Comparison of Some Properties of Selected Co-Cr Alloys Used in Dental Prosthetics

Narowska-Sobieraj A.a, Myszka D.b*

a Department of Dental Prosthetics, Medical University of Warsaw
b Department of Metal Forming and Casting, Faculty of Production Engineering, Warsaw University of Technology
*Corresponding author. E-mail address: d.myszka@wip.pw.edu

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Abstract

Corrosion resistance and mechanical properties of cobalt alloys for dentures strongly depend on the manufacturing technology. The basic alloying elements include chromium (18% to 30%) and molybdenum (2.5% to 9.0%), as well as other elements such as W, C, Fe, Mn, Si and Ti. Due to the presence of chromium and molybdenum, cobalt-based alloys are characterized by satisfactory corrosion resistance at normal and elevated temperatures. The aforementioned elements enhance the resistance to acids, provide good resistance to pitting and crevice corrosion in acidic and neutral environments, and high resistance to stress and fatigue corrosion. Casting cobalt alloys have the structure of non-homogeneous austenite with heavy chemical microsegregation. The element that is most susceptible to segregation within the dendritic area is chromium, followed, though to a lesser extent, by molybdenum. The casting process by which the dental prostheses are made exerts a strong influence on alloy structure with the consequence that, as shown in the article, the properties differ significantly in the raw condition and after precision casting process. The four Co-Cr alloys selected for the study contained different fractions of Si, W and Mo. The microstructure and hardness of these alloys as well as the impact of manufacturing process on casting surface roughness were determined.

Keywords:
Co-Cr Alloys; Dental Alloys; Microstructure; Casting Roughness; Mechanical Properties.

1. Introduction

Metal alloys are the primary material used for dental restorations, both fixed and removable. They have been used in dentistry continuously since 1907 [1], when the technique of lost wax casting, also known as the investment casting process, was developed. The essence of this process consists in shaping the manufactured prosthetic restoration in a wax pattern, coating the pattern with a refractory material, melting out the wax and filling up the free space left by the wax with metal
introduced by centrifugal force or pressure [2]. In prosthetics it is essential to cast a very exact replica of the wax pattern, both in terms of the overall dimensions and surface details. The quality of final prosthetic restoration is largely affected by the technique adopted in its execution, mainly the compliance with relevant conditions at each stage of the casting process, including proper treatment and handling of materials [3]. It is absolutely necessary to keep in mind the fact that each modification introduced to the technological process can change the quality of resultant casting, i.e. its mechanical, physical and chemical properties. A high-precision casting characterized by the smooth surface and compact structure is less susceptible to the effect of oral environment [2].

The quality of investment castings depends on a number of different factors, including wax contraction, refractory material expansion, mould preheating temperature, length and thickness of the sprue, casting method, alloy shrinkage, and final treatment of castings [2].

The wax pattern may suffer deformation due to flow, stress release or thermal expansion. Therefore, immediately after having been made, it should be embedded in a refractory material, as otherwise changes in its shape may occur due to stresses released in the wax material [4].

The sprue, designed before the wax material is separated from the plaster model, should be of an adequate length and thickness, both of which depend on the shape of dental restoration. The use of a short channel with large diameter ensures metal solidification in the sprue in the last stage of the casting process, which prevents the formation of shrinkage cavities in the cast element [2,3].

The ceramic material in which the wax pattern is embedded should match the thermal properties of the cast alloy to make sure that its expansion can compensate the alloy shrinkage. Properly selected value of the refractory material expansion is the best guarantee that a high-quality casting with smooth and non-porous surface is obtained [3].

The removal of wax from the casting mould is achieved by heating the ceramic material in a casting ring and burning out the wax. The heating temperature depends on the type of the ceramic material used. With proper temperature obtained, the corresponding thermal expansion and inversion expansion can also reach the required values. Pouring of the ceramic mould should be carried out immediately after heating the ring to prevent cooling down of the ceramic material prior to alloy casting [4]. Failure to do so can lead to mould cracking and casting distortion.

A very important step in the whole process of casting is melting of alloy. Insufficient heating of the melt can result in insufficient castability of the metal, which will not allow for an exact reproduction of the thin-walled model. In contrast, excessive heating of metal may cause the possibility of cracks appearing in the ceramic mold [3].

As regards cobalt-chromium alloys, the required melting temperature produced by a heat source should be comprised in the range of 1400° to 1600°C [2]. To achieve this temperature, it is recommended to use an induction furnace powered with high frequency current [3]. The furnace consists of a crucible and a high-frequency coil. The installation provides uniform melting temperature within the entire metal volume, and process is run under an atmosphere of inert gas (argon) without access of oxygen to prevent metal oxidation. The furnace is an electronic component of the induction casting set commonly used in prosthetic laboratories. The set also includes a mechanical component, which is an electric motor-driven centrifuge. The casting process begins with setting the arm of the centrifuge in melting position, remembering that the metal ring holding the crucible should be placed slightly above the high-frequency coil. The preheated crucible is set in a proper position on the centrifuge arm to be filled next with an adequate amount of metal. The casting mould after the burnout process is placed in the centrifuge bearing and its equilibrium position is found and fixed. Then the air surrounding the crucible is pushed out by a stream of argon and melting of the metal starts. When the metal melts down completely, the centrifuge is put in operation [2]. After casting, the ceramic mould is cooled either at room temperature or in water [4].

The properties of the ready casting depend not only on the technological process by which it is made, but also on further treatment that it receives after having been cast. In the case of dental restorations, this treatment consists in mechanical polishing and electroplating. In addition to make the surface smooth and shiny, polishing is also carried out to preserve or upgrade the metal properties [12]. The process of mechanical polishing is carried out using increasingly fine abrasive materials and various kinds of brushes as well as felt deposited on electric grinding machines [4]. Electrolytic polishing, including polishing used in the case of removable partial denture frameworks, consists in the anodic dissolution of metal. This method enables polishing the areas hard to reach for machining. The casting must be first prepared by mechanical smoothing and degreasing, because surface irregularities may not exceed 1-3 microns [2]. In this process, the cast structure acts as an anode. The current flowing between this anode and the cathode, which remains neutral after immersion in the electrolyte, has an impact on the anode surface. Products of the electrolysis are collected in the hollows of the rough casting surface, while protrusions are dissolved.

Despite the complexity of the casting process and later treatment of castings, alloys of metals, due to their
mechanical strength, ease of processing and price, will remain for long time the basic material for prosthetic reconstructions [1]. They are applicable in rebuilding the absence of a single tooth and also in the reconstruction of extensive tooth losses.

Dental alloys may contain in their composition up to thirty different types of metals [1]. These include both precious metals (gold, platinum, palladium) and non-precious ones (nickel, copper, cobalt, silver, zinc, titanium). As regards the percent content of individual metals, dental casting alloys are classified according to the ANSI-ADA specification [4]. They are divided into three groups: high noble (precious) alloys (60% of precious metals, including at least 40% of gold), noble (semi-precious) alloys (at least 25% of precious metals), and non-precious (base) alloys (less than 25% of precious metals). The chemical composition of the alloy significantly affects the casting properties, such as density, hardness, bending strength, and corrosion resistance [6].

Before admission to trading, metal alloys must meet certain requirements concerning their physical and chemical properties, which are specified by ISO standards. Qualification of metal alloy for sale is preceded by testing its physical and mechanical properties. All these tests are performed prior to alloy casting. The values of some physical and mechanical parameters obtained on metal alloys after casting may differ from the values specified by the manufacturer. This reflects the impact of the casting process on alloy properties, the fact usually disregarded by manufacturers of these materials in their studies [8].

Remembering that the current state of knowledge clearly indicates the importance of mechanical properties in the assessment of non-precious metal alloys used by dentists, the aim of this article is to compare the structure and some properties of selected Co-Cr alloys after casting. Knowledge about correlations between chemical composition and structure of the cast would allow to choose appropriate alloy for prosthodontic cure.

2. Research methodology

Four types of Co-Cr alloys were tested. They are used for the manufacture of removable partial denture frameworks in dental laboratories and are characterized by the chemical composition similar to alloys, such as BIOSIL F, WIRONIT EXTRAHART, REMANIUM GM 800+, REMANIUM STAR. Chemical compositions of the tested alloys and of the alloys offered by manufacturers on the prosthetic market are compared in Tables 1 and 2. To evaluate the as-cast and surface-treated metal properties, samples were cast in the form of plates 15mm high, 15mm wide and 2 mm thick (Fig. 1). Twenty samples of each of the tested metal alloys were prepared under the conditions as close as possible to the standard manufacturing conditions of skeletal prostheses (casting temperature - min.1450°C, foundry mould temperature - min. 950°C).

Table 1. Chemical composition of the examined alloys [wt% ].

<table>
<thead>
<tr>
<th>Alloying constituent</th>
<th>BF</th>
<th>WE</th>
<th>R8</th>
<th>RS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>64.63</td>
<td>61.98</td>
<td>59.02</td>
<td>59.31</td>
</tr>
<tr>
<td>Cr</td>
<td>29.84</td>
<td>32.56</td>
<td>31.59</td>
<td>30.56</td>
</tr>
<tr>
<td>Si</td>
<td>0.61</td>
<td>0.87</td>
<td>1.09</td>
<td>1.51</td>
</tr>
<tr>
<td>Mo</td>
<td>4.92</td>
<td>4.59</td>
<td>6.96</td>
<td>-</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>-</td>
<td>1.34</td>
<td>8.62</td>
</tr>
<tr>
<td>Cl,Fe,Mn,N,Nb</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of commercial prosthetic alloys [wt%] according to data from manufacturers.

<table>
<thead>
<tr>
<th>BIOSIL F</th>
<th>WIRONIT EXTRAHART</th>
<th>REMANIUM GM 800+</th>
<th>REMANIUM STAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co – 64.8%</td>
<td>Co – 63.0%</td>
<td>Co – 58.3%</td>
<td>Co – 60.5%</td>
</tr>
<tr>
<td>Cr – 28.5%</td>
<td>Cr – 30.0%</td>
<td>Cr – 32.0%</td>
<td>Cr – 28.0%</td>
</tr>
<tr>
<td>Mo – 5.3%</td>
<td>Mo – 5.0%</td>
<td>Mo – 6.5%</td>
<td>-</td>
</tr>
<tr>
<td>Si – 0.5%</td>
<td>Si – 1.1%</td>
<td>Si – 1.0%</td>
<td>Si – 1.5%</td>
</tr>
<tr>
<td>Mn – 0.5%</td>
<td>Mn,C &lt;1.0%</td>
<td>Mn,C,N &lt;1.0%</td>
<td>N,Mn,Nb&lt;1.0%</td>
</tr>
<tr>
<td>C – 0.3%</td>
<td>-</td>
<td>W – 1.5%</td>
<td>W – 9.0%</td>
</tr>
</tbody>
</table>

Fig.1. View of model set with test samples and casting.
To determine the surface roughness of each of the examined alloys after casting, samples were polished in the same manner as cast partial denture. This operation comprised mechanical polishing using a prosthetic micromotor with embedded eraser for polishing of metals and a unipolar grinding - polishing kit with sequentially applied polishing brushes with the canvas and cotton bristles, and polishing brush with cotton thread (the whole operation corresponded to fine polishing in the dental studio). For comparison, surfaces of additional castings were polished on laboratory grinders (the whole operation corresponded to rough polishing in the laboratory). Cross sections of castings were also prepared to check the microstructure and measure hardness of each of the examined materials. Compression mounting of each alloy samples was performed (pressure 15kN, temp. 180 °C - 4 min, cooling - 4 min). Then they were cut transversely by the grinding wheel, polished on Struers LaboPol -21 (sandpaper: #300, 600, 800, 1200, 1500, 2000 , 2500; cotton cloth with diamond paste 1 μm and distilled water), rinsed in distilled water and dried with a cold air flow.

Samples prepared in this way were subjected to the following tests:
- Measurement of surface roughness was carried out using 5 mm at the contact measurement section on a tester Hommel T1000 contact profilometer - three measurements on each sample.
- Macro- and microscopic examinations using light and electron microscopes - Olympus SZX9, Olympus IX70 and HITACHI TM3500N. The polished surfaces of castings cross sections were etched with 50% HCl, 25% HNO₃, 25% H₂O mixture.
- Microhardness tests µHV100g was performed on two samples per alloy, with five measurements for each alloy at the cross-sections of samples.
- Chemical analysis were made for each alloy by SEM EDS.

### 3. Results and discussion

Roughness measurements showed significant differences between the sample surfaces in as-cast condition and polished (Table 3). Using these results and, additionally, selected roughness parameters (the arithmetic mean of the profile deviation from the mean line - \( R_a \), the height of the roughness profile in a ten point roughness scale - \( R_z \), individual alloys were compared with each other.

Surface roughness is the property strongly dependent on casting treatment and as-cast surface condition. Despite optimal casting conditions developed for the examined alloys, the as-cast surfaces showed different roughness states. The least favourable profile had the alloy designated as BF. It was also found that the condition of the as-cast surface shaped the condition of the surface after fine polishing. A significant difference was observed between the sample surfaces subjected to fine polishing in the dental studio and surfaces rough polished with ordinary polishing wheels in the laboratory. The measurement results have proved that surface roughness of samples after fine polishing largely depended on the condition of the as-cast surface.

<table>
<thead>
<tr>
<th>Alloy designation</th>
<th>Surface as-cast</th>
<th>Surface fine polished in dental studio</th>
<th>Surface rough polished in laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_a ) [µm]</td>
<td>( R_z ) [µm]</td>
<td>( R_a ) [µm]</td>
</tr>
<tr>
<td>alloy BF</td>
<td>5.48</td>
<td>29.58</td>
<td>1.00</td>
</tr>
<tr>
<td>alloy WE</td>
<td>3.55</td>
<td>21.71</td>
<td>0.53</td>
</tr>
<tr>
<td>alloy R8</td>
<td>2.59</td>
<td>10.09</td>
<td>0.42</td>
</tr>
<tr>
<td>alloy RS</td>
<td>2.71</td>
<td>18.20</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Detailed analysis of the images of sample surfaces before polishing has revealed the presence of mild porosity, external metal buildups and small misruns (Fig. 2). Examinations by light microscopy of the images of casting cross-sections after etching showed the presence of the precipitates of carbide phase (probably \( \text{Cr}_2\text{C}_6 \) carbides) on the interdendritic spaces of \( \gamma \) phase - solid solution of alloying elements in \( \text{A1} \) crystal lattice of cobalt. Well visible is a layered, oriented crystallographic systems of carbides the precipitates of this phase and a clear outline of the grain boundary. This is particularly well visible at a 50x magnification in alloys BF and WE. SEM examinations have revealed the presence of porosity, also noted on the interdendritic spaces. The highest rate of porosity was observed in castings made from alloys BF and R8. The solidification rate of metal alloys during conventional casting process is relatively high, and therefore it strongly affects the formation of fine-grained dendritic microstructure in the cast elements. The size of grains was comparable in all the examined alloys. Tungsten was observed to reduce the dendritic segregation strongly associated with the presence of molybdenum, but by no means this element can be considered a substitute for molybdenum, mainly because absence of the molybdenum, even in the presence of high tungsten content (> 8%), significantly deteriorates the properties of Co-Cr alloys.

The technique of alloy casting and processing is to a great extent responsible for its structure, and hence for
Fig. 2. Appearance (LM, 16x) of the sample surface cast from: a) alloy BF, b) alloy WE, c) alloy R8, d) alloy RS.

Fig. 3. Macrostructure on the cross-section of samples cast from: a) alloy BF, b) alloy WE, c) alloy R8, d) alloy RS.
Fig. 4. Microstructure (SEM, 300x) on the cross-section of samples cast from: a) alloy BF, b) alloy WE, c) alloy R8, d) alloy RS.

Fig. 5. The results of hardness measurements.

The chemical, physical and mechanical properties [5]. Among the chemical properties, it is the resistance to corrosion that mostly depends on alloy structure; in the group of mechanical properties, these are hardness, ductility and strength, while in the group of physical properties, alloy structure is responsible for the thermal and electrical conductivity. As confirmed by relevant studies, even size of the casting can change the alloy microstructure [7]. To eliminate the effect of different casting conditions, all samples used in these studies were made from the wax patterns of the same size and using the same casting technique. This procedure excluded the sample size and shape and casting process variations as possible causes of differences in the results obtained.

Hardness measurements taken on respective samples showed that the lowest values were obtained in alloy RS. This can be due to the presence of numerous micropores, but primary reason seems to be the absence of molybdenum forming precipitates responsible for the alloy hardening process (Fig. 6). The relationship between alloy porosity and hardness is well known, and well known is also the low level of hardness typical of alloys with the composition similar to Remanium Star [7,9]. Defects such as pores clearly deteriorate the strength properties. Hardness measurements showed slight differences between individual alloys, but obviously the lowest values were found in alloys RS and BF. Microscopic examinations revealed the presence of porosity in all the examined alloys, but in alloy BF this defect occurred mainly on the interdendritic boundaries. Alloy RS was characterized by a uniform distribution of the resulting pores. The lowest porosity was observed in alloy WE which, jointly with alloy R8, boasted the high hardness values.

It has been assumed [16] that in cobalt alloys, depending on the chemical composition and processing conditions, carbides with different structures can arise,
starting from MC through M$_{23}$C$_6$, M$_6$C, M$_3$C$_2$ and in M$_7$C$_3$ ending. Most frequently, it is the M$_{23}$C$_6$ carbide that is identified in alloys of this type [18]. Its characteristic feature is that, appearing in the matrix of cobalt-based solution, it allows for a wide range of the content of various alloy constituents. In a typical case [16], this is the content (wt%) of 30% Cr, 45% Co and 22% Mo, with strong microsegregation observed in the volume of grains.

Fig. 6. Point analysis of alloy BF - marked are measuring points for the quantitative analysis of chemical composition.

<table>
<thead>
<tr>
<th>Measuring point</th>
<th>Content of element [% wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>1</td>
<td>0.57</td>
</tr>
<tr>
<td>2</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
</tr>
</tbody>
</table>

Carbide phase enhances the hardening effect in cobalt-based alloys; it increases the alloy ultimate strength and temporary high-temperature endurance [14]. At the same time, carbide precipitates can nucleate microcracks, both within their own volume and at the carbide/matrix phase boundary, dangerously reducing the ductility, impact strength and fracture toughness of these alloys, particularly when a continuous film of carbides is present on the grain boundaries, accompanied additionally by the occurrence of cellular precipitates [14]. Carbide precipitates also reduce the corrosion resistance of cast cobalt alloys [15] and affect casting hardness [14]. Both size and surface area of the carbide phases decrease significantly with the increasing rate of alloy cooling. Therefore the method of cooling is also one of the factors that contribute to the hardness of resulting alloy [4]. Cooling down of casting at room temperature makes it hard and more resistant, while rapid cooling in water makes it “soft”. [4] All cast test samples were cooled at room temperature to exclude the cooling rate effect on casting hardness. So, the factor that can be responsible for different hardness values obtained in the tested alloys and at the same time for the size and distribution of the precipitated carbide phases is the chemical composition of the alloy cast. This means that further studies are welcome to detect other correlations between alloy microstructure and mechanical properties.

4. Conclusions

From the comparative studies described in this article, the following conclusions can be drawn:
- The presence of alloying elements such as Si, Mo and W added to the Co-Cr alloys in an amount higher than 0.5% has a significant effect on both structure and properties of these alloys.
- All tested alloys were characterized by a very high castability and full applicability in the manufacture of dental prostheses.
- All tested alloys had a dendritic as-cast structure, but the most homogeneous structure was obtained in alloy RS without the addition of molybdenum.
- All tested alloys showed some degree of microporosity, which assumed the highest value in alloys BF and R8.
- Studies included the effect of tungsten on hardness of alloys R8 and RS. It has been found that tungsten in the presence of molybdenum increases alloy hardness, but when molybdenum is absent, even large amounts of vanadium introduced to Co-Cr alloys reduce their hardness level.

References