-e shows the SEM microstructures and EDS maps of alloying elements of investigated alloys. Major differences of microstructures can be observed. The eutectic that corresponds to CoCrMoSi5Mn1 alloys have coarse lamellas, and its surface area are higher. Within interdendritic zones, M₂₃C₆ carbides having 1 μm up to 5
μm sizes can be observed. In the case of CoCrMoSi5Mn1 alloy, the arms of γ (fcc) dendrites have sizes greater than the sizes of dendrite of CoCrMoSi5Mn1. A fine eutectic can be observed for CoCrMoSi1Mn1, and other phases cannot be observed. A good correlation between XRD patterns and SEM/EDS analysis was established.

### Mechanical properties

In figure 5 are presented examples of strain-stress curves for the both alloys. The shape of the two tensile curves is similar. In table 3 is observed that the both alloys have an adequate mechanical behaviour, with adequate average values for yield and fracture strengths, and acceptable average values of the elongation. The statistical analysis of experimental values derived from tensile tests showed that only tensile stress and elongation values are significantly different. This result corresponds with microstructural analysis, namely a higher content of Si lead to a higher fraction of carbides, which implies the decrease of fracture strength and elongation values. Also, the average values of HV hardness are found in the table 3. Statistical analysis indicated the occurrence of a significant difference between the average values of HV hardness. Again, an increased Si content lead to higher value of hardness, result that are correlated with observed microstructure and mechanical properties resulted from tensile tests.

### Conclusions

By alloying with 5% silicon, it appear combinations from type CoXMoY and CrYCoXSiZ (identified by qualitative analysis with X-ray diffraction) which modify radically the mechanical properties of the alloys. Based on experimental determinations, at the original variant of CoCrMoSi5Mn1 alloy, the elongation decreases at values under 10.3%. This fact is in directly correlation, both of microstructural modifications (interdendrite agglomerations), and with the mechanical resistance, due to excessive increase of hardness to values up 500 HV. The measurements of hardness made on CoCrMo alloys, provided the information about the mechanical resistance, imposing or not the utility of heat treatment applications. The additions of silicon added at the commercial variant of the alloy from CoCrMo system, improved the mechanical characteristics, especially the hardness, with the formation of solide solutions with cobalt and chemical compounds types CrSi and MoSi, favouring in same time a structure with fine grains.

The original variant of CoCrMoSi5Mn1 alloy, whose properties are improved by the increase of silicon addition, may be used in medical applications only after achieving of a heat treatment (quenching to put into solution), which have the role to reduce the quantity of secondary phases. The heat treatment may be made in function of the destination which will have the original variant of alloy, but in function of the realized structure due of thermodynamic conditions of the solidification process.

### References


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