Characteristic of intermetallic phases in cast dental CoCrMo alloy

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Abstract

Apart from chromium and molybdenum, casting alloys of cobalt usually contain also up to 0.35 % of carbon. With significant content of carbon, presence of carbide-forming alloying elements results in creating carbide phases. These alloys are characterised by dendritic structure of solid solution of chromium and molybdenum in cobalt with interdendritically precipitated carbides. Because of high chromium content, dominating are M23C6-type carbides, but chromium-rich carbides can be also of M7C3 and M3C2-types. The other elements in the alloy result in creating M6C and MC-type carbides. In the case of low carbon content, creating carbides and forming intermetallic phases based on the alloying elements and cobalt become limited.

The presented research was aimed at characterising structure of the cobalt-based dental alloy containing trace quantity of carbon. Characterised were intermetallic phases hardening the alloy. Micr oscopic examinations using light microscopy, SEM and TEM were carried out. Chemical microanalysis of the precipitates using X-ray analyser EDS was performed, as well as phase analysis using selected area electron diffraction.

Keywords: wear resistant alloys, mill rolls, heat treatment, cast iron, bainite, pearlite

1. Introduction

Cobalt alloys have found wide application as dental alloys, mostly for manufacture of prosthetic implants. An important factor that forms structure of these materials is high solubility of the alloying elements in γ solid solution. This gives a possibility of not only solution hardening but also of its controlled decomposition that leads to creating stable phases resulting in precipitation hardening [1].

Carbon content in cobalt-based dental casting alloys can reach 0.35 %. Precipitation hardening in such alloys is caused by interdendritic precipitates of carbides of the alloying elements. Contents of chromium (reaching 22 wt%) and of the other elements are so selected that the matrix is composed of solid solution of chromium and molybdenum in cobalt, with A1 (γ) lattice [1-4]. Both molybdenum and tungsten – often present in these alloys – are added to obtain the solution hardening effect. These two element are usually applied interchangeably [5,6].

Depending on concentration of carbon and the alloying elements, the process of precipitating can proceed due to the eutectic reaction or simple precipitation [7]. Because of the presence of chromium, the M23C6-type carbides dominate in the cobalt-based alloys [7,8], but the chromium-rich carbides can be also the M7C3 and M3C2 carbides. The other elements present in the alloy can form the M6C and MC carbides [7,9,10]. The most widespread carbide occurring in all the cobalt alloys is M23C6. It is created during solidification of the alloys with high chromium-to-carbon ratio and in the alloys containing additives of high-melting metals. It is characterised by very differentiated morphology [1].

After saturating these alloys, the M23C6-type carbides dissolve in the solid solution or are converted to M6C according to the equation [9,11]:
\[ \text{M}_{23}\text{C}_6 + \text{M} \rightarrow \text{M}_6\text{C} + \gamma. \]  

(1)

In cobalt alloys with tungsten and molybdenum concentrations over 4 wt%, the \text{M}_6\text{C} carbide is often formed instead of \text{M}_{23}\text{C}_6. The former is more stable than the latter and can have complex chemical composition. The secondary \text{M}_6\text{C} carbide can be also formed as a result of the reaction between \text{MC} and solid solution [9,11]:

\[ \text{MC} + \gamma \rightarrow \text{M}_6\text{C}. \]  

(2)

During ageing the alloys, the \text{M}_6\text{C} carbide can be again converted to \text{M}_{23}\text{C}_6. The formed then secondary carbide is fine-dispersive, which profitably affects mechanical properties of cobalt alloys [2].

The \text{M}_7\text{C}_3 and \text{M}_3\text{C}_2 carbides are created in cobalt alloys with low chromium content and thus this type carbides are not formed in dental alloys [1,4].

At lower carbon content, possibility of forming carbide phases is reduced. No data exist in the available literature on intermetallic phases that are formed in dental cobalt alloys in place of carbides.

An example of cobalt alloys with low carbon content are abrasion-resistant alloys of the group Tribaloy (Co-Mo-Cr-Si). However, this group differs from the examined alloy in decidedly higher molybdenum content (from 22 to 28.5 wt%) and lower chromium content (from 8.5 to 17.5 wt%). Silicon is present in the similar range from 1.2 to 3.4 wt%. Structure of the Tribaloy alloys with molybdenum content at the lower limit is characterised by the presence of secondary precipitates of the Laves phases (forming laminar eutectics with solid solution) distributed in interdendritic spaces of the solid solution [6,12]. Higher concentration of molybdenum and silicon in these alloys changes the solidification process from hypoeutectic to hypereutectic [12]. Composition of the created Laves phases MgZn2-type, containing Co, Mo and Si, is determined as Co$_3$Mo$_2$Si or CoMoSi [12÷15]. It was found that silicon can be replaced by chromium, forming a Co$_2$MoCr structure [12,14].

2. Material, methodology and assumptions

2.1. Examined material

The examined material was the cobalt-based dental alloy with chemical composition given in Table 1. Beside the main alloying element – chromium, the alloy contains also molybdenum and silicon.

Table 1.
Chemical composition of the examined alloy (manufacturer's data)

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration [wt%]</td>
<td>rem.</td>
<td>31.5</td>
<td>5</td>
<td>2</td>
<td>–</td>
</tr>
</tbody>
</table>

A characteristic feature of the examined alloy that decidedly distinguishes it from typical alloys used in dentistry is lack of carbon in its chemical composition. As a consequence, creation of carbidizes and intermetallic phases based on cobalt and alloying elements is limited.

2.2. Methodology

The performed examinations included light microscopy using a microscope NEOPHOT 32 and scanning electron microscopy (SEM SE, SEM BSE, EDX) using a microscope JEOL JSM 6610A coupled with an X-ray microanalyser JEOL–EX 230. Microstructure examinations on electrolytically prepared thin foils were carried out using a transmission electron microscope JEOL JSM 2010 FX with accelerating voltage 200 kV. Phase analysis was performed on the grounds of the obtained electron diffraction patterns.

Vickers hardness measurements were carried out acc. to EN-ISO 6507-1, using a hardness meter Zwick 321, under 90.07 N for 15 s.

2.3. Analysis of equilibrium diagrams

It can be seen from the Co-Cr diagram that solidification of the alloy containing 31.5 wt% should start at ca. 1420 °C (fig. 1). According to the manufacturer's data, melting point of the alloy is within 1240 to 1350 °C what indicates that molybdenum and chromium reduce the melting temperature.

Because of chromium content, the alloy should solidify omitting the eutectic transition at 1397 °C. The \( \gamma \) phase (FCC, A1) that solidifies directly from liquid is stable till ca. 950 °C, when the martensitic-like transformation to \( \varepsilon \) phase (HCP, A3) should start [13]. However, according to the literature data, the \( \gamma \) phase in dental alloys remains stable down to the ambient temperature [1÷4].

![Fig. 1. Two-component phase equilibrium diagram Co-Cr][3]

At lower temperatures, at chromium concentration range including that of the examined alloy, the eutectoidal decomposition \( \varepsilon \rightarrow \text{Co}_2\text{Cr} + \text{Co}_3\text{Cr} \) is observed. At higher Cr concentration, its equation is \( \varepsilon \rightarrow \text{Co}_2\text{Cr} + \text{Co}_3\text{Cr}_2 \) (Fig. 1).
Analysis of the Co-Mo diagram indicates that melting point of molybdenum is indeed higher than that of cobalt (Mo – 2623 °C, Co – 1495 °C), but eutectic mixture is created at 1335 °C for ca. 40 wt% Mo. That fact could be the reason for lowering the melting point of the examined alloy.

It was found on the ground of analysis of the Cr-Mo alloy that chromium and molybdenum make a spinoidal mixture. Silicon can create with molybdenum intermetallic phases Mo₅Si₃ and Mo₃Si.

The examined material is a multicomponent alloy, so some complex phases can be created in its structure, absent in the above two-component diagrams.

3. Results

3.1. Light microscopy

On the ground of microscopic examinations, a cellular-dendritic structure was found, with visible precipitates in interdendritic spaces of cobalt-based solid solution, see Fig. 3.

3.2. Scanning electron microscopy

The SEM examinations confirmed interdendritic nature of the precipitates, see Figs. 4 and 5.

Nature of the precipitates observed at larger magnifications indicates creation of local eutectic mixture, see Figs. 6 and 8.
Local chemical analysis carried out with an X-ray microanalyser showed distinct micro segregation. In the matrix, higher concentration was found of cobalt (ca. 62 at%), but lower concentration of chromium, molybdenum and silicon. Reduced concentration in the matrix was especially visible in the case of molybdenum, whose decidedly major part was bounded in the precipitates located in interdendritic areas. Concentration of cobalt in the eutectic areas was ca. 44 at%, lower than in the solid solution, see Fig. 7 and Table 2.

Table 2.
Chemical microanalyses obtained for the locations A, B and C in Fig. 7 (in at%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location A</td>
<td>44.60</td>
<td>40.45</td>
<td>9.02</td>
<td>5.93</td>
</tr>
<tr>
<td>Location B</td>
<td>44.26</td>
<td>40.21</td>
<td>9.92</td>
<td>5.61</td>
</tr>
<tr>
<td>Location C</td>
<td>61.83</td>
<td>33.07</td>
<td>1.97</td>
<td>3.14</td>
</tr>
</tbody>
</table>

Fig. 7. Precipitates of intermetallic phases formed in interdendritic areas of cobalt-based solid solution. Marked are locations of microanalyses. SEM SE, etched electrolytically.

On the grounds of linear EDX microanalysis it was found that chromium, molybdenum and silicon diffuse to interdendritic areas. Particular increase of the reflexes intensity was observed for molybdenum, proving rise of its concentration. On the other hand, cobalt remains in the solid solution, see Fig. 9.

These observations are confirmed by analysis of the alloy solidification in the Co-Cr equilibrium diagram. It can be found that the solidifying γ phase should contain less chromium than liquid. Moreover, concentration of molybdenum in the γ phase solidifying in Co-Mo alloys is reduced. This means that, in the case of unbalanced solidification resulting in chemical segregation, both elements show a tendency to remain in interdendritic areas of the solid solution. Since the phase precipitating during solidification of Co-Cr and Co-Mo alloys is impoverished in the alloying element, it should be expected that in the alloys containing both Cr and Mo the solidifying solid solution will be impoverished in both these elements. Impoverishing the solid solution in chromium and molybdenum results in enriching the interdendritic spaces in these two elements.

Results of EDX microanalysis of the structure shown in Fig. 8 are settled in Table 3.

Table 3.
Chemical microanalyses obtained for the locations D and E in Fig. 8 (in at%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location D</td>
<td>54.13</td>
<td>34.69</td>
<td>5.38</td>
<td>5.80</td>
</tr>
<tr>
<td>Location E</td>
<td>46.12</td>
<td>41.56</td>
<td>7.78</td>
<td>4.54</td>
</tr>
</tbody>
</table>

Fig. 8. Eutectic mixture of intermetallic phases in interdendritic areas of cobalt-based solid solution. SEM SE, etched electrolytically.
3.3. Transmission electron microscopy

Examinations of thin foils carried out using TEM confirmed the presence of $\gamma$ solution of cubic face-centred lattice with precipitates of intermetallic phases. Numerous stacking faults were found in the $\gamma$ phase grains, which would be subject to further investigations. The occurring solution hardening resulted in increased lattice parameter $a$ with respect to Co$\gamma$. The parameter $a$ calculated for the diffraction patterns obtained from various places ranged from 0.365 nm to 0.372 nm. For cobalt solidifying in cubic face-centred lattice, the theoretical parameter $a$ is 0.35446 nm.

Diffraction pattern acquired from a precipitate found on the image taken from a thin foil and its interpretation are shown in Fig. 10. No Laves phases CoMoSi or Co$_3$Mo$_2$Si-type of hexagonal lattice were found on the obtained diffraction patterns. Cross-section of the reverse lattice in the plane (011) shows a very good correlation of crystallographic parameters with the intermetallic phase Co$_5$Cr$_3$Si$_2$ of cubic face-centred lattice Im3m.

Local chemical analysis carried out with an X-ray microanalyser revealed molybdenum in the analysed phases. Molybdenum solidifies in the same lattice as chromium, has similar lattice parameters and atomic radius (cubic face-centred lattice). In the case of carbides, chromium is easily substituted by molybdenum. With this respect it is highly probable that chromium can be also easily substituted by molybdenum in the forming precipitates. Then, their formula can be determined as Co$_5$(Cr,Mo)$_3$Si$_2$. It should be also noted that cobalt creates with molybdenum a solid solution, which proves that this element as well can be substituted in the lattice by molybdenum or chromium atoms.

Theoretical chemical composition of the obtained phase indicates also that it should have higher concentration of silicon than that obtained from chemical microanalysis. The literature data indicate that silicon can be replaced by chromium [12,14].

3.4. Hardness measurements

The measured hardness of the examined material is 443±14 HV10. Hardness of the other materials tested by the authors, also reinforced by interdendritically precipitated carbides of the alloying elements, did not usually exceed 400 HV10. Higher hardness of the examined alloy should be related to the presence of intermetallic phases of higher hardness than that of carbides.
4. Conclusions

- The examined alloy is characterised by cellular-dendritic structure of solid solution $\gamma$ with reinforcing phases precipitated in interdendritic spaces. This phase shows a very good correlation of crystallographic parameters with the Co$_5$Cr$_3$Si$_2$ phase solidified in the cubic face-centred lattice Im$ar{3}$m.
- Local chemical analysis revealed molybdenum in the created phase. It is highly probable that atoms of chromium in the precipitates are replaced by atoms of molybdenum that solidifies in the same lattice with similar parameters. Then, the formula can be determined as Co$_5$(Cr,Mo)$_3$Si$_2$.
- The examined alloy shows strong segregation of chromium and molybdenum. Concentration of chromium ranges from 33 at% in the solid solution to 42 at% in the precipitates. Concentration of molybdenum ranges from 2 at% in the dendrites to 10 at% in the interdendritic areas.
- Nature of the precipitates indicates their creation as a result of an eutectic transformation, which is probably related to segregation of the components in front of the solidification front.
- The examined alloy is characterised by higher hardness in comparison with the alloys containing carbides of the alloying elements.

References