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Chapter 6

Investigations on Dental Alloys Using Metallographic Observation, Scanning Electron Microscopy, and Energy-Dispersive X-Ray Spectroscopy

Lavinia Ardelean, Lucien Reclaru, Cristina-Maria Bortun and Laura-Cristina Rusu

Additional information is available at the end of the chapter

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Abstract

Alloys are used in various areas of dentistry, but mainly in prosthetics. Their properties, behavior, and corrosion resistance are of great importance for the success of the prosthetic treatment. Among the investigations used for assessing dental alloys, in this chapter, we focus on metallographic observation, scanning electron microscopy, and energy-dispersive X-ray spectroscopy and present the ways we investigated several types of dental alloys. We obtained important data concerning their structure and corrosion potential that could explain certain shortcomings which appeared after luting of the fixed partial dentures.

Keywords: dental alloys, metallographic observation, scanning electron microscopy, energy-dispersive X-ray spectroscopy, corrosion

1. Introduction

Alloys are used in various areas of dentistry, but mainly in prosthetics. Noble-metal alloys and base-metal alloys are used for manufacturing different prosthetic pieces: crowns, inlays, fixed partial dentures, and metallic frames of removable partial dentures. The field of dental alloys is a very extensive one, in constant development, encompassing both the materials themselves and the manufacturing methods [1].

In the past, the use of high-nobility alloys, with a high content of gold or noble metals, generally ensured quality for fixed partial dentures. However, later, the use of low-nobility alloys gained
interest due to economic pressures. As a consequence of this trend, problems regarding chemical stability of this type of alloys have emerged. Accordingly, more attention was paid to the quantification of the chemical stability of dental alloys in terms of their corrosion behavior.

In time, the necessity to introduce a large number of alternative casting alloys of low cost has become more obvious. Base alloys containing nickel, chromium, cobalt, etc., and non-noble metals, also had to be accompanied by the continuous check of corrosion resistance to assure a long-term durability and good aesthetic result [2]. Classes of dental alloys used for dental applications are listed in Table 1.

<table>
<thead>
<tr>
<th>Class</th>
<th>Type and area of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>High-gold-content alloys for the metalo-ceramic technique</td>
</tr>
<tr>
<td>B</td>
<td>High precious metals content alloys for the metalo-ceramic technique</td>
</tr>
<tr>
<td>C</td>
<td>Pd-based alloys for the metalo-ceramic technique</td>
</tr>
<tr>
<td>D</td>
<td>High-gold-content alloys for the conventional technique</td>
</tr>
<tr>
<td>E</td>
<td>Low-gold-content alloys for the conventional technique</td>
</tr>
<tr>
<td>F</td>
<td>Ag-Pd-based alloys for the conventional technique</td>
</tr>
<tr>
<td>1</td>
<td>Co-Cr base alloys for the metalo-ceramic technique</td>
</tr>
<tr>
<td>2</td>
<td>Ni-Cr base alloys for the metalo-ceramic technique</td>
</tr>
<tr>
<td>3</td>
<td>Fe-Ni-Cr base alloys for the conventional technique</td>
</tr>
<tr>
<td>4</td>
<td>Co-Cr base alloys for cast partial denture frameworks</td>
</tr>
<tr>
<td>5</td>
<td>Ti 4th grade for implants and the metalo-ceramic technique</td>
</tr>
<tr>
<td>6</td>
<td>Ti-6Al-4V for implantology pieces</td>
</tr>
<tr>
<td>7</td>
<td>Ti-Ni alloys for wires and endodontic use</td>
</tr>
</tbody>
</table>

Table 1. Classes of dental alloys.

The alloy’s microstructure is influenced by heat treatments. Varying the solidification rate and post-solidification anneals leads to the modification of the grain size. The homogenization anneals, alloy composition, and casting conditions influence the degree of segregation in a casting. Furthermore, the particularity of low-gold alloys is that they exhibit both precipitation and ordering reactions that affect their chemical stability. However, the desirable features of low-gold-content alloys are large grains, a minimum of segregation, and the absence of precipitates and ordered phases.

Cobalt-based alloys are often used to manufacture different types of devices implanted in the body. In dentistry [3, 4], cobalt-chromium alloys are mainly used for manufacturing removable partial dentures and metal ceramic fixed partial dentures, and also in fine framework constructions. These alloys are characterized by excellent corrosion resistance and superior mechanical properties [5]. Dental Co-Cr alloys have diversified over time, aiming at creating...
both new products and new technologies to process them [6], including attempts to combine them with precious metals or to manufacture them by sintering instead of casting.

The alloy performance when processing is an important factor affecting its selection. Properties such as castability, surface roughness, and deformation resistance affect the usability of an alloy [7].

At present, there is no perfect dental alloy. Alloys are mixtures of two or more metals. Metals, when cooling after melting, usually result in a solid solution with higher values of hardness, resistance, and flexibility than the initial components. Due to their grain-type structure, alloys are predisposed to corrosion. The oral cavity provides an ideal environment for conducting electrochemical corrosion phenomena, which takes place in the presence of moisture. Other shortcomings involve the manufacturing technology, which, in case of casting, is quite laborious. Incorrect manufacturing technology or improper finishing may also contribute to corrosion debut.

Corrosion results in a visible alteration of the material and also affects the metallic device’s function, so the major goal for any alloy used in the oral cavity is to have a good corrosion resistance.

The degree of corrosion damage on the prosthetic restoration depends on different factors such as the type of alloy, the presence of soft or hard deposits on its surface, the relation with the oral tissues, existing fractures of the veneering material, the age of the restoration, and the composition of saliva [7]. Alloy-related internal factors include composition, structure, impurities, and surface condition, and the external factors being electrolyte related (composition, concentration, temperature, oxygen content, pH, heterogeneity, etc.) [8]. Parameters related to topography (surface ratio of the two materials, geometric distribution, etc.) may also play a role in developing corrosion.

Grain size and structural heterogeneity influence corrosion; impurities between grains and large grains are favourizing factors. The tendency to corrode is lower in case of a more homogeneous distribution of metallic atoms in the alloy. That is the reason why most alloys are submitted to a homogenizing heat treatment, to minimize the possibility of electrochemical corrosion.

The surface condition depends on the polishing degree, surface properties, and absence of pores or cracks in the primary protective layers [9].

The correlation between pH and corrosion may be summarized as follows: low in a neutral environment, generally high in an acidic environment, and variable in a basic environment. The increase of the electrode potential is frequently the consequence of an increased electrode potential [10]. The temperature’s effect is an important but indirect one. Concentration of the metal’s specific ions, in the vicinity of the electrode surface, is influenced by the movement of the solution and may cause variations. The process depends on the duration of exposure.

To assess the quality of a fixed partial denture and its corrosion potential, investigations such as metallographic observation, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) are of much effectiveness.
Metallography is essentially the study of the structural characteristics or constitution of a metal or an alloy in relation to its physical and mechanical properties. Besides the crystallographic nature of a material, imperfections inside a material have an even greater influence on the mechanical properties, that is, tensile, fatigue, creep, fracture toughness, and impact properties. Some defects such as missing atoms and dislocations cannot be observed optically except by their effects, that is, strain, etch pits, and slip lines.

Scanning electron microscopy, an electron microscopy technique based on the principle of electron-matter interactions, enabled us to produce high-resolution images of the sample’s surface.

Energy-dispersive X-ray spectroscopy permitted us to do the elemental analysis or chemical characterization of the samples. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure, allowing unique set of peaks on its X-ray emission spectrum.

2. Metallographic observation, scanning electron microscopy and energy-dispersive X-ray spectroscopy in corrosion behavior investigation of different types of dental alloys

2.1. Low-gold-content alloy

In case of a fixed prosthetic restoration (Figure 1), made of a low-gold-content conventional class E alloy (Au, Ag, Pd, Cu, Zn), a severe color change and the loss of the metallic shine occurred only a few months after luting, dark and shiny appearances or areas being present at the surface. Removing was decided in order to analyze the causes that lead to its failure.

Figure 1. The deteriorated surface of the prosthetic restoration.

After removing it, we prepared two samples, one was used to analyze the damaged surface using SEM and EDX, without any surface alteration, and the other one was used to observe the superficial structure of the alloy, after transversally sectioning it.
Figure 2. Surface image using retro diffused electrons (chemical contrast) of the sample.

Figure 3. (a) EDX spectrum of area 1 (without sulfur). (b) EDX spectrum of area 2 (rich in copper and sulfur). (c) EDX spectrum of area 3 (rich in silver and sulfur).
The surface analysis with retro-diffused electrons (Figure 2) and EDX (Figure 3a–c) were performed. They indicate the correlation between coloration and a non-homogeneous surface composition. The presence of areas without sulfur (area 1, Figure 3a), areas rich in copper and sulfur (area 2, Figure 3b), and areas rich in silver and sulfur (area 3, Figure 3c) are shown.

Retro-diffused electron analysis and the location of the elements (Au, O, Cu, S, and Ag) (Figure 4) show that the shine loss in area 2 is related to the presence of high amount of sulfur and copper. The presence of oxygen is related to copper localization.

SEM section analysis using secondary electrons (Figure 5a) reveals an important millimetric internal porosity, localized in the external part, in some areas merging into the surface. Figure 5b reveals a dendritic non-homogeneous structure in the vicinity of the surface (SEM analysis with retro-diffused electrons).
Au, Ag, and Cu (main alloy elements) are positioned close to the surface and in the vicinity of the porous areas, in a non-homogeneous way. This non-homogeneity is more important in the sub-superficial darkened areas than in the sub-superficial shiny areas. The porosities are colored in black and are characterized by the presence of tiny inclusions very rich in Cu (Figure 6).

![Figure 6](image.png)

Figure 6. Observation of the sub-superficial layer of the dark area with retro diffused electrons (chemical contrast) and element allocation (Au, Ag, and Cu).

The differences between the nominal chemical composition of the analyzed areas (areas I, II, III, and IV) are shown in Table 2. The four areas where the relative chemical composition in Au, Ag, and Cu was measured are as follows: I and II, internal composition of the matrix and external composition of the inclusions; III, inclusions rich in Au and Ag (Figure 4); and IV, inclusions rich in Cu (Figure 7). The corrosion resistance is negatively affected by any change in the alloy’s composition (decreasing or increasing with one or more elements) [11], the corrosion being accelerated by the unstable phases in the alloy structure. In our case, the shine loss represents the result of selective corrosion subsequent to the appearance of a galvanic cell between these unstable phases and the alloy matrix [2]. Composition analysis reveals the presence of sulfur and oxygen. The presence of a high amount of copper or silver in the darkened areas is explained by their reaction with the sulfurous compounds in the saliva. Formation of insoluble chemical products (sulfides, copper, and silver) is involved in the selective corrosion process [12].

<table>
<thead>
<tr>
<th></th>
<th>Au*</th>
<th>Ag*</th>
<th>Cu*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>560</td>
<td>243</td>
<td>197</td>
</tr>
<tr>
<td>II</td>
<td>574</td>
<td>237</td>
<td>189</td>
</tr>
<tr>
<td>III</td>
<td>611</td>
<td>354</td>
<td>35</td>
</tr>
<tr>
<td>IV</td>
<td>253</td>
<td>123</td>
<td>624</td>
</tr>
</tbody>
</table>

* % weight

Table 2. Relative chemical compositions of the four areas.
The failure is subsequent to the incorrect alloy melting. This caused the internal porosities and areas with very different superficial compositions. Furthermore, the surface was not properly polished, causing surface porosity. The porous and chemically non-homogeneous surface, led to decreased corrosion resistance and subsequent degradation of the prosthetic restoration, in a short time after luting.

2.2. High-gold-content alloy

For determining corrosion causes of a fixed prosthetic restoration made of noble alloys with high content of gold, shortly after luting, we used SEM and EDX, applied to the restoration surface and in section. The fixed prosthetic restoration consisted of a cast part and a metal-ceramic part [13].

When superficially analyzing the cast part (Figure 8) using SEM, three different areas appeared.

- Areas with no deposits and free from corrosion deposits. EDX reveals a normal nominal alloy composition.
- Areas in bluish-black color, without deposits. In these areas, the surface analysis by laser ionization revealed the formation of copper and silver sulfides, concentration decreasing rapidly in the depth.
- Areas characterized by whitish deposits. In these areas, sulfur, sodium, and potassium chlorides are present, as well as calcium phosphates. A high concentration of copper was also noticed, compared to that measured at the nominal composition.
Section analysis by EDX shows that the segregations are nodules of copper and zinc oxide. Metallographic observation of a section through the cast part reveals no defects in the internal structure of the alloy. On the other hand, SEM, with a 5000× magnification, shows an important segregation in the cast part (Figure 9).

The nodules observed originate from the internal oxidation of the less noble alloy elements [12]. Our conclusion is that, in this case, we are dealing with localized corrosion in which the less noble parts of the surface consist of copper and zinc oxide nodules.
Thus, a mixed potential (corrosion potential) has been created on the same surface due to the areas of different chemical composition [14], the anodic parts being areas consisting of copper and zinc oxide nodules. Corrosion was caused by the appearance of a mixed potential on the surface of the cast part as a consequence of incorrect manufacturing.

### 2.3. Cobalt-chromium alloys doped with precious metals

To improve corrosion resistance, a new generation of cobalt-chromium alloys doped with precious metals (Au, Pt, and Ru) was created [15]. We used EDX to determine the microstructure of this new generation of alloys by testing four different products in order to determine if they have improved corrosion resistance compared to classic Co-Cr alloys. The alloys were also micrographically and electrochemically tested. The compositions of the four tested alloys and of a classic Co-Cr alloy are listed in Table 3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Co-Cr</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
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<td>63.5</td>
<td>52.0</td>
<td>50.6</td>
<td>59.3</td>
</tr>
<tr>
<td>Cr</td>
<td>28.9</td>
<td>21.0</td>
<td>25.0</td>
<td>18.5</td>
<td>25.0</td>
</tr>
<tr>
<td>Mo</td>
<td>5.3</td>
<td>4.5</td>
<td>3.0</td>
<td>5.0</td>
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</tr>
<tr>
<td>Ga</td>
<td>4.5</td>
<td>6.0</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>Trace</td>
<td>5.0</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>Trace</td>
<td>2.0</td>
<td>15.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td></td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.8</td>
<td>6.5</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>2.0</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.1</td>
<td></td>
<td>0.5</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td>Trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** Chemical composition of the tested alloys (wt %).

The alloys were micrographically analyzed, analysis of phases by EDX was carried out, and hardness properties were also tested [15–17].

Metallographic structures of the tested alloys are shown in Figures 10–13. Phase compositions are listed in Tables 4–7.
Investigations on Dental Alloys Using Metallographic Observation, Scanning Electron Microscopy, and Energy-Dispersive X-Ray Spectroscopy

Figure 10. Microstructure of alloy 1.

Figure 11. Microstructure of alloy 2.

Figure 12. Microstructure of alloy 3.
Figure 13. Microstructure of alloy 4.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Mn</th>
<th>Ga</th>
<th>In</th>
<th>Fe</th>
<th>Pt</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.15</td>
<td>28.42</td>
<td>4.39</td>
<td>1.06</td>
<td>0.50</td>
<td>4.89</td>
<td>-</td>
<td>0.58</td>
<td>-</td>
<td>-</td>
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<tr>
<td>2</td>
<td>1.30</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4. Phase composition (wt %) of alloy 1.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Ti</th>
<th>W</th>
<th>Ga</th>
<th>In</th>
<th>Pt</th>
<th>Au</th>
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<tr>
<td>1</td>
<td>63.48</td>
<td>25.71</td>
<td>3.55</td>
<td>-</td>
<td>-</td>
<td>4.85</td>
<td>2.41</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>28.46</td>
<td>32.83</td>
<td>22.98</td>
<td>1.74</td>
<td>0.95</td>
<td>11.31</td>
<td>-</td>
<td>-</td>
<td>1.73</td>
<td>-</td>
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</table>

Table 5. Phase composition (wt %) of alloy 2.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Mn</th>
<th>W</th>
<th>Ti</th>
<th>Nb</th>
<th>Pt</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.96</td>
<td>17.48</td>
<td>3.44</td>
<td>1.02</td>
<td>0.70</td>
<td>1.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.44</td>
</tr>
<tr>
<td>2</td>
<td>42.75</td>
<td>19.51</td>
<td>11.76</td>
<td>4.36</td>
<td>0.88</td>
<td>1.56</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.25</td>
</tr>
</tbody>
</table>

Table 6. Phase composition (wt %) of alloy 3.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Ga</th>
<th>In</th>
<th>Pt</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.61</td>
<td>28.04</td>
<td>5.37</td>
<td>0.63</td>
<td>6.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.44</td>
<td>0.76</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7. Phase composition (wt %) of alloy 4.
The microstructures of alloys 1 and 4 are characterized by round inclusions. The diameter of these inclusions is up to 0.1 mm. The chemical analysis of these zones showed In (between 42 and 51%), Pt (around 28%), and Au (between 18 and 27%). The Vickers tests of the zones with inclusions for alloy 4 showed a mean hardness value of 147 HV. Compared to the overall hardness value of the alloy (326 HV) this is more than twice lower [15–17]. The hardness values are given in Table 8.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>1 overall</th>
<th>2 overall</th>
<th>3 overall</th>
<th>4 overall</th>
<th>4 zone 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV 0.2</td>
<td>333</td>
<td>435</td>
<td>338</td>
<td>326</td>
<td>147</td>
</tr>
</tbody>
</table>

Table 8. Vickers hardness of the tested alloys (n = 5).

For electrochemical measurements, artificial saliva of the Fusayama type was used, with the rotating electrode technique. The cathodic and anodic potentiodynamic polarization curves were measured from 1000 mV to + 1250 mV vs. saturated calomel electrode and showed important differences in the behavior of all the four studied alloys, compared to the classic Co-Cr alloy. The worst behavior was shown by the alloys 1 and 4 that contain only gold. This confirms the existing results which state that Au is not miscible to Co and Cr [18].

Alloys 1 and 4 are characterized by a very complex microstructure. The round inclusions with a diameter up to 0.1 mm are in part non-miscible phases with a very low corrosion resistance. The classic Co-Cr alloy has the best corrosion behavior, followed by alloys 2 and 3 (addition of, respectively, 4% and 25% precious metals). Alloys 1 and 4 (with only addition of 2% Au) have the worst behavior. Adding of precious metals deteriorates the corrosion behavior of Co-Cr alloys in a significant way. Gold doping, in particular, produces heterogeneous microstructures that are vulnerable to corrosive attack [15, 16, 19].

In conclusion, Co-Cr dental alloys doped with precious metals do not make sense, due to their poor behavior; using them as an alternative to conventional Co-Cr alloys is not justified [15–17, 19].

2.4. Laser-sintered cobalt-chromium prosthetic elements

Co-Cr alloys are traditionally manufactured by casting. Alternative modern technologies include the CAD/CAM systems. In this case, a ring-shaped material is used and most of the alloy is therefore lost, only a limited part of the material being actually used [20, 21]. Another alternative modern technique that does not have the disadvantage of losing material is the laser sintering.

By means of a laser, using a well-established energy/local surface unit, a fine alloy powder is locally sintered to form the prosthetic element (Figures 14 and 15) [22, 23].
The topography of the respective restorations is designed by numerical monitoring after having scanned the devised objects. Several objects are numerically programmed on the tray. Subsequently, a computer-based program orders the laser beam. The laser is programmed in a way that it only becomes active at the site where the elements should be achieved. The alloy particles will consequently be sintered by the laser energy (Figure 16) [22, 23].

The programmed objects, virtually presented, are obtained by superposing several layers, a process during which, after each period of laser exposure, the tray is raised by 60–80 μm and is subjected to another laser exposure after the application of each additional layer of powder.
Thus, the whole reconstruction process is achieved layer by layer. This results in a fast prototype making process (Figure 17) [22, 23].

Figure 16. The bridge, immediately after separation from the tray, on the model.

Figure 17. Co-Cr sintered frameworks.

The powder has to be as spherical as possible and its granulometry has to be below 20–30 μm, which represents the space between the sintered layers. The composition of the alloy used by us is 64–67% Co, 28–30% Cr, and 5–6% Mo.

After sintering, the prosthetic elements are cut down from the tray. The result is clinical satisfactory, with a precision of 25 μm (Figure 16). The surface has a stratified structure matching the granulometry of the basic powder (Figure 18). From the mechanic point of view, the breaking limits of the sintered metalo-ceramic elements are comparable to casted metalo-ceramic elements, the average hardness being 395 HV.
Figure 18. The internal surface of two crowns, immediately after sintering.

The metallographic observation (50× magnification) shows a slight porosity in the horizontal sample (compared to the sintering plane) (Figure 19), while in vertical sample, the pore lines are uninterrupted (Figure 20).

Figure 19. Metallographic observation of a horizontal sample, without chemical attack.

Figure 20. Metallographic observation of a vertical sample.
The chemical attack shows (50× magnification), similar to the surface, a very fine layered structure roughly corresponding to the original granular structure of the base powder (Figure 21).

![Figure 21. Metallographic observation of a horizontal sample, after chemical attack.](image)

The local chemical composition is characterized by a high regularity: Co between 62.6 and 64.1%, Cr between 29.3 and 30.5%, and Mo between 4.9 and 6.4%. Mn and Si are less than 1%.

Our conclusion was that the laser sintering technique makes possible the manufacture of extremely accurate prosthetic elements with mechanical properties that correspond to any clinical requirement, but it seems to be a rather significant risk of internal porosity that might lead to fracture, cracking, or corrosion [22, 23].

3. Conclusions

The biocompatibility of dental casting alloys is of great importance because these alloys are in long-term intimate contact with oral tissues [24].

Alloys used for fixed prosthetic restorations must have an appropriate corrosion resistance to avoid the release of cytotoxic or sensitizing elements into the biological milieu [25]. The manufacturing conditions are of great importance as well as the environmental ones. The corrosion of dental alloys may be significantly increased by improper processing (formation of pits and crevices). Good corrosion resistance is an important criterion for alloy selection. Corrosion influences other properties of an alloy, such as esthetics and strength.

Electrochemical corrosion of alloys involves the ionization of elements that are released into the environment, for example, saliva [26], initially uncharged elements loose electrons and become positively charged ions as they are released into solution. The released elements may or may not cause problems [27]. One of the main factors that influence element release is the alloy’s composition. Elemental release and corrosion occurs regardless of type or composition of the alloy. The elements with higher tendencies to be released include copper, zinc, and...
nickel. Gold and palladium show a low release tendency [27]. Element lability is also influenced by the phase structure of the alloy. If multiple phases are present, the risk of element release is greater because of the potential electrochemical corrosion among the phases [28]. The element release is also influenced by the surface characteristics of the alloy as roughness and the presence of oxides. Surface roughness increases elemental release because it exposes more atoms to the external environment. The oral environment also plays a role in corrosion. Low pH increases corrosion, especially when nickel-based alloys are involved. Corrosion is also particularly high in retentive areas such as crevices, pits, gingival, and sulcus [29].

The surface composition of the alloy may vary from the composition of the bulk of the alloy [30]. The surface composition may have a direct influence on which elements are released [31, 32]. Base dental alloys (Co-Cr) have an inferior corrosion resistance than the noble alloys.

To determine the degree of internal porosity, in case of a major surface porosity we used metallographic observation. Failure due to incorrect alloy usage may occur when the alloy’s normal melting conditions are not respected. This incorrect melting may be the cause for the internal porosities and for the areas with very different superficial compositions. A not properly polished surface, porous and chemically non-homogeneous, may be a result of incorrect melting and surface treatment, and leads to decreased corrosion resistance and subsequent degradation, after luting.

We also used it to determine the quality of laser-sintered Co-Cr prosthetic elements, in horizontal and vertical samples, with and without chemical attack. Our conclusion was that there seems to be a rather significant risk of internal porosity which might lead to fracture, cracking, or corrosion.

For determining the corrosion causes of a fixed prosthetic restoration made of noble alloys, with high content or low content of gold, shortly after luting, we used scanning electron microscopy and energy-dispersive X-ray spectroscopy, applied to the restoration surface and in section. Using SEM we were capable of producing high-resolution images of the surface of a sample. SEM limits itself to solid samples of certain size, but this was not an issue in our case. In case of EDX, the accuracy of the spectrum can be affected by various factors, including the nature of the sample, but generally has a statistical precision of ±1%.

EDX enabled us to do the elemental analysis or chemical characterization of the samples and was also used to determine the microstructure of the new generation of cobalt-chromium alloys doped with precious metals (Au, Pt, Ru) by testing four different such alloys to determine if they have improved corrosion resistance compared to classic Co-Cr alloys. We concluded that attempts to obtain alloys with better properties by doping Co-Cr alloys with precious metals were not successful. Some cheaper alloys such as copper, aluminum, and bronze, also developed to substitute gold dental alloys, proved to be a great failure.

For minimal biological risks, dentists should consider alloys with low corrosion potential, mainly high-noble metal or noble alloys with single-phase microstructures. The alloy should be selected for each patient using corrosion and biologic data from the manufacturer [27]. Success or failure of a prosthetic restoration depends on many factors: the producer, the proper manufacture, and some related to the patient itself.
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