Effect of Chromium and Molybdenum Increment on the Crystal Structure, Nanoindentation, and Corrosion Properties of Cobalt-Based Alloys

Shaukat Ali Lone, Dichu Xu, Richard Barker Cook, and Achim Walter Hassel*  

This study investigates the influence of chromium and molybdenum content (Cr: 20–35 wt%; Mo: 5 and 10 wt%) in a cobalt–chromium–molybdenum alloy system on the phases present in the microstructure, the nanomechanical, and electrochemical behavior of the alloys. A linear increase in the hardness is found in relation to the increasing chromium content for both 5 and 10 wt% Mo contents, whereas reduced modulus demonstrates an inflection at 30 wt% Cr, which is influenced by the molybdenum content. The open-circuit potential, polarization resistivity, and linear sweep voltammetry disclose that passivity of Co–Cr–Mo alloys improves in line with increasing Cr until 30 wt%, with any further increase causing a depreciation in the corrosion properties. X-Ray diffraction and optical metallographic analysis confirm that as the chromium content transitions through the 25–30 wt% range, the sigma (σ) phase begins to develop within the combined matrix of hexagonal close pack martensite (ε) and face-centered cubic austenite (γ) phase.

1. Introduction

Within the field of orthopedics, there has been a huge amount of attention paid to developing new alloys and materials that can enhance the performance of joint replacements, particularly for younger and more active patients. One of the key alloy groups are the Co–Cr–Mo alloys, due to their outstanding wear performance, mechanical stability, and corrosion resistance.¹⁻² While the alloy compositions for Co–Cr–Mo alloys are restricted by the ASTM standards (F75-18 and ASTM F1537-20),³⁻⁴ they provide compositional ranges within which there is scope to generate a range of alloy compositions with different microstructures and phase makeup, providing an allowance to tailor the mechanical properties and electrochemical performance.⁵⁻⁶

The mechanical and tribological properties of Co-based alloys originate from the crystallographic structure and metallurgical microstructure of the alloys which are both governed by the alloy composition. A key element in Co–Cr–Mo alloys is carbon (C); while C has a zero solubility in Co, the alloy is able to form carbides with both Cr and Mo which act as precipitates within the matrix impeding dislocation slip.⁷⁻⁸ The carbides are recognized to strengthen the alloy, but their influence on the tribological performance varies depending on the alloy’s treatment (as-cast, as-cast heat treated or forged) as these treatments influence the composition, morphology, distribution, and volume fraction of the carbides within the matrix which are crucial to how they influence the performance of these alloys.⁹⁻¹⁰

Co, Cr, and Mo all have the ability to exist in a single-phase solid solution alloy in both the face-centered cubic (FCC) and hexagonal close pack (HCP) phases. Pure Co transforms from FCC structure to HCP structure at a temperature of ≈417 °C, but the transformation temperature increases when alloyed with HCP stabilizers Cr and Mo, for example, in a Co27Cr5Mo0.05C alloy the HCP region expands and the transformation temperature increases to ≈970 °C.¹⁰ However, the allotropic diffusionless martensitic transformation from FCC to HCP is kinetically sluggish, meaning the majority of Co–Cr–Mo alloys consist of a predominantly metastable FCC structure.¹¹⁻¹² The FCC phase in Co–Cr alloys has an increased ductility and a high yield strength, but the low stacking fault energy of the alloy means that the dislocation cross-slip is restricted, and during deformation the alloy work hardens initially through forest hardening, but as dislocation glide is restricted further deformation occurs through the generation of twins and wide stacking faults which enable the strain-induced transformation to the HCP phase.¹³⁻¹⁴ These changes are, however, advantageous to the alloy’s tribological performance. Changes that do not occur is a harder surface to the alloy, but the friction coefficient obtained from single crystals
HCP Co was found to be approximately 50% less than FCC Co under the same condition and sliding velocity.\(^{[16,17]}\) This is why Co–Cr–Mo alloys are often cold or high-temperature work hardened to obtain an increased HCP phase presence at the surface.\(^{[16,17]}\) Thus, an increase in the mechanical properties and tribological performance of Co–Cr–Mo alloys can be acquired by enhancing the amount of the HCP phase within the microstructure. While HCP, FCC, and the carbide dominate in the microstructure, a third phase can form: the sigma (\(\sigma\)) phase. Sims\(^{[18]}\) disclosed the existence of intermetallic or tetragonal close-packed (TCP) compounds (i.e., \(\sigma\), \(\pi\), \(\mu\), and \(\rho\)) and emphasized that these phases impart mostly deleterious effects to the alloy. The presence of these phases can be attributed to high temperatures or exceeding concentrations of refractory metals depleting the amount of the HCP phase within the microstructure. While \(\sigma\) (\(\sigma\)Cr(OH)\(_2\) and \(\sigma\)Cr\(_2\)O\(_3\)) on the alloy surface,\(^{[20]}\) the passive phenomena are further supported by the presence of Mo either in the form of oxides or metal (at low potentials).\(^{[21,22]}\) As a general rule, the higher the concentration of Cr in the alloy, the more compact and protective the oxide is.\(^{[23]}\) The protective oxide can be worn down by mechanical means and consequentially the dissolution of undesired Co(II), Cr(III), Cr(VI), and Mo(VI) ionic species is unavoidable.\(^{[24]}\) Although the presence of Cr, Co, and Mo is essential for certain metabolic activities in the human body,\(^{[25]}\) the increment from a certain level is ought to be unfavorable due to potential biological inflammatory reactions and pseudotumor-like tissue formation associated with wear phenomena.\(^{[24,26]}\) Such corrosion of debris and its monitoring is part of ongoing studies.\(^{[27]}\)

Considering the fact that the composition of the Co–Cr–Mo system is an important factor, the present work is focused on the preparation of various compositions of Cr and Mo in complementary Co heat treated at a temperature of 970 °C. The resulting effects on the crystal structure were studied using X-ray diffraction (XRD). Moreover, an effort was undertaken to find the best composition of the Co–Cr–Mo alloy system which has improved mechanical properties without sacrificing the corrosion resistance.

2. Experimental Section

Two series of Co–Cr–Mo samples as shown in Table 1 were prepared by melting in an argon-enriched compact vacuum arc melter (Edmund Bühler GmbH, Germany). Pure Co, Cr, and Mo granules with the size (<6 mm) were purchased from (HMW Hauner GmbH & Co. KG, Germany) with a purity of 99.9%. Before the fusion of Co, Cr, and Mo granules, the melting chamber was evacuated \((\approx 10^{-5} \text{ hPa})\) and flushed with argon consecutively 3 times. The alloys were upturned and remelted 7–8 times to obtain a homogeneous composition. The final shape of all samples was a meniscus with the maximum diameter of 7–8 mm.

The arc melted alloys were further annealed at a temperature of 970 °C for a time period of 12 h. The samples were enclosed in a quartz glass ampoule to overcome the possibility of oxidation during the heat treatment and quenching process. For this purpose, the quartz glass tube \((\sigma = 1 \text{ cm})\) was sectioned in the middle (Figure 1a) and the sample was introduced into the tube through the open end. The argon was purged in with the help of a pipe and the respective end was spontaneously connected to the vacuum chamber (Figure 1b). Finally, the glass tube was molten and fused to form an ampoule by flaming the glass around 10 cm away from the sample (Figure 1c). The suction produced by the vacuum pump draws out not only the extra argon but also assists the fusion of the molten glass.

The glass ampoules with sealed samples were hung vertically into the Bridgman oven with the help of a stainless-steel wire. Once the annealing time period is over, the wire was cut and the samples were quenched into the water by free fall motion. The samples were taken out from the ampoule and cut into two halves with the help of a saw machine (MICRACUT 201, Metkon Instruments). One set of halved samples was spot welded with copper wire (for electrochemistry) and subsequently embedded in an epoxy resin while the other set was embedded in a condenser.

### Table 1. Two series of Co–Cr–Mo alloys with their intended compositions.

<table>
<thead>
<tr>
<th>No. of series</th>
<th>Alloy 1</th>
<th>Alloy 2</th>
<th>Alloy 3</th>
<th>Alloy 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co20Cr5Mo</td>
<td>Co25Cr5Mo</td>
<td>Co30Cr5Mo</td>
<td>Co35Cr5Mo</td>
</tr>
<tr>
<td>2</td>
<td>Co20Cr10Mo</td>
<td>Co25Cr10Mo</td>
<td>Co30Cr10Mo</td>
<td>Co35Cr10Mo</td>
</tr>
</tbody>
</table>

### Figure 1. a) Sectioning of the glass tube from the middle via hydrogen gas flame. b) Introducing the Co–Cr–Mo sample and argon gas to create an inert atmosphere. c) Connecting the vacuum pump and fusion of the glass tube to form a glass ampoule. d) Annealing the sample at 970 °C in Bridgman furnace and finally cutting the suspended wire for water quenching.

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without any copper wire. The initial grinding of embedded samples was undertaken in an aqueous medium with SiC sand papers (300, 800, 1000, and 2500), respectively, using an automated polishing machine (DIGIPREP 251, Metkon Instruments). Final polishing was done for 500 s by using silica-based suspension (1H2O2:5SiO2) with a fine polishing cloth (PT Chem Perforiert, Cloren Technology GmbH, Germany).

The composition of all Co–Cr–Mo samples was acquired by scanning energy dispersive X-ray spectroscopy (SE-EDX) equipped with a Si drift detector (remX GmbH). An accelerating voltage of 30 kV was utilized to produce X-Ray with a spot size of 500 μm. Three consecutive spectra were obtained for each sample, spatially 1.5 mm apart from each other. Obtained spectra were quantitatively analyzed by a software (IDFix software, remX GmbH). In the present work, the composition of all alloys is given in weight percentage before each metal symbol, i.e., Co20Cr5Mo contains 20 wt% of Cr, 5 wt% of Mo, and complementary Co. XRD analysis was performed to obtain the crystal structure of various Co–Cr–Mo alloys with an X-ray diffractometer (Philips X’pert Pro) using Cu Kα radiation at 40 mA and 40 kV. All XRD spectra were recorded in a Bragg–Brentano mode from 20° to 90° in 20 with a scan rate of 0.01° s⁻¹.

The Co–Cr–Mo samples were etched in aqua regia for 60 s at room temperature and the resultant etched structure was analyzed under a polarized light microscope (Carl Zeiss AG, Germany). Nanoindentation tests were conducted using a NanoTest Vantage system (MicroMaterials Ltd., Wrexham) using a Berkovich diamond tip at room temperature. For each alloy specimen, a 20 × 20 array of indents was performed with the indent spacing of 10 μm in both the x and y direction, resulting in a total of 400 indents for each specimen. The nanoindentation tests were performed in load control to a maximum load of 50 mN. The loading and unloading occurred over 10 s, with a dwell period of 10 s at the maximum load. A maximum depth termination was set to 500 nm, with the aim of avoiding interaction volume overlap between neighboring indents. The nanoindentation hardness (H) and reduced modulus (E₁) were calculated using the Oliver-Pharr method. The reduced modulus E₁ involves Young’s modulus of the diamond indenter and the specimen and can be expressed by Equation (1)

$$\frac{1}{E_1} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i}$$

(1)

where E₁ is Young’s modulus of the indenter (1141 GPa for diamond indenter), E_s is Young’s modulus of the specimen, ν_i is the Poisson’s ratio of the indenter (0.07), and ν_s is the Poisson’s ratio of the specimen.

Electrochemical measurements were conducted using a potentiostat (Ivium Technologies BV, The Netherlands) at a temperature of 37 °C in chloride-rich Ringer’s solution (pH = 7.4). A three-electrode electrochemical cell was utilized containing a counter: Au wire, reference: Ag|AgCl|3.5 M KCl, and the working electrode: Co–Cr–Mo sample. The samples were kept initially in open-circuit condition for 500 s. A potential sweep of ±100 mV versus E_cell was applied at a rate of 1 mV s⁻¹ for Tafel extrapolation. The anodic and cathodic slopes (b_a and b_c) were obtained by linearly fitting the anodic and cathodic branches of Tafel plots while the exchange current density (i_ex) was determined by the intersection of both lines. Finally, all acquired data were substituted in Equation (2) to evaluate the resistivity (R_p).

$$R_p = \frac{b_a - b_c}{2.303(b_a + b_c)(i_ex)}$$

(2)

Lastly, the linear sweep voltammetry (LSV) experiments were performed by scanning the potential from −0.8 to 1.5 V versus Ag|AgCl|3.5 M KCl at a scan rate of 1 mV s⁻¹.

3. Results and Discussion

Figure 2a–d shows the EDX spectra and averaged evaluated compositions of various Co–Cr–Mo alloys. All alloys achieved the intended targeted composition with a small change (≤ ±2 wt %). It is observable that the alloys carrying higher Cr and Mo content show comparatively higher compositional deviations (e.g., Co35Cr5Mo and Co30Cr10Mo exhibited an increase in Cr content by ≈1.6 wt% in comparison to the targeted composition). Considering the fact that the Cr and Mo are more refractory metals relative to Co and precipitation of secondary phases (σ) in Co-based alloys may impart inhomogeneity and resultant compositional deviation.

As shown in Figure 3, the quenched alloys after heat treatment at 970 °C are partially consisted of retained FCC phase (γ and majorly martensitic HCP phase (ε). The major occurrence of ε can be inherently conjoined to the rapid quenching of high temperature FCC (γ). The inherently rich stacking faults in FCC (γ) convert to Shockley partials due to low stacking fault energy and initiate the formation of HCP embryo on every plane where glide is possible. According to P. Huang et al.,[31] the nonequilibrium quenching process can produce sessile local supersaturation of vacancies exerting enormous osmotic force on the intrinsic dislocations. This osmotic force can aid in the rearrangement, pinning or climbing of local dislocation forming a martensitic (ε) embryo. The heat treatment step at a high temperature (i.e., 970 °C in the present work) can also encourage the growth of the martensitic embryo.

R. T. Estrada et al.[32] found a maximum transformation of FCC into the HCP phase as a function of temperature at 940–950 °C. On one side, the high-temperature aging decreases the required activation energy for HCP formation while on the other side Cr and refractory metal-enriched dual phases mediate the martensite nucleation and growth. The formation of dual phases has been declared to cause the compositional zoning in their surroundings ensuing in the development of pearlitic type and interdendritic martensitic structures.[18]

Various carbides and TCP phases (σ, μ and R) are commonly reported in the Co–Cr–Mo–C-based alloys and their formation is inevitable as the proportion of Cr and Mo increases above a certain limit.[13] In the present work, no additional carbon was added, thus the carbides are extinct; however, the existence of the secondary σ phase is evident especially with the raise in Cr content above 30 wt% as shown in Figure 3a–b. The peaks originating due to the sigma phase are represented by the magenta dotted lines and are noticeably more pronounced regarding intensity and numbers with the increase in Mo content (i.e., when comparing the Co35Cr5Mo with Co35Cr10Mo alloys).

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Morphologically, it can be noted in Figure 4 that below a percentage of 25 wt% Cr, the etched surface of each alloy regardless of Mo content exhibited no presence of additional phases except the white matrix consisting of $\varepsilon + \gamma$ as detected by XRD data. The formation of the martensitic phase in the form of long needle and lath like structure can be seen in Figure S1, Supporting Information (see Supporting Information). The preferentially attacked pits are a result of exaggerated etching of defects (especially Co20Cr5Mo in Figure 4a) inherently formed during the alloy solidification. As Cr increases more than 25 wt%, the dark secondary phase either in the form of small precipitates (Figure 4c) or thin interconnected lining (Figure 4d,g,h) at the grain boundaries is clearly visible corresponding to the $\sigma$ phase. These findings are completely in agreement with the most recent results obtained by Wang et al. In their work, the presence of only three phases (FCC, HCP, and $\sigma$) has been reported up to a maximum composition of (Cr ≈ 31 wt%) and (Mo ≈ 9 wt%). They found the $\sigma$ phase in the form of interconnected thick linings embedded in the matrix of HCP and FCC. It is interesting to note that the dark phase ($\sigma$) on the grain boundaries is attaining more prominence with increasing Cr and Mo content (Figure 4d,g,h). Considering the fact that the $\sigma$ phases (Co$_7$Cr$_8$...
and Co2Mo3) are usually formed by soaking up the Cr and refractory metals, i.e., Mo, the increase in the $\sigma$ can be directly related to the presence of Cr and Mo in higher amounts.[18]

For both Cr5Mo and Cr10Mo alloys, the average $H$ values linearly increased with increasing Cr content (Figure 5a,b), with Cr10Mo alloys showing higher average values than the corresponding values of Cr5Mo alloys at the same Cr content. The standard deviations increased with the increased Cr content for Cr5Mo alloys, while they first increased and then decreased with the increased Cr content for Cr10Mo alloys. The trendlines of best fit for the hardness values with the Cr content ($x$ wt%) were $H$ (GPa) = 0.2125 $x$ (wt%) – 0.2181 for Cr5Mo alloys group and $H$ (GPa) = 0.1681 $x$ (wt%) + 2.461 for Cr10Mo alloys group, respectively. The linear trend for Cr5Mo alloys was steeper than that of Cr10Mo alloys. The average $H$ value of Co–Cr–Mo alloy was found aligned with the hardness values of Cr5Mo with a much smaller standard deviation. The hardness trend results from two processes: the first is the increased solid solution strengthening which results from the additions of increasing amounts of Cr into the matrix; the Cr10Mo alloys start higher as the matrix already has a higher solution strengthening influence resulting from the higher Mo content. The second effect relates to the development and increase in the $\sigma$ phase within the microstructure which provides a precipitation hardening effect, with the intermetallic particles restricting the dislocation motion. The increasing deviation within the hardness results originates from the $\sigma$ phase development, as each 500 nm indent has an interaction volume from which the results are obtained. The variation in balance between the $\gamma$, $\epsilon$, and $\sigma$ phases results in a higher deviation in the results obtained.

The average $E_r$ values and standard deviations were not significantly changed with increasing Cr content, for both Cr5Mo and Cr10Mo alloys (in Figure 5b). The average $E_r$ values of Cr10Mo alloys were slightly higher than the values of Cr5Mo alloys, except for the specimens with 30 wt% of Cr content. The standard deviations were found similar between the two alloy groups. The average and standard deviation values for nanoindentation hardness and reduced moduli for each Co–Cr–Mo alloy specimen are summarized in Table 2. The modulus trend stems from a different origin to the hardness data. For the 20, 25, and 30 wt% Cr5Mo alloys, the initial increase is related to the increased Cr content within the matrix affecting the interatomic bonding and

Figure 4. a–d) Light microscopic images were taken after etching in aqua regia for 60 s for the CoXCr5Mo alloy series and e–h) CoXCr10Mo alloy series while X represents the Cr wt% on the left top side of each image.

Figure 5. a) Comparison of the hardness ($H$) and b) reduced modulus ($E_r$) between various alloy samples with different Cr and Mo content.
Co35Cr alloy heat treatment, leaving the Cr content in the 35 wt% Cr5Mo alloy shows a modulus drop due to the preferential formation of the γ phase (Co2Mo3) during the alloy heat treatment, leaving the γ and ε matrix depleted in Mo and with a lower modulus. The same effect is evident in the Cr10Mo alloys, but the peak modulus occurs at 25 wt% Cr due to the increased Mo content, with the modulus reduction at 30 wt% Cr due to the Mo segregation into the γ phase (Co2Mo3), with the subsequent increase at 35 wt% Cr resulting from the increased γ phase within the indent interaction volume. The polished Co–Cr–Mo samples were treated electrochemically under open-circuit potential. Figure 6a,b shows the OCP behavior of both series of Co–Cr–Mo alloys. The potential of last 100 s was taken as final OCP where the slope of OCP with respect to time was in a range of (±0.01–0.12 mV s\(^{-1}\)). Both series of alloys show nobility in the potential with the increase in Cr and Mo content up to a maximum of 30 wt% Cr (Figure 6c). As an example, the open-circuit potential of Co20Cr5Mo is \(\approx -0.39\) V which increases to a peak value of \(-0.04\) V for Co30Cr5Mo. However, after attaining the respective peak value the OCP declined in both cases (CoXCr5Mo and CoXCr10Mo). This analogous tendency is followed by the polarization resistance evaluated from Tafel plots as presented in Figure 6.

The polarization resistivity increases from 27.6 to 62.9 kΩ cm\(^2\) as the Cr in CoXCr5Mo series increases from 20 to 30 wt%. Additional increase in Cr content outcomes in a subsequent reduction in resistivity. The respective decline in \(R_p\) is particularly more prominent in the case of CoXCr10Mo series alloys. More Mo content (≈10 wt%) in series alloys appears to be advantageous in terms of polarization resistance for the Co–Cr–Mo alloys contingent when the Cr is lower than 30 wt%; otherwise, a detrimental effect on passivity is expected. Figure 7a,c illustrates the linear sweep polarization (LSV) behavior of various CoCrMo alloys in 0.15 M Cl\(^-\) electrolyte. The LSV curves can be principally distributed into cathodic and anodic branches. The cathodic current mainly depends upon the reduction of water or dissolved oxygen at the native passive oxide.\(^{36,37}\) As the potential exceeds in the positive direction, a sharp transition occurs from the cathodic to anodic region. Apparently, the transition region from cathodic to anodic branch behaves nearly the same as the Tafel plots shown in Figure 6d,e, except for a slight shift to negative potentials consequently due to starting potentials of \(-0.8\) V versus Ag|AgCl|3.5 M KCl. It is important to note again that the Co30Cr alloys irrespective of the Mo content exhibit the lowest anodic current in both alloy series. Any change in Cr content results either in a shift of the Tafel region to a negative direction or an increase in the anodic polarization current. In the anodic branch section, several

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### Table 2. Average values and standard deviation for the hardness and reduced modulus values of Co–Cr–Mo alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(H) [GPa]</th>
<th>(E) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrMo</td>
<td>5.02 ± 0.33</td>
<td>222.94 ± 8.22</td>
</tr>
<tr>
<td>Co25Cr–5Mo</td>
<td>4.17 ± 0.40</td>
<td>188.50 ± 9.40</td>
</tr>
<tr>
<td>Co25Cr–5Mo</td>
<td>4.75 ± 0.65</td>
<td>195.52 ± 10.64</td>
</tr>
<tr>
<td>Co30Cr–5Mo</td>
<td>6.43 ± 0.97</td>
<td>217.45 ± 10.40</td>
</tr>
<tr>
<td>Co35Cr–5Mo</td>
<td>7.16 ± 1.69</td>
<td>207 ± 11.55</td>
</tr>
<tr>
<td>Co20Cr–10Mo</td>
<td>5.81 ± 0.74</td>
<td>206.03 ± 12.04</td>
</tr>
<tr>
<td>Co25Cr–10Mo</td>
<td>6.76 ± 1.17</td>
<td>214.46 ± 10.49</td>
</tr>
<tr>
<td>Co30Cr–10Mo</td>
<td>7.40 ± 1.40</td>
<td>204.58 ± 10.97</td>
</tr>
<tr>
<td>Co35Cr–10Mo</td>
<td>8.41 ± 0.74</td>
<td>214.73 ± 9.75</td>
</tr>
</tbody>
</table>

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Figure 6. a) Open-circuit potential recorded during 500 s of immersion time in Ringer’s solution at a temperature of 37 °C for CoXCr5Mo, b) CoXCr10Mo, and c) averaged OCP for last 100 s plotted with respect to the Cr content. d) Tafel plots obtained for CoXCr5Mo, e) CoXCr10Mo, and f) polarization resistivity tabulated by Tafel extrapolation for both Co–Cr–Mo alloy series.
chemical and physical changes occur at the Co–Cr–Mo oxide surface. Co being the major component of the parent alloys can convert into anhydrous CoO and Co(OH)2; however, the chloride ions may form Co complexes (CoCl+ and CoCl2) which are water-soluble and give rise to the preferential dissolution of Co.\\cite{19,38} This phenomenon will lead to the surface enrichment of Cr in the form of Cr2O3, Cr(OH)3 and CrOOH. According to I. Milošev et al., the enriched passive layer on the F75 Co–Cr–Mo alloy (below EAg|AgCl|3.5MKCl < 0.34 V) is \(\approx\) 3.1 nm thick and consists of more than 90% of Cr2O3.\\cite{39} The extent of less passivating Co dissolution and Cr oxide enrichment mainly depends upon Cr content in the alloy. As an example, in Figure 7a if we compare the anodic branch in the potential range (0–0.6 V) of Co20Cr5Mo and Co30Cr5Mo, the current density in the latter case is considerably lower. This is due to the fact that Cr forms a meshwork of (Cr–O–Cr) on the alloy surface and its 3D connectivity mainly depends upon the Cr availability.\\cite{40} The increase in Mo content from 5 to 10 wt% (see Figure 7c) also retards the dissolution kinetics significantly, i.e., CoXCr10Mo alloy series demonstrates improved passivation in comparison to CoXCr5Mo with regard to the anodic current. Mo either in the elemental form (due to its bigger size) or absorbed MoO4^{2-} can block the intromission of chloride ions.\\cite{21,22,41} Owing to the surface enrichment, oxide film thickness remains increasing as a function of applied potential and continues even in the transpassive region.\\cite{42,43}

As the potential increases more than the transpassive region (\(E_{Ag|AgCl|3.5MKCl} > 0.7 V\)), the Cr(III) transforms into Cr(VI) species and transports outward through the oxide layer under the action of an increasing electric field across the oxide. The respective solid-state reaction in combination with the outward motion of Co(II) and Mo(III) ionic species and inward transport of O^{2-} and OH^- ions increases the thickness of the passive oxide film and also changes the chemical composition.\\cite{42,43} The transpassive region (Figure 7a–d) is represented by the exponential increase in the current above 0.7 V. Alongside the water oxidation (O2 evolution), the dissolution of Cr(III), CrO4^{2-}, Mo(VI), and Co(II) occurs continuously in the transpassive region and is not significantly affected by their bulk composition as shown in Figure 7b,d.

Surprisingly, the improvement in the passive behavior does not continue after the Cr content of 30 wt%. The lack of passive behavior can be associated with the change in the microstructure of the alloy. Some micrographs of the CoXCr5Mo alloy series taken by a polarized light microscope after LSV experiments are given in Figure 8a–d. The martensitic plate-like structures are clearly apparent for Co20Cr5Mo and Co25Cr5Mo (Figure 8a,b). Co30Cr5Mo shows randomly arranged sigma particles which are seemingly less affected by the applied voltage; nevertheless, dark regions in their vicinity manifest the existence of chromium deficient regions. As already discussed previously, the increase in Cr content above 30 wt% causes the formation of the secondary phase (a) which can be electrochemically more stable due to high Cr and Mo content. However, compositional zoning introduced by these phases may create electrochemical potential inhomogeneities along the surface. Furthermore, the
grain boundaries formed by the presence of these phases can be potentially vulnerable sites for corrosion attacks. Finally, the sigma phase in Co35Cr5Mo is relatively thicker, and dark regions in the form of lines and around their neighborhood demonstrate a comparatively higher dissolution.

This work is part one of the study on this material class. Further investigations are presently performed that should evaluate the differences in different crystallographic orientations. Another aspect will be the in situ indentation and the influence of the passive layers formed on these alloys.[46,47]

4. Conclusion

Two series of Co-based Co–Cr–Mo alloys (CoxCr5Mo and CoxCr10Mo) were produced by using vacuum arc melting and subsequent annealing at 970 °C for 12 h while \( x \) changes from 20 to 35 wt%. All targeted compositions were achieved with a small variation in Cr content in the range of 0–2 wt%. XRD analysis performed on the samples showed that the crystal structure is mainly composed of martensite hexagonal structure and high-temperature FCC structure. Increases in Cr above 25 wt% were responsible for the formation of a secondary sigma phase (\( \sigma \)) either in the form of small precipitates or thin interconnected linings. Hardness and reduced elastic modulus were measured by nanoindentation, and a linear slope of 0.213 GPa wt\% \(^{-1}\) and 0.168 GPa wt\% \(^{-1}\) was obtained by linear fitting the hardness with respect to Cr content for CoXCr5Mo and CoXCr10Mo. The reduced modulus with respect to Cr did not show a linear relation due to ambiguous behavior at 30 wt% Cr; however, the values lie in the range between 188 and 222 GPa. The open-circuit potential and polarization resistivity revealed an increase with respect to Cr content till a maximum was obtained in both Co-based CoCrMo alloy series at 30 wt% Cr. Further increases in Cr content resulted in a decline due to the presence of secondary phase and formation of grain boundaries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

cobalt–chromium–molybdenum alloys, corrosion, linear sweep voltammetry (LSV), nanoindentation, sigma phase (\( \sigma \)), X-Ray diffraction

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Figure 8. Polarized light microscopy images taken after LSV for a) Co20Cr5Mo, b) Co25Cr5Mo, c) Co30Cr5Mo, and d) Co35Cr5Mo.