Investigation of microstructure, mechanical and temperature effects on biomedical Co-25Cr-9,5W-3,5Mo-1Si alloys fabricated by Additive Manufacturing

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Abstract: The Wolfram (W), Silicium (Si) and Molybdenum (Mo) doped Co-Cr biomedical alloy were fabricated by additive manufacturing method, which is part of powder methodology. The mixture of Wolfram (W), Silicium (Si), Chrome (Cr) and Cobalt (Co) alloy is known good wear and corrosion resistance among of biomedical applications. By addition of Molybdenum (Mo) into the structure of alloy, the structure become more stable also increase the corrosion and wear resistance. In addition, the effects of secondary annealing process on the alloy were investigated. The microstructure of the produced alloy was analyzed by X-ray diffraction method XRD, Energy Dispersive X-Ray Analysis EDX and scanning electron microscope SEM. Moreover, Electrochemical corrosion test, micro hardness and density measurements were performed to investigate the mechanical properties of the alloy. As a result of the analyzes, the effects of Molybdenum (Mo) doped and secondary annealing on the microstructure and mechanical properties of bioalloying were determined.

Keywords: Additive Manufacturing; Biomedical Alloy; Micro Structure; Mechanical Properties.

1. Introduction

Biomaterials are natural or artificial materials that perform the functions of tissues and organs in human body partially or completely [1]. The basic properties expected from biomaterials can be listed as; high corrosion resistance, mechanical suitable for human body and tissue, provide high life, bioactivity, non-reactivity with tissues and organs. Corrosion of the biomaterials which are in constant contact with the dynamic liquids in the human body is inevitable. Therefore, one of the most important issues to be considered in surgical implantations is corrosion of these metals. These metals, which cause ion release in the body as a result of wear, may enter into carcinogenic or allergic reactions with tissue. All these factors make corrosion resistance the most important feature for bimetalts [1-5]. Alloys used in biomedical applications are expected to be biocompatible. Co-based metallic alloys known for their biocompatibility which are known for their corrosion, high temperature resistance and good wear resistance [6]. In general, Co-based alloys obtained by casting method were first introduced in the medical field as a dental implant. Subsequently, many mechanical and dynamic tests performed in the body environment have shown that Co-based alloys are biocompatible and can be used as bio implants [7]. Co-based alloys are strengthened by the addition of Cr and the addition of Mo results in a fine-grained structure that improves mechanical properties. Mainly Co-Cr and Co-Cr-Mo are used in dentistry, newly developed artificial joints, hip and knee joints as prosthetic stem material [8-9]. Co-based alloys produced by casting and various methods are produced as an advantage to the limitation of use due to their high cost despite the
superior properties of noble metals. Major Co-based alloys produced by conventional methods are respectively Co-Cr-Ga Nb, Co-Cr Ni-Mo, Co-28 Cr-6Mo-0.7Mn-0.5Si-0.5C, Co-Cr-Mo, Co-Cr-Ni Mo, Co-Ni-Cr-Mo- W-Fe, Co-Cr-W-Ni, Ni-Cr-Si-Mo. These alloys are used as a prosthetic handle material in knee joints with high resistance to fatigue and tensile strength, arm, hip and leg construction where artificial joint construction load requires more. It is seen that the production technique of bio metallic alloys has significant effects on the microstructure and grain size of metals [10-13]. Microstructure and grain size have been suggested by researchers to have a significant effect on the mechanical properties of metals. In the production of metals and alloys; it is undoubtedly the best method for complex component production, the possibility of lightweight parts, efficient use of material, tailor-made design, low cost, reproducibility, wide design possibilities and repetition. Additive manufacturing production techniques, which offer all these possibilities together, have started to manifest themselves as a production method in medical sector as in many other sectors in recent years and have emerged as a highly preferred production method in the production of today’s bio metals. Co-Cr alloys are suitable for the manufacturing of metal ceramic restorations, bridges, partial dentures and secondary formwork structures as well as the above mentioned applications. Cobalt-Chromium (Co-Cr) alloys consist mainly of three elements: Cobalt (Co), chromium (Cr) and molybdenum (Mo). The major Co-Cr alloys produced by additive manufacturing methods are respectively, Co-Cr W-Si Co-Cr-W-5.4 Mo-Si Co-Cr-W-3.5 Mo-Si Co-Cr-W-5 Mo-Si. The amount of W-Mo-Si metal used as an doped in Co-Cr alloys can be used by adding the quantities according to the expected property at different scales, but in general the chemical composition determined by the powder suppliers is used in industrial products. If a generalization is made about the chemical compositions of Co-Cr metal powders produced by the additive manufacturing production method, the contribution of powders used in the manufacturing companies and academic publications by weight in the alloy was found to be as follows [19-22].

58<=Co <= 64.00, 24<= Cr <=33, 4<=W <= 9, 1<= Si <= 3, 3<= Mo <=6 [18].

Layered production of metal powders is an important process step of the additive manufacturing production process. The size, geometric structure and quality of metal powders used in the production of bio metallic alloys have been shown to have a significant effect on the mechanical properties of the material [23]. Contamination that is likely to occur in metal alloys produced by conventional methods is almost negligible in alloys produced by additive manufacturing production techniques. Furthermore, since there is a huge difference between yield cost and quality, it is anticipated that additive manufacturing methods will dominate the market in producing biometallic alloys in a short period of time. Also, when the samples produced by additive manufacturing method and samples produced by conventional production techniques are examined, it is seen that better powder morphology, fluency and diffusion ability of the additive manufacturing method improve the improvement of powder and bed density [24 26].

2. Experimental Procedure

W-Si-Mo doped Co-25Cr-9,5W-3,5Mo-Si bioalloys were produced by additive manufacturing production method in this study. Two samples were produced on MYSINT 100 Dual Laser machine produced by SISMA under nitrogen gas atmosphere. One of the samples produced was annealed in the PLF series furnace supplied by Protherm for 4 hours (to investigate the effects of secondary annealing on microstructure and mechanical properties after production). The sample produced and annealed is shown in Figure 1.
The powder mixture of the alloy produced is provided by Scheftner Dental alloy. The chemical composition of the alloy is given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cobalt</th>
<th>Chrome</th>
<th>Wolfram</th>
<th>Silicium</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>59</td>
<td>25</td>
<td>9.5</td>
<td>1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The chemical components of the produced bulk samples were presented in Table 1. After completing the chemical production processes, XRD analysis were performed in the θ-2θ and Rocking curves by the scanning rate of (20-100) ° using XRD-6100 Shimadzu device to figure out the possible phases. The measurement details of Cu X-ray tube target, voltage = 40.0 (kV), and current = 30.0 (mA) was used. The surface morphology images of the samples were taken by FEI XL30 Sirion Scanning Electron Microscope (SEM) tool. The standard data of EDX analysis of the samples produced by SLM were performed by using an in-situ tool of SEM device. The micro hardness values of the samples were obtained by FM-310 type hardness tester tool. Vickers test was applied for micro hardness test by FM series micro hardness tester under a constant 100 g load and 10 seconds loading time. The micro hardness values of the samples were repeated for 5 times for as-cast and heat treated W and Si-doped Co-Cr powders. Archimedes’ principle was applied for determining the densities of the samples through the tool XB 320M. Electrochemical corrosion values were determined by Tafel extrapolation method.

3. Results and discussions
3.1. XRD analysis of Alloys

In Figure 2, XRD graph of As-cast and annealed samples produced by additive manufacturing is given. The structure determining the main phase for both samples is face centered cubic structure (FCC). The phases that determined the main structure in both samples appeared at 44,40, 51,60, 75,60 and 930 degrees and these structures are Co-based (FCC) structures. Co3Mo structure was evident in as cast sample, Co7Mo6, Co2Mo3, Co3Mo and Co, Cr, Mo and Cr-Co structures were observed in minor phases. Si and SiO2 phases were also observed in the annealed sample. Generally, it has been concluded that annealing promotes the introduction of doped metals into the structure.
Figure 2. W, Mo and Si-Doped-Co-Cr Alloys Produced by Additive Manufacturing

The FCC structure that forms the main phases of the alloy stems from Co and Cr. However, with the contribution of W, Si and Mo, a little hexagonal closed package (hcp) structure was formed in the alloy. This situation is more evident in the annealed sample.

3.2. SEM and EDX analysis of Alloys

Additive manufacturing production technique appears as a powder metallurgy production technique. In powder metallurgy production technique, powders are generally treated as sintering in suitable gas atmosphere after being mixed and pressed in appropriate proportions. As a matter of fact, nitrogen atmosphere was used to protect our powders produced by additive manufacturing from oxygen affinity. It is an advantage that no pressing is required in the method. However, our production method will be analyzed according to oxygen content, porosity and grain size properties as in powder metallurgy production methods. Dispersion X-Ray Analysis EDX results of W, Si and Mo doped Co-Cr alloys produced by additive manufacturing method are given in Figure 3/4 and the ratios are given in Table 2. Co-Cr is the main phase component in EDX analysis. At the same time, it is seen that the addition metals W, Si and Mo peaks occur. It has been found that the annealed sample is partially oxidized. However, it is worth noting that the protective gas atmosphere is not used for the annealing process.

Figure 3. EDX analysis of sample. Figure 4. EDX analysis of annealed sample
In Table 2, the chemical composition of all alloys used in the samples was found by EDX analysis. Analyzes show that the annealed sample is slightly more oxidized. In addition, it is seen that the structure does not change significantly in the mixing ratios of the metals forming the alloy and generally depends on the initial production composition.

**Table 2.** Chemical composition of alloys found by EDX analysis.

<table>
<thead>
<tr>
<th>Composition Co-Cr-Mo-W-Si</th>
<th>As-cast</th>
<th>Heat Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Wt %</td>
<td>At %</td>
</tr>
<tr>
<td>CoK</td>
<td>61,99</td>
<td>60,94</td>
</tr>
<tr>
<td>CrK</td>
<td>26,51</td>
<td>29,54</td>
</tr>
<tr>
<td>WL</td>
<td>7,82</td>
<td>2,47</td>
</tr>
<tr>
<td>MoL</td>
<td>1,35</td>
<td>0,82</td>
</tr>
<tr>
<td>SiK</td>
<td>1,37</td>
<td>2,84</td>
</tr>
<tr>
<td>OK</td>
<td>0,94</td>
<td>3,4</td>
</tr>
</tbody>
</table>

SEM mapping, which is formed according to the K and L shell energies of the doped metals, is given figure 5 with the annealed sample in and figure 6. The produced samples are left to right, as will be seen in the energy shell mappings given in Figure 5/6; CoK, CrK, sample section, MoK, MoL, slightly formed oxide, SiK and WL are available. In many cases it is difficult to obtain data from heavy metals such as W and Si, but as can be seen from SEM mapping, the amounts of W and Si added to the structure in the alloy are quite obvious. Mapping also gives us an idea of the compounds that can be formed in the element, for example the presence of CoK, CrK, MoK in the upper black region of figure 5, which tells us that a combination of the elements Co, Cr and Mo is formed in the main structure.

![Figure 5. SEM mappings depending on the shell energies of W, Si, Mo doped Co-Cr alloy.](image-url)
SEM images of W, Si and Mo doped Co, Cr alloy produced by additive manufacturing production method are given in figure 7 and images of annealed sample are given in figure 8. In Figures 7 (a), (b), (c) the images are taken from 10µm, 20µm and 200µm respectively. Production in powder metallurgy is directly related to the structure and shape of the powder. In additive manufacturing production methods, powders are produced layer by layer. The first three pictures were taken without any secondary treatment on the surface of the produced material. It was aimed to show the spherical grains with prominent distribution and proper production of the grains produced. The average size of the grains on this surface is between 3µm and 15µm. The size of the powders prepared to be produced was 30µm, which shows that we have achieved the targeted production process because one of the main objectives in powder metallurgy is the desire to reduce the grains in the alloy produced after the production stage.
The grains seen in Figure 7 (c) are bar-shaped and the lengths of several grains are measured as 4.5 µm, 6.3 µm, 11 µm, 13 µm, 14 µm, 36 µm and 537 µm respectively. After the surface SEM treatments, the produced alloys were broken into two pieces and the diameter of the grains and pores were analyzed better. In Figures 7 (d), (e) and (f) the pictures are taken from the cracked surface. SEM images taken in Figure 7 (d) 1 µm 118nm, 178nm, 208nm, 264nm, 273nm, 278nm and 304nm diameter porous structures were measured. In Fig. 7 (e) pores of 110nm, 161nm, 100nm, 185nm, 205nm, 244nm and 591nm diameters were measured respectively. The hexagonal bead apertures shown in FIG. W, Si, Mo doped Co-Cr alloy is known to contain both FCC structure and HCP structure.

Figure 8 SEM images of the annealed sample are given. Figures 8 (a) and (b) were taken from 5 and 10 µm respectively. Samples were not treated at this stage. The diameter of the spherical grains was observed to be reduced compared to the non-annealed sample, but slight fractures and cracks occurred on the sample surface. It was observed that the spherical structure was again finely dispersed. In the (c) untreated sample after the surface treatment, rod-like grains were also observed and their lengths were measured as 6.35µm, 4.01µm, 4.95µm, 4.75µm, 4.89µm, 7.82µm and finally 948µm, respectively. A significant decrease in the size of these structures has been observed with annealing. Fig. 7 It was seen that the hexagonal grains on the cracked surface shifted here into a digangular structure, the lengths of which were measured as 1.1 µm, 1.03 µm, 807 nm, 291nm, 579nm, 731nm, 179nm, 576nm, 690nm, 269nm, respectively.
3.3. Measurement of Micro Hardness and Density of Alloys

The hardness and density characteristics can show the abrasion resistance and penetration of a sample, and can form a broad network of ideas about the characteristics of the material. Vickers hardness measurement is the least destructive test method among the material tests. Similar properties have been reported between Vickers hardness and mechanical properties of a material. Vickers hardness notching machine (Micro Hardness Tester FM-310) was used to obtain the hardness values of the surface of the samples. Hardness values were taken under 100 g load for 10 sec. Hardness values were taken from 5 different points on the surface of each sample. The average of 5 Vickers values was accepted as the final hardness value. As seen in Table 3, annealing increases the micro hardness value of the alloy. On the other hand, annealing reduced the density value of the alloy.

Table 3. Micro hardness values of heat treated (in the upper) and as-cast (in the lower) samples produced by SLM.

<table>
<thead>
<tr>
<th>The micro hardness test</th>
<th>As-cast sample, HV (kgf/mm²)</th>
<th>Heat treated sample, HV (kgf/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W, Si and Mo-doped Co-Cr powders</td>
<td>371.3</td>
<td>330.1</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>440.9</td>
</tr>
<tr>
<td></td>
<td>386</td>
<td>449.6</td>
</tr>
<tr>
<td></td>
<td>398.8</td>
<td>452.7</td>
</tr>
<tr>
<td></td>
<td>432.2</td>
<td>485.5</td>
</tr>
<tr>
<td>Average value</td>
<td>387.26</td>
<td>431.76</td>
</tr>
</tbody>
</table>

By means of Archimedes’ principle, the densities of the samples were determined from the varying parts of each sample in different atmosphere. In the density calculation stage, the following formula was used:

\[ D_g = \left[ \frac{W_a}{(W_a - W_b)} \right] \times D_{H_2O} \] (1)

Where \( D_g \), \( W_a \), \( W_b \), and \( D_{H_2O} \) are visible density of the sample, weight of the dry sample in air, hanging weight of the sample in water, and water density, respectively. The calculated density values for as-cast and annealed W, Si and Mo doped Co-Cr alloys were found to be 8.769 and 8.691 g/cm³, respectively. The measured micro hardness average value was 387.26 HV, while the annealed sample was 431.76 HV. There was an 11.4% increase in micro hardness. Density values have caused a decrease of 1.008%.

3.4. Electrochemical Corrosion Testing of Alloys

Nowadays, many corrosion measurement techniques are available. Among these techniques, the most prominent one is the electrochemical corrosion measurement method according to the others. Electrochemical corrosion is based on the creation and use of anodic and cathode polarization curves. Electrochemical corrosion is based on the measurement in wet environments. In metallic biomaterials, metals and alloys in the wet environment of the body undergo electrochemical degradation as a result of environmental interaction. This negative condition causes corrosion tissue and organ poisoning, but also changes the physical or chemical properties of the material. Our alloys...
were analyzed in ringer solution in artificial body fluid. One ringer tablet was calcined in 500 ml of pure water at 121 °C for 15 minutes. Typical chemical composition of the tablet used is Ammonium Chloride 0.00525; Sodium Hydrogen Carbonate 0.005; Calcium chloride-2-hydrate 0.04; potassium chloride 0.00525; sodium chloride 1,125. Corrosion testing of pure metal and alloys is made of high mesh sandpaper and ultrasonic cleaning. Then, the alloyed metal alloys were connected as electrodes and placed in the corrosion apparatus. Tafel curves and open circuit voltages were obtained in the potential range determined by using electrode and graphite cathode. The reference electrodes used in response to working electrodes (our Co-Cr based alloys) are calomel. Gamry’s interface 1000 serial electrochemical analyzer is used for all corrosion measurements. Graphite was used as cathode. The samples were allowed to reach the open-loop potential (Ecorr) within 40 minutes prior to testing.

![Figure 9](image1.png)

**Figure 9.** The open-loop potential of the samples is shown.

![Figure 10](image2.png)

**Figure 10.** Tafel extrapolation graph of the alloys is given.

In Figure 9/10, the green lines show the data of the annealed sample. Figure 9 shows the open circuit potential measurements of the samples in the ringer solution for 40 minutes. The annealed W, Si and Mo doped Co-Cr sample showed thermodynamically stable behavior during the measurement period. The open-circuit potential was measured at -95mV. The main alloy coded sample deviated in a positive direction and completed the measurements at higher values than the potential it started.
Samples that exhibit such behavior are caused by a protective oxide layer formed on their surface. This protective layer is thought to be caused by Molybdenum (Mo) contribution. Figure 10 shows that unstable data potentials exist in the anodic part of the annealed sample. Since the anodic part in most samples is opposed to dissolution, surface dissolution is observed due to the rapid occurrence. When we look at the corrosion current values, the current value of the annealed sample is lower. ICORR; anneal Co-Cr-W-Mo-Si 12.80nA, ICORR Co-Cr-W-Mo-Si 29.30nA. However, the corrosion potential values of ECORR; annealed Co-Cr-W-Mo-Si is -145.0mV and ECORR Co-Cr-W-Mo-Si is 50.70mV. When we look at the corrosion rates of the annealed sample’s corrosion value is 410.5e-3 mpy, while the normal sample corrosion value is 11.15e-3 mpy. As can be seen, annealing showed an increasing effect on corrosion.

Conclusions

W, Si, Mo doped Co-Cr alloy produced by additive manufacturing method was produced in this study. The characteristic and morphological properties of the alloys were investigated by various tools. Molybdenum (Mo) doped generally makes Co-Cr alloys more excellent. It has been observed that a secondary annealing process in additive manufacturing production methods causes significant changes to the microstructural and mechanical properties of the material. Although it is seen that secondary annealing causes the formation of smaller grains in the alloys produced by additive manufacturing, larger pore diameters are seen in the annealed sample. It is noteworthy that the maximum pore diameters in both alloys are ~1 micron. It was observed that secondary annealing reduced the density value (%1,008 g/cm³) and increased the micro hardness value (%11.4 HV). Again, secondary annealing had adverse effects on the corrosion properties of the alloy. Mo additive is observed to form a strong layer against corrosion. In SEM and XRD analyzes, secondary annealing caused more compound formation of XRD measurements and caused changes in grain size and pore diameters of the alloy.

References


