# MICROSTRUCTURE FEATURES OF DENTAL PROSTHESES FROM Co-Cr BASED ALLOY AFTER SELECTIVE LASER MELTING AND THERMAL TREATMENT

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**Abstract**

Co-Cr based alloys usually produced by conventional casting or newly by direct metal laser sintering (DMLS) have been widely used in dentistry as dental prostheses. This work is focused on the powder size and chemical composition of initial powder particles of a commercial Co-Cr based alloy, as well as on the microstructure after DMLS and heat treatment. Material used in this study is a Co-Cr-Mo-W based alloy in a fine powder form (EOS Cobalt Chrome SP2 type). Its composition corresponds to type 4 CoCr dental materials in EN ISO 22674:2006 standard. It also fulfils the chemical and thermal requirements of EN ISO 9693 for CoCr PFM (porcelain fused metal). In order to solve the problem of porosity and shape stability of prostheses after high temperature annealing, microstructure and phase evaluation using optical and scanning electron microscopies completed by EDX analysis were performed.

**Keywords:** CoCr alloys, direct metal laser sintering, heat treatment, microstructure, porosity

## 1. INTRODUCTION

Materials used in dental prosthetics include metal alloys, ceramic materials and polymers. All-ceramic materials exhibit good biocompatibility, absence of allergic reactions, corrosion resistance, low thermal and electrical conductivity and they can be produced in varied colour shades (aesthetic reasons). A higher price, hardness and brittleness of the material are disadvantages [1].

As to their composition, physical and mechanical properties, dental alloys can be divided to high noble alloys (Au-Pt, Au-Pd, Au-Cu-Ag-Pd), noble alloys (Au-Cu-Ag-Pd, Pd-Cu-Ga, Pd-Ga, Ag-Pd) containing 25 % of noble metals at minimum and base alloys (Ni-Cr-Be, Ni-Cr, Co-Cr, Ti etc.). For dental prosthetics Co-Cr based alloys are used, consisting of a solid solution containing Co and Cr in approximately 3:1 ratio. Other alloying elements are particularly Mo and W, in an amount of 5 - 7 wt. %. Other metals are contained in a negligible amount. A content of carbon C is primarily related to the precipitation of carbidic particles and an increase in hardness. Chemical composition of the alloy strongly affects its structure and properties. A method of thermo-mechanical processing is not less important, however, Co-Cr-Mo based alloys for dental implants have been used mainly as cast alloys so far [2].

The best known Co based alloy is Vitallium, an alloy containing Co, Cr, Mo elements and possibly other metals. Other modifications can be alloys with a composition of 60 % Co, 20 % Cr, 5 % Mo + other metals [3] or CoCr27Mo5Ni3 [4]. Vitallium 2000 alloy is a widely used dental material for removable partial dentures [5, 6]. Oralium and Oralium Ceramic are Co-Cr dental alloys of the Czech origin (Safina a.s.) with high strength and applicable also for a design of removable dentures. The alloys feature very high corrosion resistance and biocompatibility. They do not contain nickel or other toxic elements, such as beryllium [7]. Remanium® alloys are manufactured by continuous casting, whereas a homogenous structure and optimized physical properties are achieved. From the medical point of view, the alloys do not contain any toxic alloying elements (Be, Ga, In, Cd, Ni, Fe). Especially the absence of nickel allows application of these implants for patients with allergic

reactions to it. The alloys are optimal in term of corrosion resistance inside the buccal cavity [8]. Mechanical properties of these alloys enable to make delicate, and at the same time firm and tough, structures resistant against fracture. The structure stability can be ensured above all by high values of modulus of elasticity. Due to its properties, ASTM F75 Co-Cr-Mo alloy is also used for demanding dental applications; its preparation is carried out in a controlled atmosphere, e.g. vacuum electron beam melting. The most frequent technological processes for the manufacture of products from this material are either conventional casting or newly the additive manufacturing (AM), including selective laser melting (SLM) or direct metal laser sintering (DMLS).

The DMLS method [9] is a revolutionary method based on the gradual smelting of very fine layers of metal powder using a powerful laser beam. This technology enables to quickly build fully functional metal parts directly from 3D CAD data, leaving out investments to production tools and technologies, thus resulting in considerable cost reductions and time savings. The DMLS method was developed in 1995 by a German company Electro Optical Systems (EOS) in cooperation with Rapid Product Innovations (RPI). At those times this was the first commercial method offering the manufacture of metal parts in a single process. DMLS allows manufacturing of several parts different in shape at the same time and also provides a wide spectrum of properties, from the controlled porosity to fully homogenous structures, which can achieve higher strength than castings and forgings [10].

SINTEO Dental s.r.o. company [11], which is specialized in the manufacture of prostheses from Co-Cr alloys, has EOSINT M270 system available (a supplier - EOS, a German company) for manufacturing of complex functional metal parts for dental prosthetics.

The aim of the work is to assess a character of the input Co-Cr alloy in a powder form and compare the structure characteristics of the alloy after the laser deposition process through the DMLS method and after heat treatment.

## 2. EXPERIMENTAL

### 2.1. Material, methods of analyses and results

For the laser deposition process a powder supplied by EOS company was used (firm EOS GmbH - Electro Opitical Systems, Munich, Germany [12]). EOS Cobalt Chrome SP2 is a Co, Cr, Mo and W based metallic material in fine powder form for production of dental restorations in EOSINT M 270 system. Its composition corresponds to type 4 Co-Cr dental material in EN ISO 22674:2006 standard. It also fulfils the chemical and thermal requirements of EN ISO 9693 for Co-Cr porcelain fused metal of dental materials (Ni content: < 0.1 %, no Cd or Be) and requirements of EN ISO 7504, EN ISO 10993-1:2003 and 10993-5:1999 regarding the biocompatibility and cytotoxicity of the dental materials. This material is ideal for producing dental restorations. Standard processing parameters use full melting of the entire geometry with 20 µm layer thickness. Typical application: dental restorations (crowns, bridges etc.).

The nominal chemical composition of SP2 alloy powder is shown in **Table 1**. Typical mechanical properties of structural parts from this alloy are summarized in **Table 2**.

**Table 1** Chemical composition (wt.%) of SP2 (supplied by EOS), according to EN ISO 22674:2006 [12]

| Element | Co | Cr | Mo | W | Si | Fe | Mn |
|---|---|---|---|---|---|---|---|
| Content | 61.8 - 65.8 | 23.7 - 25.7 | 4.6 - 5.6 | 4.9 - 5.9 | 0.8 - 1.2 | max. 0.50 | max. 0.10 |

**Table 2** Typical physical and mechanical properties of parts at 20 °C (according to EN ISO 22674:2006) [12]

| Properties | In as manufactured condition | After stress relieving at 750 °C for 1 hour and firing at 880 °C for 5 minutes |
|---|---|---|
| Density (g/cm$^3$) | 8.50 | |
| Ultimate tensile strength (MPa) | 1050 ± 100 | 1100 ± 100 |
| Proof strength $Rp_{0.2}$ (MPa) | 750 ± 80 | 900 ± 80 |
| Elongation at break $A_5$ (%) | 14 ± 2 | 10 ± 2 |
| Young's Modulus (GPa) | 200 ± 20 | 200 ± 10 |
| Hardness HV 10 | 360 ± 20 | 420 ± 30 |

An image analysis of powder particles was performed through Scanning Electron Microscopy (SEM) and X-ray diffraction analysis (EDX) using the electron microscope of JEOL JSM-6490LV type. A spherical character of the particles is shown in **Figure 1**. The results of EDX analysis of EOS powder are summarized in **Table 4**.

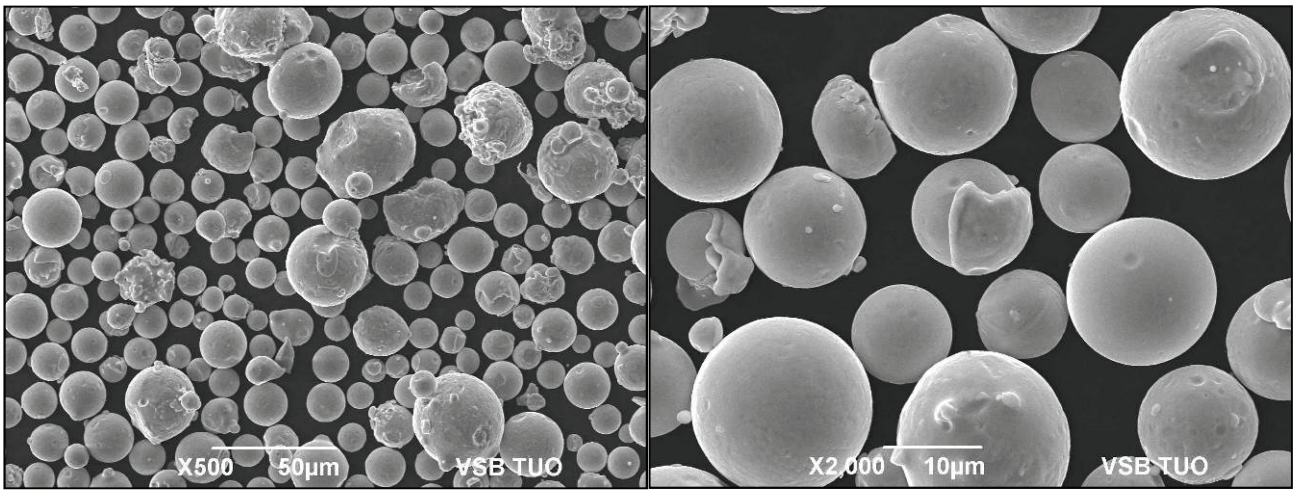


**Figure 1** SEM morphology of the raw powder material (firm EOS)

On the basis of SEM images (**Figure 1**) an image analysis of SP2 powder was performed and the results can be seen in **Table 3** and in **Figure 2**. 208 particles were analyzed in total. The largest proportion (46 %) comprises particles of 10 to 15 µm size.

**Table 3** Results of the image analysis of SP2 powder

| Particle size (µm) | Number | Percent | Cumulative volume (%) |
|---|---|---|---|
| 0 - 5 | 7 | 3.37 | 3.37 |
| 5 - 10 | 43 | 20.67 | 24.04 |
| 10 - 15 | 94 | 45.19 | 69.23 |
| 15 - 20 | 42 | 20.19 | 89.42 |
| 20 - 25 | 8 | 3.85 | 93.27 |
| 25 - 30 | 5 | 2.40 | 95.67 |
| 30 - 35 | 7 | 3.37 | 99.04 |
| 35 - 45 | 2 | 0.96 | 100.00 |
| **Summary** | 208 | 100 | |

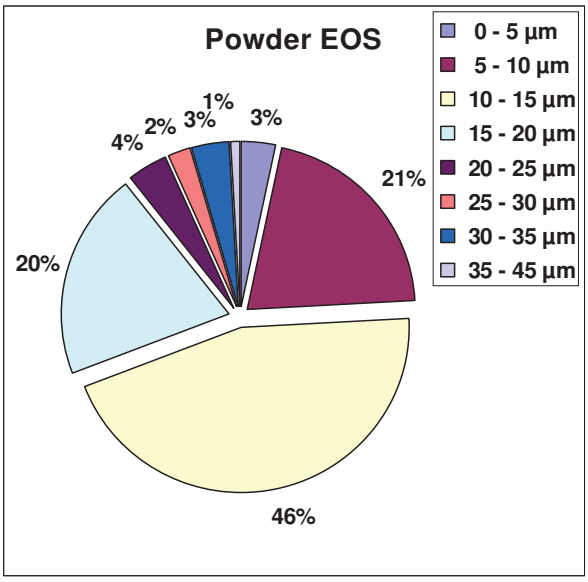


**Figure 2** Powder size distribution of SP2

**Table 4** Results of EDX analysis of the commercial SP2 powder (wt.%)

| Element | Al | Si | Cr | Co | Mo | W |
|---|---|---|---|---|---|---|
| Content | 0.78 | 1.08 | 25.89 | 61.21 | 5.46 | 5.83 |

### 2.2. Microstructure after DMLS processing and annealing

Investigation of the microstructure was performed for the specimens after the DMLS deposition and subsequent heat treatment involving various regimes.

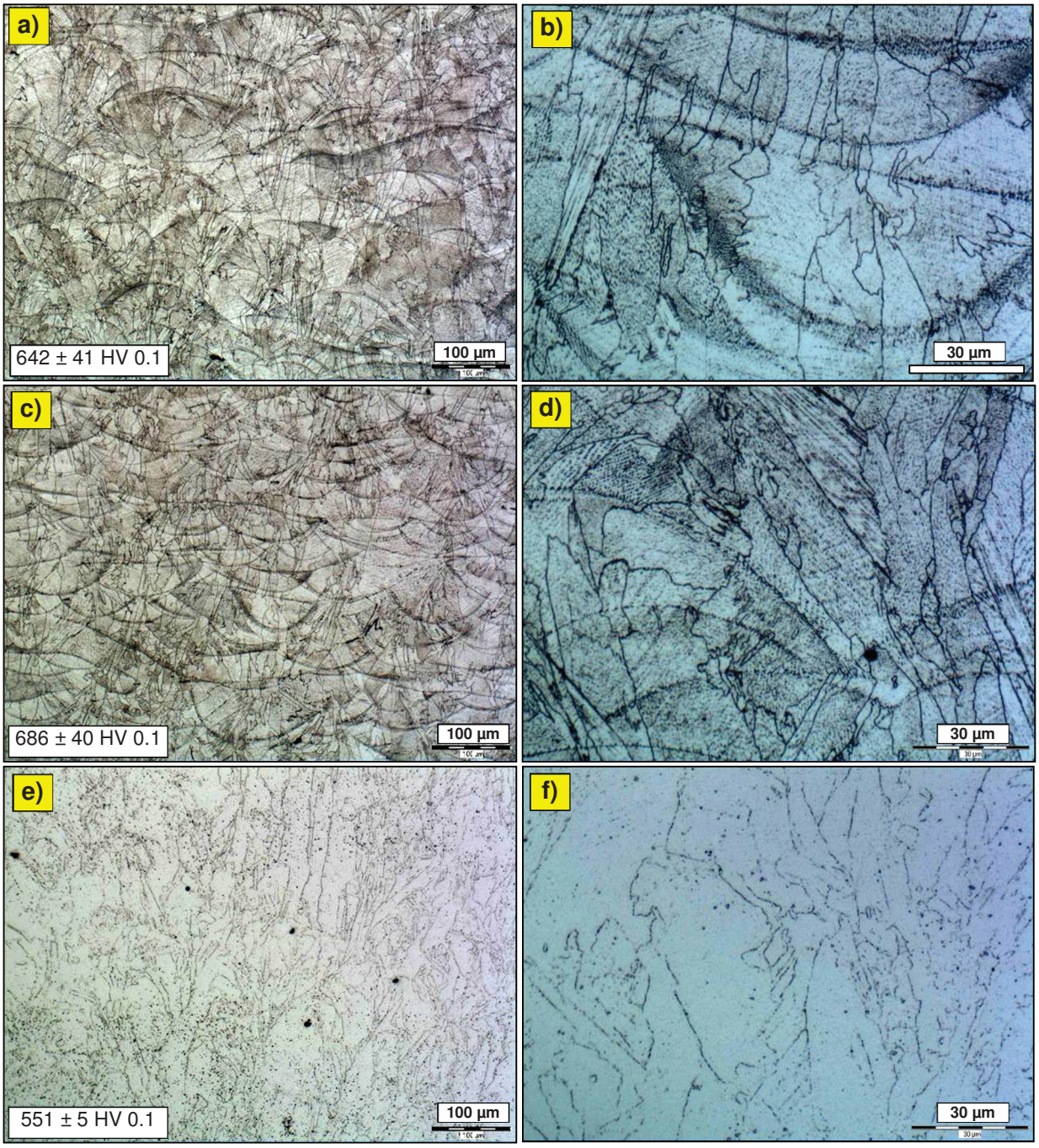


**Figure 3** Microstructure of Co-Cr-Mo-W alloy specimens in different stages of heat treatment: a) and c) "fish scale" structure; e) and f) homogenized coarse grained structure - see text below. Microhardness HV 0.1 values are completed

**Figure 3** documents the microstructure of the specimens after various heat treatment methods following the laser deposition: three-step annealing in air in a chamber furnace at a regime of 450 °C/45 min + 650 °C/45 min + 750 °C/60 min + rapid cooling in an open furnace (**Figure 3a, b**); followed by vacuum annealing at 750 °C/60 min + free vacuum cooling (**Figure 3c, d**); followed by further vacuum annealing at 1000 °C/180 min + free vacuum cooling (**Figure 3e, f**). Figures also show microhardness values after the respective processing regimes. In all the specimens, porosity and the presence of inclusions were detected. Their area proportion ranged around 0.43 % and changes in their size and frequency of occurrence depending on the heat treatment regime were not observed.

A structural phase analysis of the microstructure through SEM/EDX analysis was performed, on the basis of which chemical composition of the matrix and present inclusions were determined - see **Figure 4** and **Table 5**.

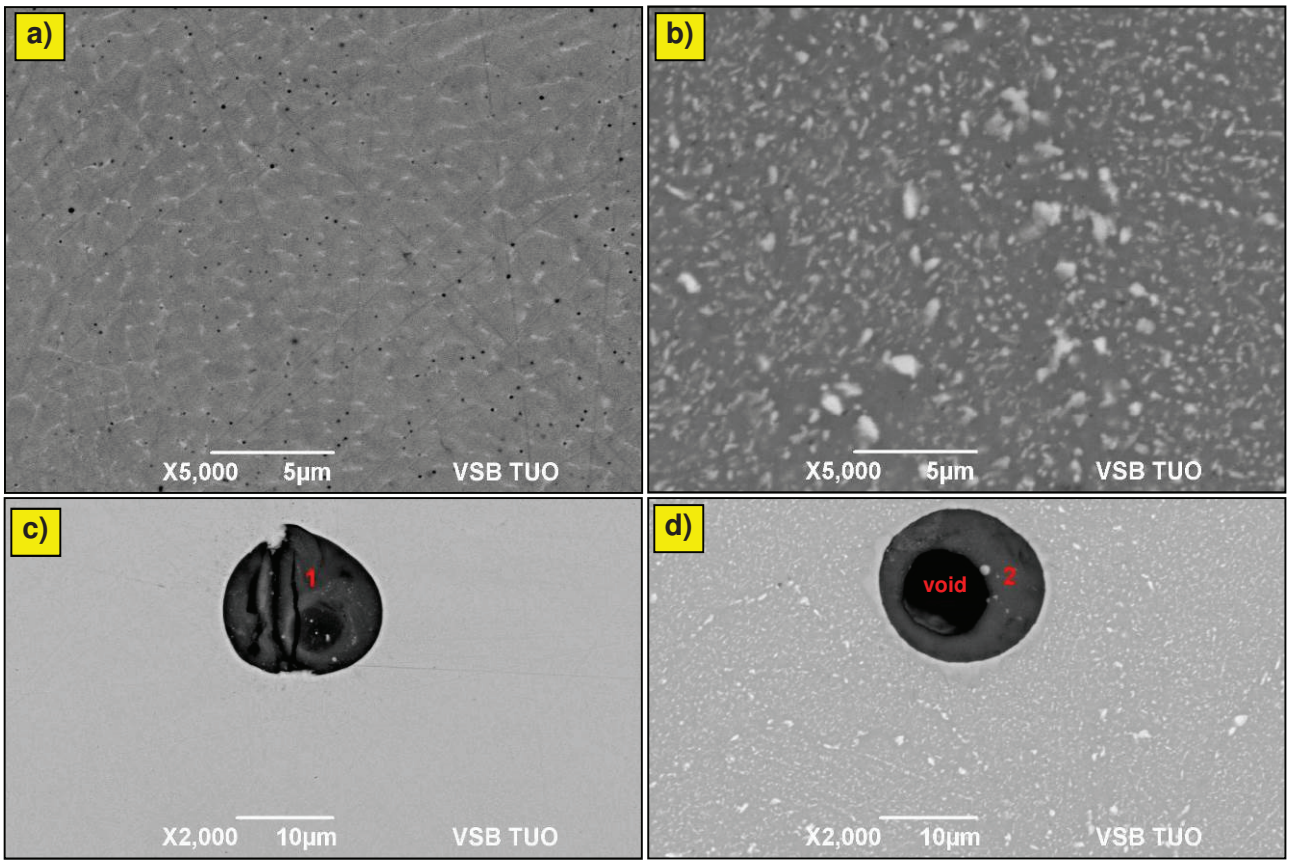


**Figure 4** SEM (BEC) images of microstructure and inclusions in samples annealed a), c) at 750 °C/1 h; b), d) at 1000 °C/3 h (after polishing, non-etched state)

**Table 5** Spot and areal EDX analyses of Co-Cr alloys after annealing at 750 °C/1 h and 1000 °C/3 h (at.%) - see **Figure 4 c)** and **4 d)**

| Element | O | Al | Si | Cr | Mn | Co | Mo | W |
|---|---|---|---|---|---|---|---|---|
| Area | | | 2.21 | 29.37 | | 61.96 | 3.90 | 2.60 |
| Spot 1 | 65.97 | 0.53 | 14.32 | 15.74 | 2.61 | 0.82 | | |
| Spot 2 | 68.97 | 0.22 | 14.93 | 13.95 | 1.34 | 0.60 | | |

The analysis of inclusions determined that these were complex oxides of $MeO_2$ type containing in particular $SiO_2$, $Cr_2O_3$ and in a less proportion $Al_2O_3$, MnO and CoO.

## 3. DISCUSSION

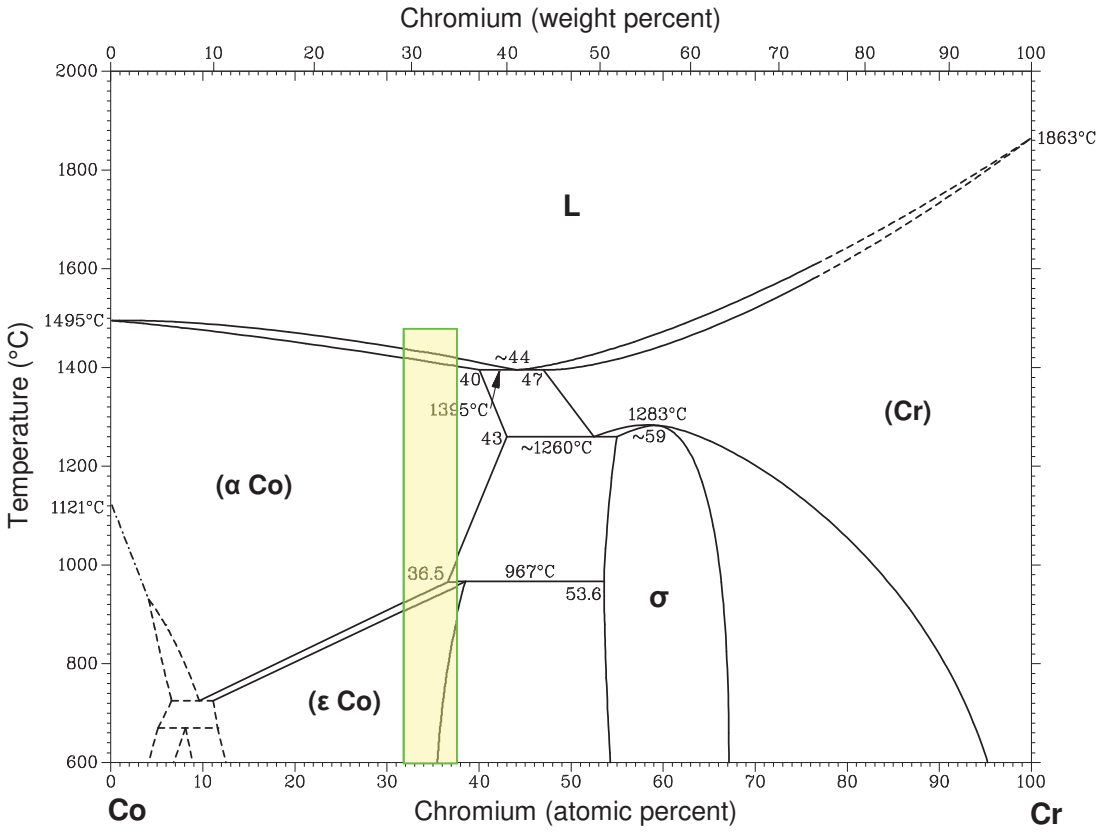


**Figure 5** Cobalt - chromium binary phase diagram [13]

**Figure 5** shows a binary diagram of the Co-Cr system. For content 62 at. % Co, which is this case, α solid solution of Co is formed directly under slow cooling conditions. Between temperatures of 1395 and 1000 °C, there is an area of α solid solution and below the temperature of 970 °C an area of ε solid solution. Below the temperature of 800 °C down to room temperature, the structure should contain a mixture of two phases with a high proportion of ε phase and a minor presence of σ phase (an approximate Cr:Co ratio - 3:2). The same also applies for ternary systems Co-Cr-Mo and Co-Cr-W [14]; there is a two-phase area (ε + σ) within temperatures below 700 °C. Therefore for Co-Cr-Mo-W alloys subjected to long-term annealing at temperatures of 750 °C or 1000 °C the presence of σ phase in the structure can be also expected.

After homogenization annealing at 1250 °C for 2 h, cooling to 750 °C at a rate of 0.166 K/s followed by isothermal aging treatments at 750 °C for 0 h, 0.5 h, 1 h, 2 h, 4 h and 6 h and water quenching, it was found that the α and ε phases only coexist in the specimens of Co-29Cr-6Mo alloy (ASTM F75) [15] when the aging time was less than 2 hours. In the case of heat treatment for longer time than 2 h, only ε phase was detected, suggesting the complete transformation of the matrix from α to ε phase. The σ phase precipitates at grain boundaries, as was found out after any time of the samples aging [15], σ phase particles being of size less than 1 μm. The area fraction of the σ phase increased along with the increasing aging time and reached 0.6 % after aging at 750 °C for 6 h. The precipitation of σ tetragonal phase at grain boundaries and interdendritic zones was detected in the as-cast microstructure formed of α dendritic matrix and $M_{23}C_6$ carbides [16].

Unlike cast Co-Cr-Mo alloys, the microstructures of parts produced by the DMLS technique [17] were formed of both α and ε phases as well as of $Me_{23}C_6$ carbides with the cubic structure. Due to high cooling rates, the equilibrium conditions of crystallization were not met during the DMLS technology and the stable α phase was

formed immediately after the laser exposure and solidification of the Co-Cr powder smelted layer. It has been proven [17], that cobalt based alloys undergo an athermal phase transformation α (fcc) ↔ ε (hcp).

The microstructure of the sintered samples was observed on the sections parallel to the laser beam direction (**Figure 3**). The observation using optical microscopy was performed on electrochemically etched specimens. The **Figures 3a)** and **3c)** show a peculiar macrostructure, similar to „fish scales", relative to the weld pools of each laser pass and to the layer stack. At higher magnification it is apparent, that an extremely fine microstructure was present inside the grains. Columnar structure has grown inside the matrix in the form of domains. The rapid cooling of the melted powder produced the formation of ε phase as small lamellae inside the α phase. The nano-lamellae formed a complex network and were responsible for the increase in hardness. Tiny black dots in **Figure 4a)** of a size below 0.5 μm might relate to carbidic particles and σ phase. Carbon concentration could not be reliably determined.

It was found out that 2 h annealing time at 750 °C increased microhardness slightly to 686 HV 0.1, while the specimen microstructure remained maintained. After annealing for 3 h at 1000 °C the microstructure character changed and microhardness decreased down to 551 HV 0.1 value, which may have related to diffusion processes at high temperatures and re-arranging of both the phases α and ε. A growth of ε phase particles in the matrix and their coagulation occurred during slow vacuum cooling (c. 6 h) from the temperature of 1000 °C down to room temperature **(Figure 4d**). It was also possible to observe that some original grain boundaries disappeared during the migration of atoms.

## 4. CONCLUSION

A Co-Cr-Mo-W alloy powder (EOS Cobalt-Chrome SP2) with the nominal composition (in wt. %) Co 61.2, Cr 25.9, Mo 5.5, W 5.8, and Si 1.0 was used as raw material with the initial structure of α phase. Direct metal laser sintering was used to produce Co-Cr-Mo-W parts for dental application. In the sintered samples the typical structure of Co based alloys with the presence of both α (fcc) and ε (hcp) phases was obtained.

The processing parameters used in the DMLS process resulted in samples with a peculiar intricate network of ε lamellae inside the α phase after heat treatment at 750 °C for 1 hour in air or in vacuum. The ε lamellae tended to aggregate and form the columnar structure observed in the OM images. An ultra-fine-grained material was obtained by DMLS, which contributed to very high strength of the Co-Cr-Mo alloys. $M_{23}C_6$ and/or $MC_6$ carbides and intermetallic σ phase could be found at grain boundaries and interdendritic zones. Annealing at 1000 °C for 3 h and slow vacuum cooling resulted in a decrease in microhardness and a growth of ε phase particles in α matrix.

The sintered samples of Co-Cr-Mo-W alloys proved to be well suitable for biomedical application on condition that heat treatment following DLMS is optimized to ensure good mechanical characteristics.

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