

# Electrochemical Corrosion and Metal Ion Release Protective Efficiency of the Multilayer TaN Coatings on CoCrMo Biomedical Alloy

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CoCrMo alloy is widely used in artificial orthopedic joint applications due to its high mechanical properties. But, high levels of the metal ion release from alloy surfaces cause variable toxic and allergic effects on the patient in vivo use. This case restricts the lifetime of the implant and results in the failure of the artificial joint. In order to enhance the corrosion resistance and to decrease the metal ion release, alloy surface was multilayer-coated by closed field unbalanced magnetron system. The protective efficiency of the coatings was determined by potentiodynamic polarization tests and static immersion tests were performed for 45, 60 and 90 days in the simulated body fluid in order to understand the effect of the coatings on the metal ion release. The metal ion concentrations in the simulated body fluids were determined by using inductively coupled plasma mass spectrometry device. The electrochemical corrosion results showed that the multilayer coatings provided 93 % protective efficiency in terms of corrosion resistance. Multilayer coatings decreased the metal ions release levels significantly, especially Co leaking was decreased approximately 52 times compared to uncoated samples.

**Keywords:** CoCrMo, biomaterial, multilayer coating, corrosion, metal ion release.

## 1. INTRODUCTION

The biomaterials which are used in hard tissue applications must have high corrosion resistance as well as high mechanical properties [1]. Although Titanium alloys have higher corrosion resistance compared to CoCrMo and 316 L steel, they are not used especially in the load-bearing applications due to its poor fatigue strength. CoCrMo alloys are preferred in these applications thanks to their better mechanical properties [2]. On the other hand, poor corrosion resistance feature and the cytotoxic effects of the released metal ions cause early failure of the implant [3, 4].

It was reported on previous studies that, released Cr<sup>+3</sup>, Cr<sup>+6</sup> ions cause aseptic loosening of the implant by accumulating in the surrounding tissues [5, 6]. Additionally, it is known that the release of Ni element into the body fluid that was added to the alloy to enhance the machinability of the alloy, causes toxic effects [7, 8]. Metal ion release can be described as the leaching of metal ions from the metal alloy into its located environment by electrochemical mechanisms [9]. Metallic biomaterials protect themselves from corrosion thanks to a self-passivated thin film layer in the corrosive body fluid environment. While this protective thin film produced by Cr on the surface of 316 L stainless steel and CoCr alloys, on Ti alloys it forms as TiO<sub>2</sub> [10]. When this protective passive thin film layer disappears instantly, body fluid acts as an electrolyte due to the content of amino acids, proteins, and various salts [11]. Then anodic and cathodic regions form on the metal surface, and electrons move towards the metal surface to the body fluid from the anodic region. The metal which loses an electron

transforms to positive charged ions and these ions release into the body fluid [11, 12]. This released ions can show different behaviours, such as binding with water molecules or anion molecules. But when they have bonded with the biomolecules which surrounds the tissues, they can cause to problems such as inflammation, aseptic loosening [13]. Since the metal ion release is an electrochemical process, previous studies had focused on the understanding of the electrochemical properties of the various protective surface coatings on the CoCrMo alloy surface [14–16]. But when the variety of the body fluid content and also method differences of the electrochemical corrosion tests considered, it is an important necessity to determining the metal ion release levels by immersion metallic biomaterials into the simulated body fluid for specific dwell times [13, 17].

Some studies had been performed on ceramic thin film coating of the CoCrMo alloy surface to enhance the corrosion resistance and decrease the metal ion release in order to overcome the problems mentioned above by enhancing the tribocorrosion properties of the alloy [18–24]. These studies aimed to eliminate the corrosive effects of the simulated body fluid on the alloy by coating its surface with an inert thin film. In a few of these studies, while metal ion emissions were examined, the vast majority were investigated for the effects of coatings on corrosion resistance. It can be said that the common result of these studies is that multilayer ceramic coatings of the alloy surface by physical vapour deposition (PVD) technique enhances the corrosion resistance significantly.

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Türkan et.al coated the surface of the CoCrMo alloy with a thin TiN film by PVD technique. They immersed the coated and uncoated samples into the simulated body fluid for specific times and then determined the metal ion levels by using inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS) devices. They reported that the TiN coating prevented the harmful metal ion release significantly [22]. Alemon et al. studied the effect of the multilayer thin TiAlVCN/CN<sub>x</sub> film coating on the tribocorrosion and metal ion release in the simulated body fluid plus bovine serum. They revealed that the amorphous multilayer coating enhanced the tribocorrosion properties and decreased the metal ion release [23]. Abdullah et al deposited multilayer Cr/CrN/CrCN/ZrN thin films on the CoCr alloy by physical vapour deposition with different coating times, and investigated the metal ion release from the samples into the simulated body fluid for different immersion times. As a result of their study, they revealed that coated samples released fewer metal ions compared to the uncoated samples except for Cr ions [24]. Hanawa has studied the metal ion release mechanisms from the metallic implant materials into the body fluids [13]. Matusiewicz reported a systematic and analytical review of the metal ion release from metallic implants. In his study, he examined previous studies, the effect of the released metal ions on the body, determination techniques of metal ion release, and comparing these techniques [9].

Although the metal ion release is a result of the electrochemical process, previous studies showed that data obtained from electrochemical corrosion studies are not with the same consistency and precision every time. Thus, it is thought that in order to confirm the biocompatibility of a newly developed metallic biomaterial, it is an important requirement to examine metal ion release in vitro. In this study, the protective efficiency of the multilayer Cr/TaN, Cr/CrN/CrCN/TaN and Cr/CrN/CrCN/ CrN/CrCN/TaN coatings deposited on ASTM F-75 CoCrMo alloy investigated in terms of electrochemical corrosion and metal ion release.

Additionally, some studies have been performed using in vitro wear simulators in order to determine Co and Cr ion release from the alloy. Wyles et al investigated the metal ion release from the Metal-Polyethylene and Ceramic-Polyethylene total hip arthroplasty simulator in plus bovine serum for a 1 million wear cycle. They obtained that ceramic-polyethylene component released much lower metal ions compared to metal-ceramic component [25]. Reyna et al investigated the ion release from multilayer CrN/CrCN/ZrN coated ASTM F-75 CoCrMo alloy total knee implant in vitro wear simulator. They determined three-fold decreased ion release concentration for the

multilayer-coated system compared to the uncoated knee system [26].

## 2. EXPERIMENTAL DETAILS

ASTM F-75 substrate materials used in this study; were supplied from a commercial implant manufacturer (Ottoman A.Ş., Malatya, Turkey). Since cutting the alloy with conventional machining methods is too hard, the laser cutting technique was used to cut the samples [27]. Substrate materials were cut off from the tibial tray component of the total knee implant as square geometry with dimensions of 20 × 20 and a thickness of 2 mm as shown in Fig. 1.

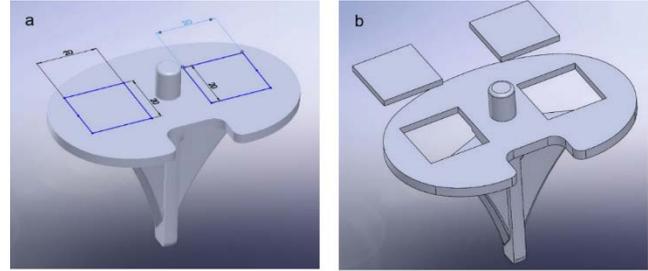


Fig. 1. Substrates were cut off from tibial insert component

The chemical composition of the CoCrMo alloy used in this study is given in Table 1. All the specimen surfaces had polished mirror-like before the coating process multilayered thin films were deposited on the substrate materials by using a closed-field unbalanced magnetron system (teer coatings). Thickness of the coatings were determined by SEM. The detailed coating parameters can be found in our previous study [28]. Coated samples were called S1, S2, and S3, and S0 was the as polished uncoated sample. Table 2 shows the coating properties such as layer numbers, thickness, coating architecture. Electrochemical corrosion measurements were performed by using a PARSTAT 4000 Potentiostat electro impedance spectrometry device. 0.9 g/L NaCl water solution was used as the corrosion environment. Open Circuit Potential (O.C.P.) measuring time was 1800 seconds for all the samples. Ag/AgCl (3.5 mol KCl) was used as a reference electrode, and the counter electrode was a pair of graphite rods. The corrosion rate of the samples was calculated accordingly to ASTM G 102 – 89 (2004) standard (Standard practice for calculation of corrosion rates and related information from electrochemical measurements).

The polarization resistance of both coated and uncoated samples was calculated from the equation given below [29]:

$$R_p = \beta_a \times \beta_c / 2.303 \times \text{CCD} \times (\beta_a + \beta_c). \quad (1)$$

Table 1. Chemical composition of the ASTM F-75 CoCrMo alloy used in the study

Element	Co	Cr	Mo	Ni	Fe	C	Si	Mn	W	P	S	N	Al	Ti	B
Mass %	Balance	28	5.96	0.25	0.2	0.22	0.7	0.5	0.01	0.01	0.005	0.15	0.05	0.01	0.006

Table 2. Properties of the coating

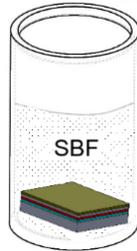
Coating	Architecture	Layer numbers	Total thickness of the coating, μm
S1	Substrate/Cr/TaN	2	1.861
S2	Substrate/Cr/CrN/CrCN/TaN	4	2.361
S3	Substrate/Cr/(CrN/CrCN) <sub>x3</sub> /TaN	8	3.614

All the values in this equation were obtained from the polarization curves and, while the  $R_p$  represents the polarization resistance value, CCD is the abbreviation of the corrosion current density,  $\beta_a$  and  $\beta_c$  represents the anodic and cathodic Tafel slopes. Electrochemical protective efficiency of the coatings was calculated accordingly the equation given below [30]:

$$P = [1 - (I_{\text{corr}} / I_{0\text{corr}})] \times 100. \quad (2)$$

In this equation, the  $P$  represents the % protective efficiency,  $I_{\text{corr}}$  represents the corrosion current density and the  $I_{0\text{corr}}$  represents the corrosion current density of the uncoated surface.

In order to understand the effect of the coating on the metal ion release of the CoCrMo alloy, both uncoated and coated samples were immersed in simulated body fluid. Simulated body fluid was prepared according to Kokubu's recipe [31]. A total amount of 500 mL simulated body fluid was prepared and the samples were immersed in 50 ml plastic cups separately. The samples were immersed in the solution as the coated face up. A schematic shown of sample immersion in the SBF was given in Fig. 2.



**Fig. 2.** Schematic shown of the specimen assembly into the SBF container

To prevent contamination; while preparing the simulated body fluid and taking the samples for inductively coupled plasma mass spectrometry (ICP-MS) analysis, metal instruments were not used. Liquid samples were removed from the incubated cups into the three 5 mL tubes for each sample in the 45, 60 and 90<sup>th</sup> days and stored in the

refrigerator at 4 °C. The plastic cups maintained in the incubator at 37 °C temperature during the all experiment period. SEM investigations were performed on the coatings surface after the static immersion tests by using Oxford Instruments scanning electron microscope operated at 25 kV. To observe the elemental changes and formations on the coating surface EDX analysis was performed by using Oxford Instrument EDX device. Co, Cr and Mo ion concentrations in the simulated body fluid were determined by ICP/MS elemental analysis. For all elements which will be detected in the liquid samples, standard solutions were prepared separately. The detection limits of the elements were given in Table 3.

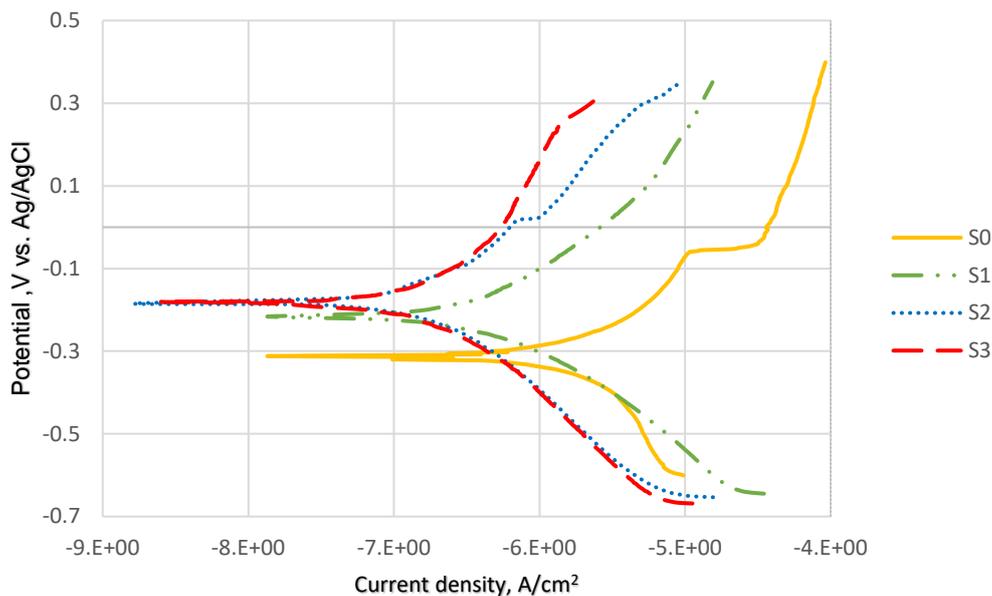
**Table 3.** Detection limits of the elements studied in the ICP-MS analyze

Element	Interior std.	Linear Range	Unit
Cr	Sc	0.5 – 50	µg/L
Co	Sc	0.5 – 50	µg/L
Mo	In	0.5 – 50	µg/L
Ta	In	1 – 50	µg/L

### 3. RESULTS AND DISCUSSION

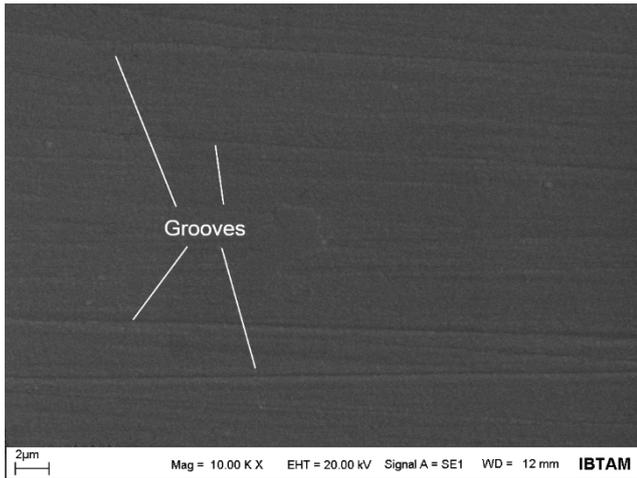
#### 3.1. Electrochemical corrosion results

Electrochemical corrosion tests are commonly used in order to understand the corrosion rate of biomaterials especially metals due to provides precision results [10, 13]. Potentiodynamic polarization curves of all samples are shown in Fig. 3. The corrosion and polarization data of the coated and uncoated samples were determined by the Tafel extrapolation method. When the polarization curve of the uncoated sample studied, it is seen that except the corrosion potential, cathodic and anodic regions, it can be seen there is a pitting potential approximately -0.05 V. The corrosion potential of the S1 shifted in a positive direction and the corrosion current density was decreased compared to the as-polished sample. The corrosion potential and current density of both S2 and S3 coatings gave fewer values compared to S1 and as-polished samples.



**Fig. 3.** Polarization curves of the samples

As can be clearly seen from Fig. 3; the polarization curves of the 4 and 8 CrN/CrCN/TaN multilayer-coated samples are quite similar. But, on the polarization curve of S2, it was seen that existing of a pitting potential at about 0.013 V. It is thought that this can be a result of the scratches that formed the polishing process before the PVD process. These scratches caused some grooves on the coating surface. Fig. 4 shows the scanning electron microscope (SEM) image of the S2 coating surface before the electrochemical corrosion tests. These grooves led to break down the continuity of the coating layers, as a result, it is thought that local corrosion formed most probably around these grooves.



**Fig. 4.** SEM image of the S2 sample surface

The corrosion potential and current density values are the key features that determine the effect of the thin film coatings on the corrosion resistance of the substrate. Table 4 represents the results obtained from the electrochemical corrosion tests. Corrosion rate of the samples was calculated according to the ASTM G 102 – 89 (2004) standard and can be seen in Table 4. Also, the polarization resistance and the protective efficiency of the coatings were calculated accordingly Eq. 1 and Eq. 2 respectively. When the data on the table is studied, it is seen that Cr/TaN coating decrease the both the corrosion potential and current density values of the uncoated samples. While the corrosion current density value of the uncoated sample was found to be 0.311 V, this value was obtained to be 0.204 V for S1 coating. Also, the corrosion current density value of the S1 is approximately 6 fold less than of the as-polished sample. The protective efficiency of the S1 coating was calculated to be 83 %, and the corrosion rate of the alloy was decreased from 0.048 mm/year to 0.007 mm/year thanks to coating.

When the electrochemical corrosion results of the S2 and S3 coatings which have CrN/CrCN bilayer are examined, it is seen that 4-layered S2 coating has 15 times less corrosion current density and 16 times lower corrosion rate than of uncoated sample. When the corrosion data of the S2 compared to S1, it is understood that the corrosion current density was 2.5 times less than of S1. The protective efficiency of the S2 coating was calculated as 93 %, and the corrosion rate was found to be 0.003 mm/year. The corrosion rate and the protective efficiency of the S2 and S3 were found same, further, the other electrochemical

properties were found very close together. Therefore, it can be said that increasing the layer number and thickness did not make a significant difference in terms of electrochemical corrosion properties. When this results are considered, it can be said that increasing the bilayer number or the thickness of the Cr/CrN/CrCN/TaN coatings did not make significance effect on the electrochemical properties. Li et al revealed contrasting results compared to our study. They reported enhanced polarization resistance and decreased corrosion current density values by increasing the bilayer number. They attributed this result to the dense microstructure and barrier effect of the bilayers provided by the increasing number of interlayers [30]. On the other hand, Beliondah et al. compared the electrochemical corrosion properties of the Cr/CrN/CrAlN thin films with different thicknesses deposited on mild steel substrates, and they found higher corrosion resistance for the 300 nm thickness coatings more than of 1500 nm thickness films [32].

Yang et al found lower corrosion current density for 20 layers TaN coating than that of 50 layers TaN coating [33]. In this regard, it can be said that electrochemical corrosion properties of the ultra-thin films with the same coating architecture, can not be directly enhanced by increasing the bilayer number or the thicknesses. But, it must be noticed that features of the deposited thin films such as microstructure, homogeneity, continuity, and the defects such as pinhole, scratches or grooves have great importance on the electrochemical corrosion properties.

Alishahi et al. have reported 99.98 % protective efficiency and 5 times lower corrosion current density for Ta/TaN multilayer coatings compared to bare 316 L stainless steel [34]. Yang et al have found  $3.3 \times 10^{-7}$  A/cm<sup>2</sup> corrosion current density for 20 multilayers TaN coating deposited onto the AISI 420 steel substrates. Mendizabal et al have studied the tribocorrosion properties of the multilayer TaN thin films deposited on the pure Titanium substrates in PBS albumin. They revealed that TaN films exhibited excellence corrosion resistance compared to bare Titanium [35]. TaN ceramic coating provided very high corrosion resistance in accordance with its excellent inertness nature [36]. It is understood that obtained results are in accordance with the previous studies, further it is thought that TaN thin films are a good candidate to use in the studies of the development of biomaterials corrosion resistance [33 – 38].

### 3.2. Metal ion release results

Released ion concentrations in the simulated body fluids for 45, 60 and 90 days were determined by ICP-MS and can be seen in Fig. 5. Tantalum ion concentration was found to be below the detection limits. The ion concentration of the Cobalt is represented in the Fig. 5 a, has been obtained by dividing a factor of 10. Co ion release of the as-polished sample was found to be 91.70 µg/L for the 45 days. It is seen that this value was increased by a very small amounts for the in the following days. Co ion concentrations of multilayered coated S1, S2 and S3 were found respectively 3.44 µg/L, 2.27 µg/L and 1.74 µg/L. It is clearly understood that Co ion release was decreased significantly by coating alloy surface with multilayer coatings.

**Table 4.** Potentiodynamic polarization data of the samples

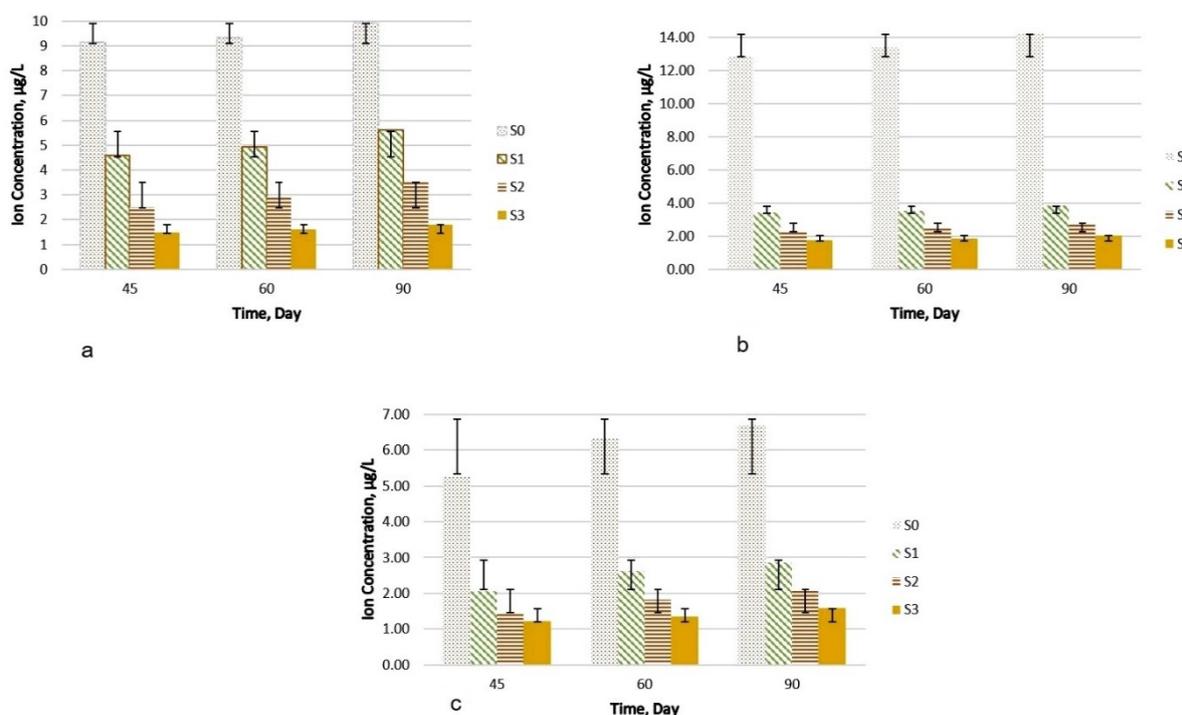
Specimen	$\beta_a$ , mV	$\beta_c$ , mV	$I_{corr}$ , $\mu\text{A}/\text{cm}^2$	CR, mm/year	$E_{corr}$ , V	$R_p$ , $\text{k}\Omega\cdot\text{cm}^2$	$P$ , %
S0	275.595	872.178	3.738	0.048	0.311	24.32	–
S1	327.225	275.587	0.622	0.007	0.204	104.43	83
S2	219.207	340.643	0.244	0.003	0.181	237.35	93
S3	262.655	345.642	0.240	0.003	0.183	270.01	93

Multilayer coatings provided a highly protective effect in terms of Co ion release and, S1, S2, and S3 coatings gave respectively 26 times, 40 times and 52 times decreased ion concentrations compared to the uncoated sample. Co ion release levels showed a similar increasing rate for the coated and uncoated samples after the 45<sup>th</sup> day by increased very small amounts. Previous studies reported that Co was dissolved quickly when the CoCrMo alloy immersed a corrosive liquid environment such as simulated body fluid [9, 10, 13, 22]. It is understood that Co has shown a similar behavior and preferentially released into the body fluid in this study. Türkan et al. have determined ion concentrations below the detection limits in their study. But it must be noticed that they have coated the bare surfaces of the alloy by resin [22]. In this study, since the only top surface of the alloy was coated with Cr/CrN/CrCN/TaN, metal ions released also from other uncoated surfaces. The results of Co ion release from the uncoated sample were similar to ours, they achieved high ion release for the first 30 days, but after following days ion release rate was very low. Espallargas et al. have found higher Co ion concentrations than the other elements in their study on the metal ion release in PBS, PBS buffered albumin and NaCl solutions [39]. Wang et al. reported higher Co ion concentration than of Cr and Mo in their study on the tribocorrosion tests of artificial hip implants in different liquid environments [40].

Cr ion concentrations obtained from the static immersion tests are given in the Fig. 5 b. As mentioned above in the introduction section, it is well known high

levels of Cr ions in the body fluids and tissues around the implant, cause toxic and infective effects. Therefore, it is of great importance to decrease Cr ion release levels in terms of the success of the coatings applied in the study. Cr ion release levels were found to be 12.88  $\mu\text{g}/\text{L}$  for uncoated samples, while this value was 4.59  $\mu\text{g}/\text{L}$ , 2.51  $\mu\text{g}/\text{L}$  and 1.47  $\mu\text{g}/\text{L}$  for multilayer-coated samples, respectively. 8 multilayered S3 coating has showed the best protective effect in terms of Cr ion release. Fig. 5 c represents Mo ion concentrations. Mo ion concentrations released from uncoated, S1, S2, and S3 samples were found to be respectively 5.26  $\mu\text{g}/\text{L}$ , 2.05  $\mu\text{g}/\text{L}$ , 1.44  $\mu\text{g}/\text{L}$  and 1.21  $\mu\text{g}/\text{L}$ . It is understood that Mo ion release continued at a very low rate following days after the 45<sup>th</sup> day. The coating has decreased the ion release effectively for all samples, especially 8 multilayered coating provided 4 times lower ion concentration level.

When all ion concentrations examined together, it can be seen clearly the ion release had formed highly till the 45<sup>th</sup> day, then following days increasing continued with very low accelerations. It is thought that high quantity ion release occurred probably before passive film forming on the samples uncoated surfaces when they immersed into the simulated body fluid. Fig. 6 represents the comparison of the Co, Cr and Mo ion levels in the simulated body fluids. In the first 45 days, 84 % of the total concentration of the released elements is Co, 11.8 % is Cr and 4.2 % is Mo element. These results are in agreement with the previous studies [39, 40].

**Fig. 5.** Released ion concentrations: a – cobalt; b – chromium; c – molybdenum

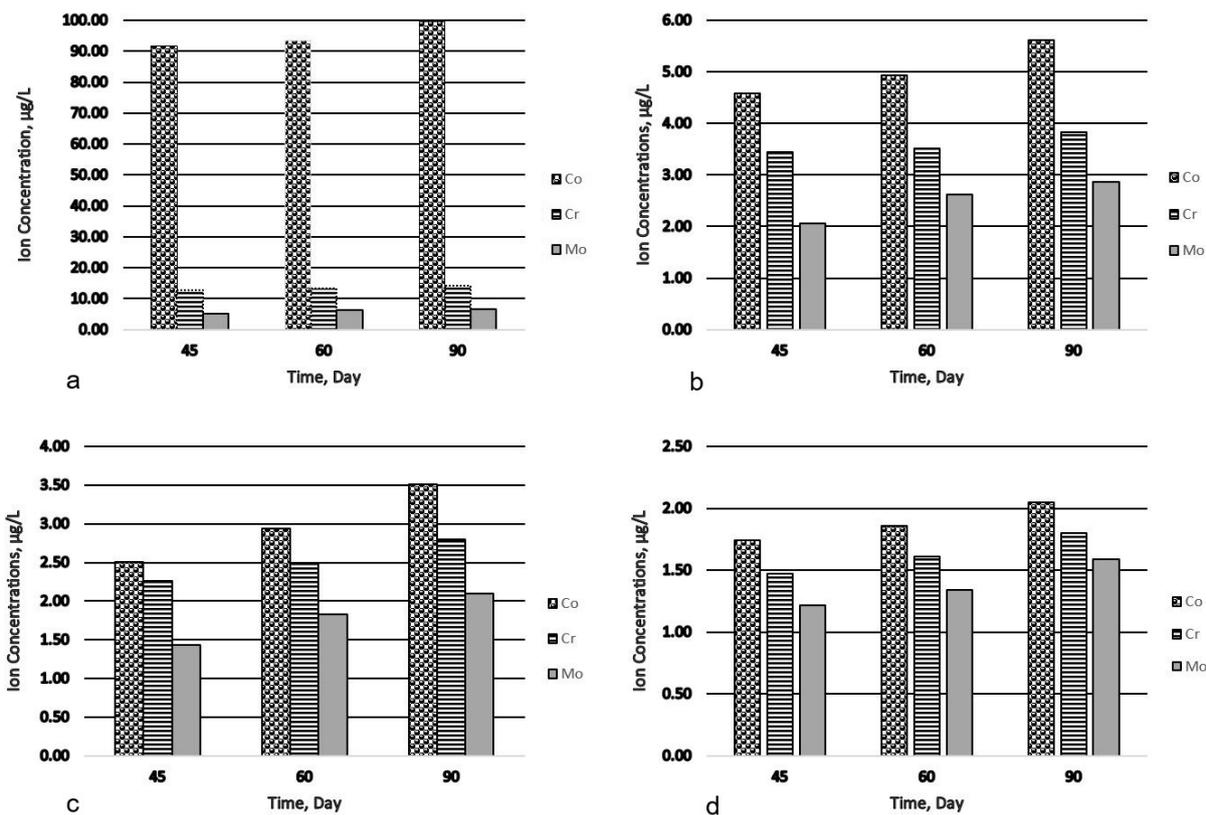


Fig. 6. Elemental ion concentrations of the samples: a – as polished samples; b – S1; c – S2; d – S3

The ion concentration of the Co from the uncoated sample is higher than the other elements similar to the coated samples. But the % rate of the elements were found different. For the Cr/TaN coated S1 sample the ion % rates were found as 45.5 % Co, 34.12 % Cr, and 20.3 % Mo. It is understood that ion release of the Co was decreased significantly by surface coating. The passive film layer formed on the surface of the CoCrMo alloy that immersed into the simulated body fluid, contains a high amount of OH and CrO, and less amount of oxides of the Co. Like the other biometals, CoCrMo alloy has an active-passive surface when immersed into a liquid electrolytic medium. The oxide film that formed on the alloy repeats the partially dissolving and reprecipitation in this electrolyte environment. Metal ion release will be occurred when the rate of the reprecipitation is lower than of the partially dissolving rate.

It is thought that high ion release levels for the first 45 days is a result of this partially dissolving and reprecipitation process. Another factor that triggers the metal ion release is the macrophages that were developed from the body to protect itself from implanted strange things [13]. But, since this study performed in-vitro, it cannot be said the existence of an ion release mechanism like that.

### 3.3. SEM and EDX results

In order to determine the structures that could be formed on the surface of the immersed samples SEM investigation was performed and given in Fig. 7. It is expected to form Ca and P compounds on the CoCrMo alloy surface since it is a biocompatible material [13, 22].

A precipitation formed on the uncoated S0 sample's surface can be seen in Fig. 7 a. EDX analysis was performed in this area in order to understand the chemical composition of the structure formed on the sample's surface. As a result of the analysis, by weight percentage, 18.27 % Ca and 12.40 % P has found, and additionally, Na, Mg, K, and Cl elements were found at lower percentages as can be seen in Fig. 8. Although the alloy has a self-passivation ability on its surface, Ca-P precipitation has formed on the alloy surface as a result of both partially dissolve-reprecipitation mechanism and decreased corrosion resistance by increasingly metal ion release. It has been observed that in the surface coated samples, such formations occur only as spot deposits on the surface of the S2 coating. This spot deposition formed on the S2 surface can be seen in Fig. 7 c and EDX results of this site were given in Fig. 9. As a result of the EDX analysis performed on this point, it was found that by weight percentage 0.03 % Mg, 1.26 % O, and 0.08 % P and 0.1 % Ca elements were present. It is thought that the scratches that formed before the coating process and the pinhole defects that formed after the coating process most probably caused this.

### 4. CONCLUSIONS

Electrochemical corrosion behaviour and the metal ion release of the CrN/CrCN/TaN multilayered coated ASTM F-75 CoCrMo alloy was investigated. Electrochemical corrosion results showed that TaN multilayer coating of this alloy had increased corrosion resistance significantly. 4 and 8 multilayered coatings showed similar corrosion resistance and decreased corrosion rate 16 times.

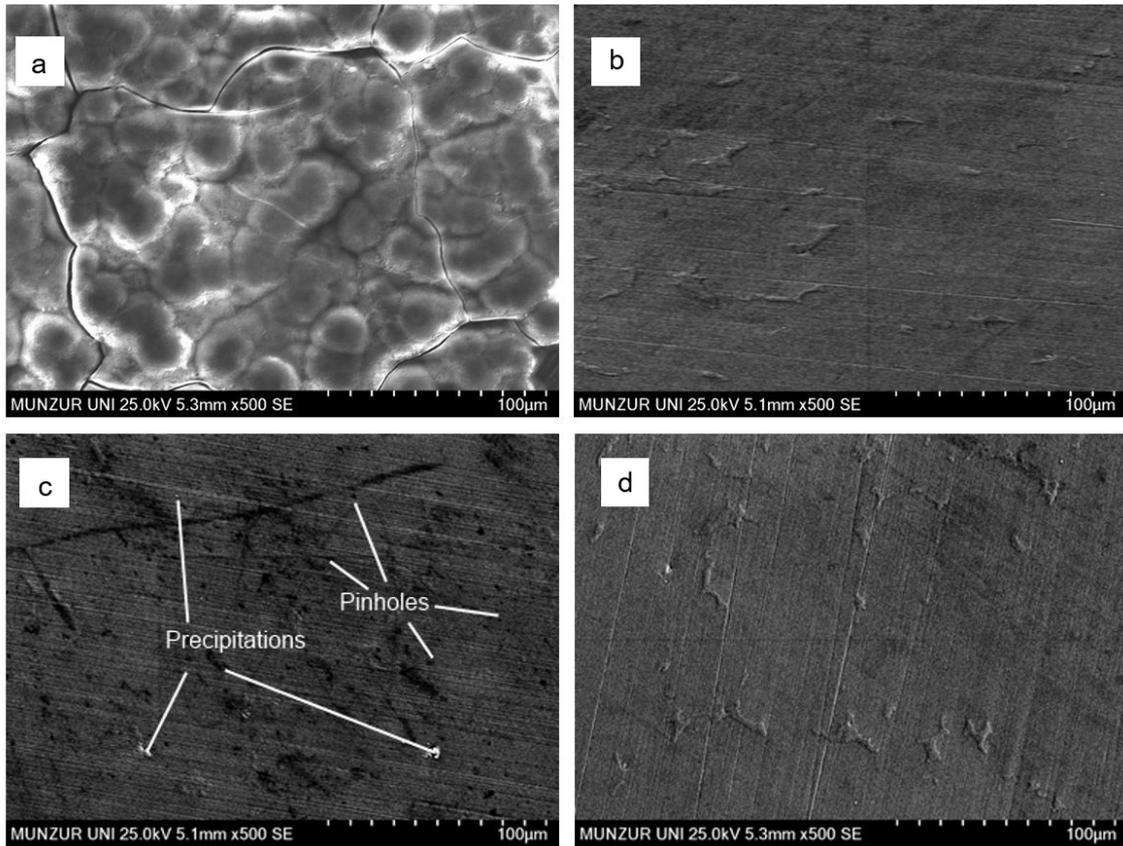


Fig. 7. SEM images of the immersed samples: a – as-polished; b – S1; c – S2; d – S3

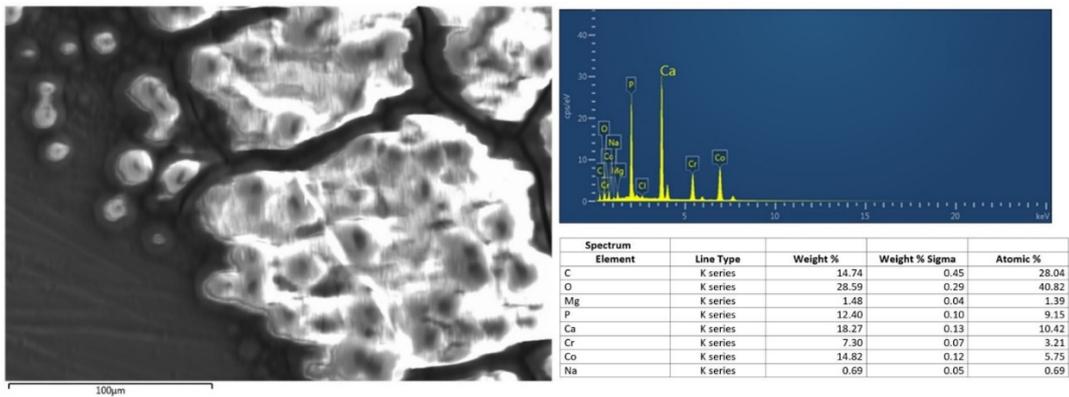


Fig. 8. EDX of the precipitation formed on the uncoated S0 sample surface

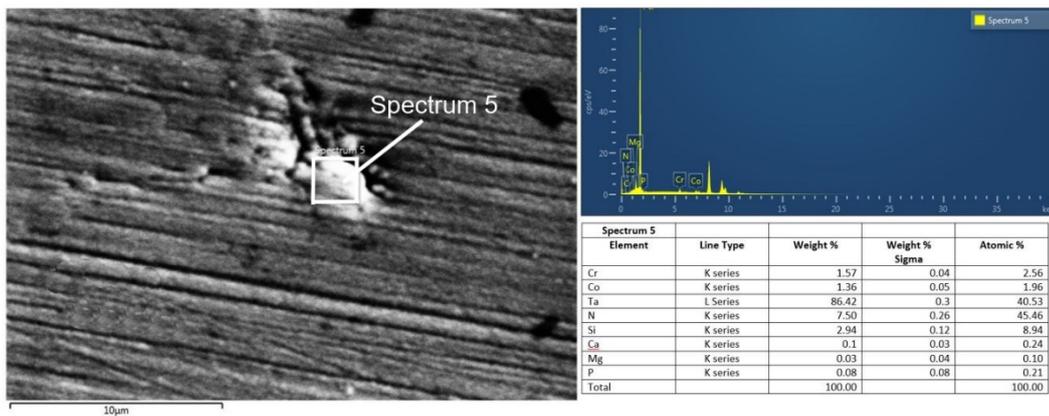


Fig. 9. EDX of the precipitation spot formed on the S2 sample surface

In the regards to protective efficiency, similar results were obtained and both coatings S2 and S3 were found 93 % efficient. It is believed that the presence of grooves on the coating surfaces of the scratches that occurred before the coating process of the samples and the pinhole defects that occurred during the coating prevented higher corrosion resistance. Therefore, it can be said that higher corrosion resistance can be achieved by more quality polishing and more quality coating process. All the multilayer coatings decreased the metal ion release from the alloy into the simulated body fluid significantly. Especially release of the Co element was decreased 52 times lower by multilayer coating. In this respect, it has been determined that the coatings show high protective properties in terms of metal ion release. It is concluded that 8 multilayer coating showed the best protective efficiency against the metal ion release. In this case, Since the 4 and 8 multilayered coatings have the same coating structure it can be said that the coating thickness is the most crucial factor to avoid the metal ion release.

When corrosion and metal ion release results are considered together, it is determined that multilayer coatings show high protective properties. 4 and 8 multilayered coatings showed better protective features that of two multi-layered S1 coating. But in terms of corrosion resistance, both showed similar protective efficiency. Considering the economic cost, it can be concluded that it will be sufficient to coating the alloy with 4 multi-layers.

In this study, the coatings were deposited on the flat surfaces. But it is known that artificial joint implants have curved surfaces. Additionally, the metal ion release levels was determined by static immersion test. Therefore, to improve the usability of this coating as an implant material, future studies should be focused on the coating of free-form shaped alloy and performing tribocorrosion tests in the simulated body fluids, so more realistic results can be achieved.

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