CHANGES IN THE STRUCTURE AND PHYSICAL PROPERTIES OF HEAT-TREATED COBALT-BASED BIOMATERIAL

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ABSTRACT

The paper describes cast cobalt alloy after thermal processing - recrystallizing annealing in 1173 ÷ 1473 K temperature range. The aim of processing was to decrease the percentage of the dendritic structure and obtain crystalline structure. The foundations of thermal processing considered the diffusion phenomenon, its parameters were determined analytically. Further, the detailed parameters of processing, results of microstructural analysis, as well as phase diffractometry, full microanalysis of chemical composition and hardness measurements are presented.

1. INTRODUCTION

Cobalt-based alloys are a group of metallic materials suitable for products for reconstructive surgery. They are characterized by a greater passivation potential in physiological solutions. Mechanical properties and corrosion resistance is determined by the chemical composition and structure depending on the type of technology and manufacturing conditions [1,2]. In this respect, cobalt alloys can be divided into casting and wrought alloys.

The main alloying elements include chromium, the concentration of which varies within 18 ÷ 30%, molybdenum in the range from 2.5 to 9%, and nickel with concentration in the range of 15 to 35%. Wrought alloys also have tungsten in an amount of 3 ÷ 8.8%. Cobalt also include coal whose maximum concentration is in the range of 0.05 ÷ 0.35%.

The basic element which undergoes segregation is chromium, the concentration of which varies in the range 19 ÷ 35%. Molybdenum is segregated to a lesser extent with concentration changing within the range of 4 to 6%.

The most commonly used cobalt alloy is Vitalism type Co-Cr-Mo casting alloy. The matrix of the Co-Cr-Mo cast alloy is made of crystallites of the solid solution of chromium, molybdenum and carbon in β -Co with A1 network. Within crystallites, there are strong dendritic micro segregation and in the interdendritic areas and along the crystallite borders there are primary separations of a continuous nature. The heat treatment of cast alloys is used to improve the mechanical and fatigue properties; the results strongly depend on the modification of the chemical composition and metallurgical quality of the casting [3].

The alloys of this type do not include iron or tungsten, the stabilizing additive is niobium. Excluding the iron from the alloy composition increases resistance to corrosion. Another factor that increases resistance, especially to pitting and intergranular corrosion, is lower carbon content, which in the presence of carbide forming alloying elements causes the formation of unfavourable $M_{23}C_6$ carbides in the alloys [3,4].

The allotropic transformation α -Co $\rightleftharpoons$ β -Co is the most important from the point of view of biomaterials.

Changing the structure from A1 (β -Co) to A3 (α -Co) can be made by forming a stacking fault on every other plane {111} in A1 network [4, 5]. As a result, the sequence of the planes changes from ABCABC the ABAB planes (0001). Such a sequence alteration may be formed by the movement of Shockley partial dislocation with Burgers vector $\frac{1}{6}\langle 211 \rangle$ on every other plane {111}.

According to a study, the conversion A1 $\rightarrow$ A3 in Vitalium cast alloys takes place mainly under thermal stress accompanying the thermal treatment, causing an intensive dissociation of dislocations, which leads to the formation of stacking faults, and with the existence of a sufficient driving force – to the formation of twin transformation and A3 separate plates [3,5].

Heat treatment of cobalt-based biomaterials results in a phase change β -Co (paramagnetic phase with A1 structure) in α -Co (ferromagnetic phase with A3 structure). These alloys include austenitic stainless steels and Co-Cr-Mo and Co-Cr-Ni alloys. The percentage share of these phases in the alloy can be adjusted by changing the heat treatment parameters.

2. DETERMINATION OF THE TEMPERATURE-DEPENDENT DIFFUSION COEFFICIENT FOR THE CO - CR - NI ALLOY

The structural analysis requires consideration of the impact of the diffusion on the degree of changes. Calculations of diffusion coefficients for a particular crystal structure of the investigated alloy were carried out using the Arrhenius law.

Figure 1: Diagram of changes in the Co self-diffusion coefficient in β -Co in the temperature range 1173 ÷ 1473 for Q and D0 on the basis of literature: A – [11], B – [6]

Figure 2: Diagram of changes in the Co diffusion coefficient in the Co + Cr + Ni alloy in the temperature range of 1173 ÷ 1473 K for Q and D0 according to the literature [7,8].

Figure 3: Diagram of changes in the Co diffusion coefficient in the Co + 10,9Ni alloy in the temperature range of 1173 ÷ 1473 K for Q and D0 according to the literature [7,10].

Figure 4: Diagram of changes in the Ni diffusion coefficient of Co + 10,9Ni in the temperature range of 1173 ÷ 1473 K for Q and D0 according to the literature [7,8].

According to some study, the Co self-diffusion coefficient depends non-linearly on the temperature with collapse at 1320 K, which however is lower than the temperature of magnetic conversion referenced in the literature [9].

The diffusion in Co – Ni and Co – Cr – Ni alloys also involved an increase in the rate of Co and Ni diffusion and the increase in temperature, and the diffusion of Co in the Ni and Cr alloy is faster than in the alloy without Cr.

3. HEAT TREATMENT

In order to determine the temperature of the effective loss of dendritic structure and to examine the effect of heat treatment on the structure and physical properties, the annealing heat treatment was performed on a series of samples taken from the ingot (21 samples).

From the Bochvar relationship $T_r = (0,4 \div 0,7) T_i$, it is apparent that the temperature range in which recrystallization should occur, assuming that $T_i = 1773$ K, is $T_r = 873 \div 1323$ K. However, this relationship refers to the temperature of recrystallization annealing (conducted after cold working). The literature on Vitalium alloys states that the loss of dendritic structure occurs above 1323 K [3]. Because the investigated alloy is a casting alloy, but has a different chemical composition than Vitalium alloys (includes Ni), the annealing temperature range was 1173 ÷ 1473 K with a step of 50 K. In this temperature range, the rate of diffusion or self-diffusion increases from $D = 3.03 \cdot 10^{-13}$ cm²/s to $D = 2.11 \cdot 10^{-3}$ cm²/s.

Annealing was carried out in air atmosphere in an electric furnace chamber for 0.75 h. The cooling was carried out in still air (a series of 3 samples were made at each temperature). In addition, at a temperature of 1173 K, annealing was performed for 12 hours in order to examine the effect of prolonged heating on the morphology and phase composition. At a temperature of 1173 K, the effect of cooling rate on the structure was also examined.

Metallographic samples were prepared in accordance with the author's own methodology based on the literature and materials from Struers. Specimens for light microscopy observation were digested with aqua regia (35% HCl + 65% HNO₃) for 5 minutes at ambient temperature (~ 295 K).

4. RESEARCH METHODOLOGY

Microstructural studies before and after heat treatment used light microscopy and optical NEOPHOT 2 (ZEISS) metallographic microscope with digital image recording. Phase analysis used diffractometry method and X-ray diffractometer. TUR M62 with HZG 4goniometer controlled by XMEASURE software. The measurements used lamp with Cu anode and Fe filter, and a gap of 0.22 mm. After the preliminary analysis, the measurement range (angle 2θ) was set at: 400 ÷ 960 in the case of the cast alloy and 400 ÷ 520 for the heat-treated alloy. The microanalysis of chemical composition used the scanning electron microscope LEO 1430VP with EDX-Rontec. Hardness tests used Brinell hardness tester. The surfaces of the structures were calculated using Image-Pro with Materials-Pro® module. The microhardness tests were carried out using Vickers method on metallographic microscope Neophot 2. Cobalt alloy after heat treatment

4.1. Microstructural analysis

4.1.1. Annealing at a temperature of 1173 K during 0.75 h

At a temperature of 1173 K, the alloy was annealed during 0.75 h and cooled in air. There are visible differences in the structure on the surface of the sample (Figure 5). The areas of dendrites (Figure 5a) and large columnar crystals are perfectly visible. Columnar crystals are visible between areas with undisclosed grain boundaries (Figure 5.b.).

Figure 5: The structure of the cobalt alloys after heat treatment 1173K/0.75 h, cooling in the open air; light microscope, digested sample.

The analysis of literature on the Co – Cr – Ni type alloys showed the possibility of changing the properties due to the speed of cooling. To investigate the effect of the rate of cooling, the tests involved annealing with cooling by water.

The analyses of microstructural images show that increasing the cooling rate after the heat treatment under the same conditions does not alter the structure. Areas with a dendritic structure obtained by prolonged cooling are also present in the samples cooled in water. Similarly, there are remnants of columnar crystals. There are also areas where it is difficult to clearly define the type of structure because grain boundaries were not etched.

Hardness measurements of samples showed an increase in average hardness by $\sim 7\%$ for the samples cooled in water (Figure 6). The resulting values for different cooling rates are as follows: for cooling in water 201 HBS 5/750, for cooling in open air 187 HBS 5/750. The sample cooled in water showed an increase in areas with a granular structure from 2.4% for the sample cooled in air to 20.9%. Samples cooled in water showed decreased areas of columnar crystals and dendritic areas, respectively $31.1\% \rightarrow 21.1\%$ and $66.45\% \rightarrow 58\%$. The absolute measurement error for the cooling in water is smaller than for air cooling.

A slight increase in hardness and slightly greater uniformity of the material after cooling in water is an evidence of achieving a low supersaturated state, leading to slightly higher uniformity of the structure. Assuming that the properties of a cobalt alloy change as in other biomaterials (Vitalium alloy), it can be concluded that other mechanical properties of the alloy change as a result of heat treatment.

Figure 6: Average hardness of the samples, Brinell hardness tester, etched samples.

The microanalysis presented in Figure 7 and 8 for the heat-treated alloy cooled at high speed did not show segregation of chemical composition, confirming that the cooling speed does not affect the segregation of alloying elements in the core area of the crystallites and at border between them.

Figure 7: Microanalysis of chemical composition of alloy subjected to annealing at 1173K/0.75h, cooling in water, a) topography of the surface, b) distribution of Co (blue), distribution of Cr (green) sample not digested, SEM + EDX

Figure 8: Full microanalysis of chemical composition of alloy annealed at 1173K/0.75 h, at the point shown in Figure 7 (a), cooling in water, sample not digested, SEM+ EDX Figure 9 shows the diffractogram of a sample cooled in water, where we can see two phases, α - Co (100%) and β - Co (40%). The analysis is restricted to 80 since the peaks of the other surfaces have a very low intensity which usually is at the background level.

Figure 9: The diffractogram of the alloy after heat treatment at 1173K/0.75 h, Cu lamp, Fe filter, 30kV/20mA, $v = 20$ /min, sample etched, cooling in water.

4.1.2. Annealing at a temperature of 1473 K

The annealing temperature of 1473K is the upper limit of the annealing temperature resulting from the melting temperature of the solution on the base of the main alloying element (Co). The microstructure in Figure 10 shows large variation. On the surface, there is a visible dendritic structure shown in Figure 10 (a), it occupies the smallest portion of the sample surface (7.71%). The surface of the crystal structure is much larger, with visible twins – Figure 10 (b, c). The size of twin crystals is different, as shown in Figure 10 b and c, and covers 71.4% of the area. It was observed that the sample surface also has areas with grain structure free of twins; these are probably α - Co grains and cover 20.9% of the sample surface.

Figure 10: Microstructure of the alloy after annealing at 1473 K during 0.75 h

The hardness of the alloy annealed at 1473 K is on average 182.2 HBS 5/750. There is a difference in the hardness of twin grains and grains free of twins, and the hardness of these areas is lower by 4%.

The diffraction studies found persistent two-phase nature of the alloy with texture effect (predominant peak β - Co (200)) (Figure 11).

Figure 11: The diffractogram of the alloy after heat treatment at 1173K/0.75 h, Cu lamp, Fe filter, 30kV/20mA, $v = 20$ /min, air cooling, sample etched.

4.1.3. Effect of heat treatment on the phase composition of the alloy

In order to determine the percentage share of the different phases in the alloy structure after heat treatment, the resulting diffraction patterns were analysed using X Measure. The percentage share was calculated and the results are shown in Figure 12. Since some alloys after heat treatment have a texture, they are not included in the comparative analysis.

Figure 12: Share of α -Co phase after heat treatment in selected states of cobalt alloy.

It can be seen that the alloy is biphasic throughout the study with predominant α - Co phase. The share of this phase increases with the increase in annealing temperature from $\sim 45\%$ to $\sim 74.5\%$. The exception is the state of 1223 K, which gave sharp increase in the share of phase α - Co, to $\sim 78\%$.

4.1.4. Effect of heat treatment on morphology of the alloy.

Figure 13 presents morphological analysis of sample surfaces. It shows that with increasing temperature, the share of grain structure is increasing and the share of dendrites is decreasing. In the case of columnar crystals, their share also decreases with increasing temperature, and after the temperature exceeds 1323K, they are no longer present on the surface of the samples. With further increase in the temperature, at 1373 K, there are visible areas with undisclosed grain boundaries. At a temperature of 1423 K, there is a fine-grained structure in interdimeric areas.

There is a quite a large percentage of the granular structure in samples annealed at a temperature of 1173 K for 12 hours, and loss of dendritic structure (1.1%); this indicates that the amount of granular structure is affected not only by temperature but also by duration.

Figure 14 presents the average hardness for the samples annealed at different temperatures, from which it follows that the hardness of the samples decreases with increasing amounts of the crystalline structure. This indicates the disappearance of the structure defects that affect the hardness of the alloy.

Figure 13: Percentage share of areas with a granular structure

Figure 14: Average hardness of the annealed samples.

5. CONCLUSIONS

Increased annealing temperature for the Co – Cr – Ni alloy causes an increase in the share of α – Co solution in relation to the β – Co phase; for 300K, the difference in the amount was about 7%.

1. The crude alloy casting showed no segregation of the chemical composition. Heat treatment (annealing) caused no secondary precipitations.
2. Change from the primary casting structure (dendrite + columnar crystals) to the grain structure occurs continuously with increasing temperature. The limit temperature, above which there are no columnar crystals and the grain structure exceeds 50%, is 1373 K.
3. Extending the annealing time is conducive to the disappearance of dendritic structure. In the lowest test temperature of 1173 K, after 12 h, the share of the grain structure was ~ 83%.
4. During supersaturation at a temperature of 1438 K, the primarily precipitated carbides $M_{23}C_6$ transform to M_6C . At a temperature of 1483 K, there is initially a high rate of dissolution of carbides, which decreases as the homogenizing period increases. $M_{23}C_6$ carbides completely dissolve after one hour, whereas M_6C carbides dissolve only partly. These carbides completely dissolve only after 64 hours. When raising the temperature to 1503 K, all types of carbides dissolve into the matrix within 15 minutes.

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