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CoCrW Alaşımının Yüzey Özelliklerinin İyileştirilmesi için ZIF-8 Sentezi ve Elektroforetik Biriktirme ile Kaplanması

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Türkçe Özet – Aşınma ve yüksek korozyon direncinin yanı sıra biyouyumluluk açısından da mükemmel özellikler sergileyen kobalt bazlı alaşımlar, diğer metalik implant malzemeleri arasında öne çıkmaktadır. Ancak döküm, dövme ve talaşlı imalat gibi geleneksel üretim yöntemleri, CoCr alaşımları gibi işlenmesi zor metalik özel parçaların üretimi için birçok endüstriyel uygulamada yetersiz kalmaktadır. Bu nedenle gelişen teknoloji ile birlikte toz metalurjisi ve eklemeli imalat gibi modern üretim yöntemlerine olan ilgi artmıştır. Lazer toz yatağı füzyonu (L-PBF) ile seçici lazer eritme (SLM), geleneksel imalat yöntemlerinin destekleyemediği karmaşık iç yapılara sahip malzemelerin üretimi için en çok tercih edilen eklemeli imalat yöntemlerinden biridir. Ayrıca diğer tüm metalik malzemeler gibi CoCr alaşımları da vücut içerisinde biyouyumluluk açısından inert özellikler sergilediğinden, bu alaşımlardan üretilen implantlarda osseointegrasyon, biyoaktivite, antibakteriyellik gibi davranışların olmaması implantın başarısını olumsuz yönde etkilemektedir. Bu açıdan bu malzemelerin yüzeylerine çeşitli yüzey işlemleri uygulanarak yüzey özellikleri iyileştirilebilmektedir. Bu anlamda, altıgen geometrisi ve gözenekli yapısıyla hidrofobik karakter sergileyen ZIF-8 metal organik çerçeve (Zn-Zeolitik imidazolat çerçeve) kaplama malzemesi, antibakteriyel ve biyouyumluluğunun yanı sıra kimyasal ve termal kararlılığıyla da dikkat çekmektedir. Bu çalışmada, ZIF-8 kaplama malzemesi ilk olarak $Zn(NO_3)_2$ ve 2-metilimidazol ile 50 °C'de metanol çözücüsü kullanılarak sentezlenmiştir. Ayrıca SLM yöntemi ile 10 x 10 x 2 mm^3 boyutlarında CoCrW alaşım numuneleri üretilmiştir. Sentezlenen ZIF-8 malzemesi elektroforetik biriktirme (EPD) yöntemi ile CoCrW numunelerinin yüzeyine kaplanmıştır. Sentez ve kaplama işlemlerinin ardından, hem ZIF-8 malzemesinin başarılı sentezini hem de ZIF-8 malzemesinin EPD yöntemiyle CoCrW numune yüzeylerine başarılı bir şekilde kaplandığını doğrulamak için yapısal (XRD) ve morfolojik (SEM) karakterizasyonlar gerçekleştirilmiştir.

Anahtar Kelimeler *– CoCrW, biyomalzeme, antibakteriyel, ZIF-8, metal organik çerçeveler*

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Synthesis and Coating with Electrophoretic Deposition of ZIF-8 for the Improvement of Surface Properties of CoCrW Alloy

Extended Abstract

Cobalt-based alloys, which exhibit excellent properties in terms of wear and high corrosion resistance as well as biocompatibility, stand out among other metallic implant materials. However, traditional production methods such as casting, forging and machining are insufficient in many industrial applications for the production of difficult-to-machine metallic special parts such as CoCr alloys. Therefore, with the developing technology, interest in modern production methods such as powder metallurgy and additive manufacturing has increased. Selective laser melting (SLM) with laser powder bed fusion (L-PBF) is one of the most preferred additive manufacturing methods for the production of materials with complex internal structures that traditional

manufacturing methods cannot support. In addition, since CoCr alloys, like all other metallic materials, exhibit inert properties in terms of biocompatibility within the body, the lack of behaviors such as osseointegration, bioactivity, antibacteriality in implants produced from these alloys negatively affects the success of the implant. In this respect, surface properties can be improved by applying various surface treatments to the surfaces of these materials. In this sense, ZIF-8 metal organic framework (Zn-Zeolitic imidazolate framework) coating material, which exhibits hydrophobic character with its hexagonal geometry and porous structure, is remarkable for its chemical and thermal stability as well as its antibacterial and biocompatibility. In this study, ZIF-8 coating material was first synthesized with $Zn(NO_3)_2$ and 2-methylimidazole using methanol solvent at 50 °C. In addition, CoCrW alloy samples with dimensions of 10 x 10 x 2 mm3 were produced by SLM method. The synthesized ZIF-8 material was coated on the surface of CoCrW samples by electrophoretic deposition (EPD) method. Following the synthesis and coating processes, structural (XRD) and morphological (SEM) characterizations were performed to confirm both the successful synthesis of ZIF-8 material and the successful coating of ZIF-8 material on CoCrW sample surfaces by EPD method.

Keywords *– CoCrW, biomaterial, antibacterial, ZIF-8, metal organic frameworks*

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I. INTRODUCTION

CoCrW alloys are frequently preferred in biomedical and aerospace applications due to their superior properties such as high temperature, wear and corrosion resistance [1]. In addition to these superior properties, other important reasons why CoCrW alloy is preferred as an implant material in biomedical applications in hip, knee and dental implants are its non-magnetic, radiopaque and MRI compatible properties [2]. However, some studies have shown that the release of Co^{2+}, Cr^{3+} and Cr^{6+} ions into the body from implants made of CoCr alloys may cause inflammatory effect as a result of hypersensitivity at the implant site [3]. In addition, since these alloys are frequently used in in-body implants, they are constantly exposed to corrosion and wear damage. On the other hand, studies show that most of the failures of metallic implant materials during application are due to bacterial invasion. Therefore, in addition to its superior properties, there are many problems to be solved, such as structural, chemical and biological incompatibilities that may lead to the rejection and failure of implants and prostheses made of CoCrW alloy by the body [4]. To overcome all these problems, the structural, chemical and biological surface properties of these structures have been investigated to improve their biocompatibility and antibacterial properties. Metal organic frameworks (MOFs) are three-dimensional porous polymeric materials in which multivalent organic ligands and metal ions come together to form a densely packed, periodic network structure [5]. MOFs are known for their high specific surface areas and porosity, which enable them to effectively store and release substances. Additionally, some MOFs can intelligently respond to pH changes, facilitating the controlled release of corrosion ions and drugs. This unique property makes them particularly promising for applications in antibacterial fields, where targeted delivery and release can enhance therapeutic efficacy [6], [7]. Zinc metal organic framework (ZIF-8), an important MOF, possesses chemical, thermal stability and hydrophobic characteristic and exhibits easy synthesis [8]. The size of ZIF-8 particles can be effectively controlled by adjusting several factors, including the molar ratio of Zn^{2+} to 2-methylimidazole, the choice of reaction solvent, the temperature of the reaction, and various other conditions. This flexibility allows for the production of ZIF-8 particles ranging from dozens of nanometers to hundreds of micrometers in size [9-11].

Furthermore, the rapid synthesis of ZIF-8 nanocrystals in aqueous system at room temperature has been developed, which can easily and environmentally friendly prepare thermally and chemically stable nanoscale ZIF-8. It is necessary to improve it by developing it with good biocompatibility [12]. Over the years, various coating techniques have been developed to enhance surface properties for biomedical applications. These techniques include immersion coating, thermal spraying, plasma phase coatings, layer-by-layer deposition, and electrochemical coatings. Each method offers distinct advantages for improving biocompatibility, corrosion resistance, and other surface characteristics crucial for medical devices and implants [13-15]. Electrophoretic deposition (EPD) offers several advantages, including low equipment cost, the ability to operate at room temperature, fast deposition times, the capability to coat porous or three-dimensional substrates, easy control over coating morphology and thickness, and the flexibility to use both aqueous and organic suspensions for coating substrates [16], [17]. In addition, the EPD method is a versatile coating technique that allows the control of process parameters such as the amount of material deposited on the base material, voltage, time, distance between electrodes or suspension properties such as concentration, pH, stability. With the EPD method, it is possible to coat a wide range of materials, including polymers, bioceramics, metals and their composites, on a suitable base material [16]. In this sense, ZIF-8, a metal organic polymer that has proven its antibacterial and osteogenic properties, has recently attracted attention [17]. Due to its excellent biocompatibility and relatively simple synthesis process, ZIF-8 has emerged as one of the most widely used MOFs in biomedical applications. Additionally, the release of Zn^{2+} ions from ZIF-8 has been shown to possess antimicrobial properties, providing long-lasting antibacterial effects [18], [19].

In a study by Ling et al. on AZ31 Mg alloy, Cu-doped ZIF-8 particles were solvothermally coated on the alloy surface and as a result of the study, they obtained a bioactive surface in terms of antibacterial, osteogenic and corrosion resistance [18]. Wen et al. coated titanium with ZIF-90, a type of Zn imidazolate framework, and as a result of the study, they found that the coating increased the antibacterial and osteogenic effect on Ti implants in orthopedic fields [19]. In the study by Tao et al., the implant material pure titanium was first anodized and the titanium oxide nanotubes formed on the surface were coated with cobalt MOF EPD method supplemented with OGP material that supports bone formation. The results of the study show that bone formation is significantly improved compared to pure titanium and MOFs will be an important step in the development of drug-assisted implants [20].

In order to increase the surface area of ZIF-8 particles and thus their surface activity, studies on smaller sized ZIF-8 are very valuable in this sense. Venna et al., synthesized ZIF-8 at room temperature using methanol. In this synthesis, they saw that if nano-sized ZIF-8 is to be synthesized, high nucleation rate and low crystallization rate are required [21]. Ordonez et al., summarized the general synthesis methods and basic applications of MOFs in their study and proved that they can be used in many applications. In their study on the synthesis of ZIF-8, it is aimed to reduce the particle size, control the crystal size and produce it in nano size. They used DMF as a solution for the synthesis of ZIF-8 and synthesized ZIF-8 with a BET surface area of 1300 m^2/g with a size of 50-150 nm at 140 ℃ [22]. In another study, Pan et al. synthesized ZIF-8 using DMF as a solution for 5 min at room temperature. It was reported that the particle size of ZIF-8 decreased as the $C_4H_6N_2/Zn(NO_3)_2$ ratio increased during this synthesis [23].

In this study, ZIF-8 particles of approximately 50-100 nm in size were chemically synthesized at 50 °C and structural and morphological analyses were carried out after synthesis. The synthesized ZIF-8 particles were coated with EPD by applying different potentials of 20 V and 40 V to CoCrW alloy with dimensions of 10 x 10 x 2 mm^3 produced by selective laser melting, an additive manufacturing method. After the coating process, structural and morphological analyses were performed and it was confirmed that the coating was successfully formed.

II. Materials and Method

Within the scope of the study, synthesis of ZIF-8, production of CoCrW samples by selective laser melting (SLM) method and coating of ZIF-8 particles on CoCrW by electrophoretic deposition were carried out. The processes carried out in the sub-headings are explained in detail.

A. ZIF-8 synthesis

The chemicals used for the synthesis of ZIF-8 were methanol, $Zn(NO_3)_2$, 2-methyl imidazole and the equipment were magnetic stirrer, centrifuge and oven. Firstly, 1 g of 2-methyl imidazole was added to 50 ml of methanol, which was previously heated to 50 °C and continuously stirred at 400 rpm in a magnetic stirrer. After obtaining a homogeneous solution, 1.4 g of $Zn(NO_3)_2$ in 25 ml of methanol was added dropwise into this solution [23]. A white solution was obtained and the solution was heated and stirred for 1 hour. After 1 hour, the heating was stopped and the solution was stirred for 6 hours. This white solution was centrifuged at 4000 rpm for 10 minutes and the white precipitate was subjected to dehumidification in an oven at 60 °C overnight.

B. Figures and Tables Fabrication of CoCrW samples by selective laser melting (SLM)

CoCrW specimens with dimensions of 10 x 10 x 2 mm^3 were produced using CoCrW powder according to ASTM F75 standard by selective laser melting, which is an additive manufacturing method that allows the production of specific, complex, difficult-to-machine materials with high melting temperatures, using the parameters given in Table 1. The manufacturings were performed using the CONCEPT LASER MLab Cusing device. Also, CoCrW alloy contain 58.85 wt% Co, 26.30 wt% Cr, 12.62 wt% W, 1.13 wt% Si and 1.1 wt% C [25].

Table 1. Parameters of manufacturing of CoCrW samples by SLM method

Parameters	Values
Laser Power	95 W
Plane scan speed	1500 mm/s
Contour scan speed	1500 mm/s
Layer thickness	30 μm

C. Electrophoretic deposition of ZIF-8

The synthesized ZIF-8 particles were coated on the produced samples by electrophoretic deposition (EPD), an electrochemical coating method.

For the coating process, 1 g/L ZIF-8 colloidal suspension was first prepared. For the suspension, 99 ml of deionized water and 1 ml of acetic acid was used as electrolyte [24], [25]. After stirring the suspension for 1 hour, the coating step was started. The coating process was carried out for 15 minutes by applying 20 V and 40 V voltages to examine the effect of voltage on the coating morphology. Figure 1 shows a schematic representation of the EPD method.

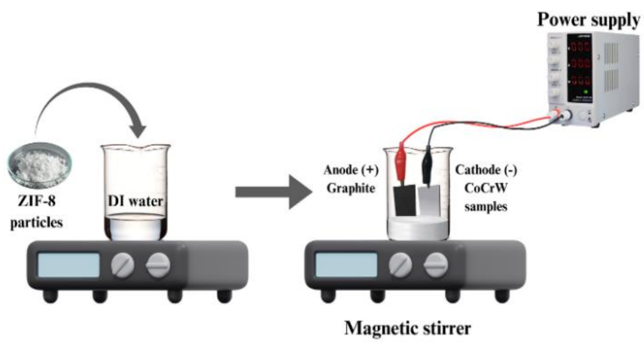

Fig. 1 Schematic representation of ZIF-8 coating by EPD method

After all procedures, structural and morphological analyses were performed.

III. Results

X-ray diffraction (XRD) and scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX) analyses were performed for structural and morphological investigations of the synthesized ZIF-8 particles, respectively. The counts-2θ graph obtained as a result of XRD analysis is given in Figure 2. According to the obtained XRD graph, the belrigin peaks confirm that the synthesis of ZIF-8 was successfully realized when compared with the literature [20-23].

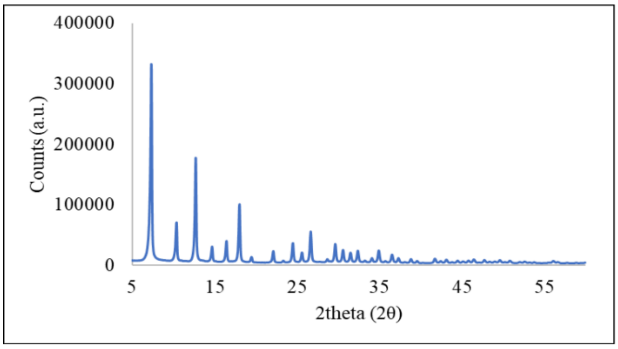

Fig. 2 XRD graph of synthesized ZIF-8 particles

Figure 3 shows the images of (a) SEM and (b) EDX analyses performed to investigate the morphological structure of ZIF-8 particles. The images confirm that porous ZIF-8 particles with a hexagonal crystal structure of approximately 50-100 nm in size were successfully synthesized. In addition, EDX results confirm that ZIF-8 particles contain Zn element densely in the desired direction.

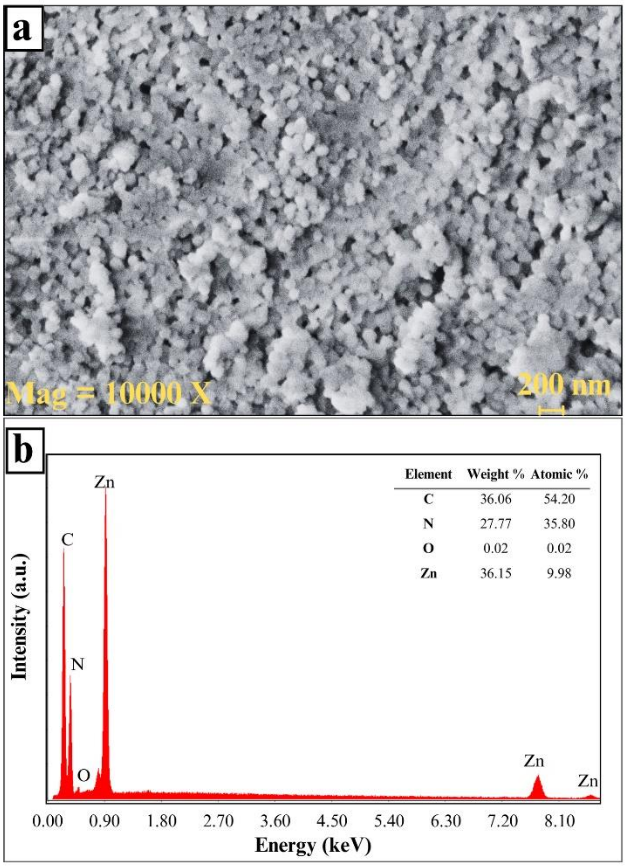

Fig. 3 (a) SEM image and (b) EDX analysis of the synthesized ZIF-8 particles

Figure 4 shows the XRD graph of CoCrW sample produced with SLM and it is confirmed by comparison with the literature that the prominent peaks belong to CoCrW alloy [24].

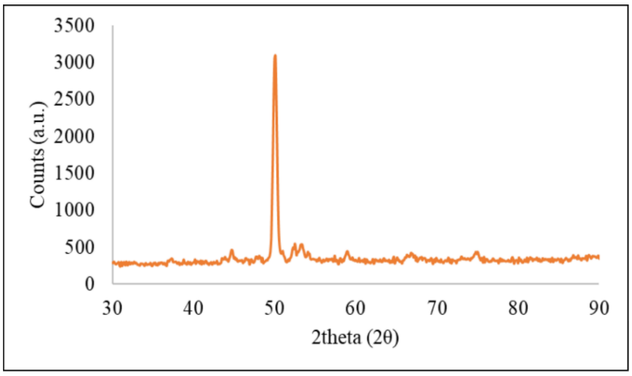

Fig. 4 XRD graph of CoCrW sample

Figure 5 shows SEM images of CoCrW specimens coated with ZIF-8 by EPD method at (a) untreated, (b) 20 V, (c) 40 V for 15 minutes. When the images are examined, it is confirmed that the coatings are realized compared to the untreated samples. When the images are examined, it is seen that the homogeneous deposition of the sample coated for 20 V - 15 minutes is more than the sample coated for 40 V - 15 minutes. This situation is considered to negatively affect the coating of ZIF-8 particles with EPD by applying more voltage.

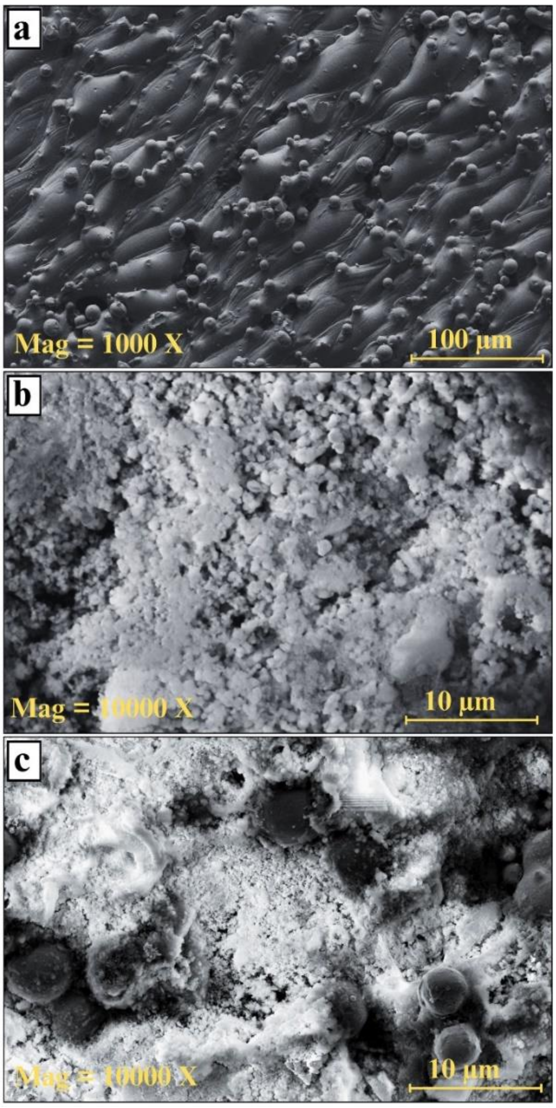

Fig. 5 SEM images of CoCrW samples: (a) untreated, ZIF-8 coated with EPD method applying for (b) 20 V-15 min, and (c) 40 V-15 min

Figure 6 shows SEM analysis and cross-sectional images of (a) 20 V and (b) 40 V coatings to evaluate the coating morphologies in terms of thickness. When the cross-section and surface images were evaluated, it was observed that the coating applied with a voltage of 20 V was both more homogeneous and thicker. Therefore, for optimum results, the coating condition of 20 V - 15 minutes is considered to be more suitable for the desired coating of ZIF-8 particles on CoCrW alloy.

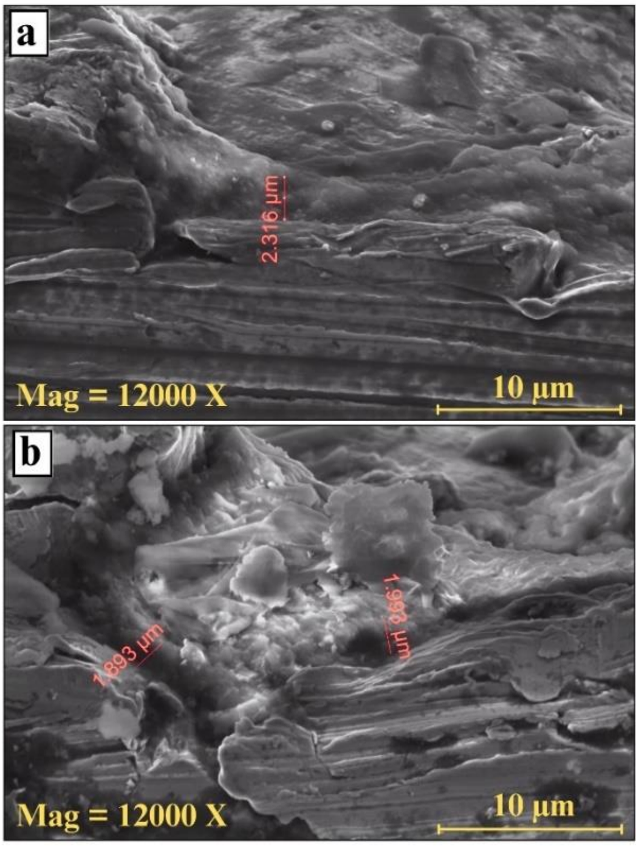

Fig. 6 SEM cross-section images of CoCrW samples: ZIF-8 coated with EPD method applying for (a) 20 V-15 min and (b) 40 V-15 min

Figure 7 shows the results of EDX analyzes of CoCrW samples (a) untreated, ZIF-8 coated with EPD method applying for (b) 20 V-15 min, and (c) 40 V-15 min. Compared to the untreated sample, Co, Cr and W elements as well as Zn, N, C elements due to ZIF-8 coating were found in the 20 V-15 min and 40 V-15 min coated samples. This confirms that the coating was successfully realized. In addition, when the analyzes are examined, the fact that the Zn, C and N ratios in the 20 V-15 min coating are higher than the 40 V-15 min coated sample indicates that the application of 20 V voltage, such as cross-sectional SEM images in terms of coating parameter, will provide a more homogeneous and thicker film.

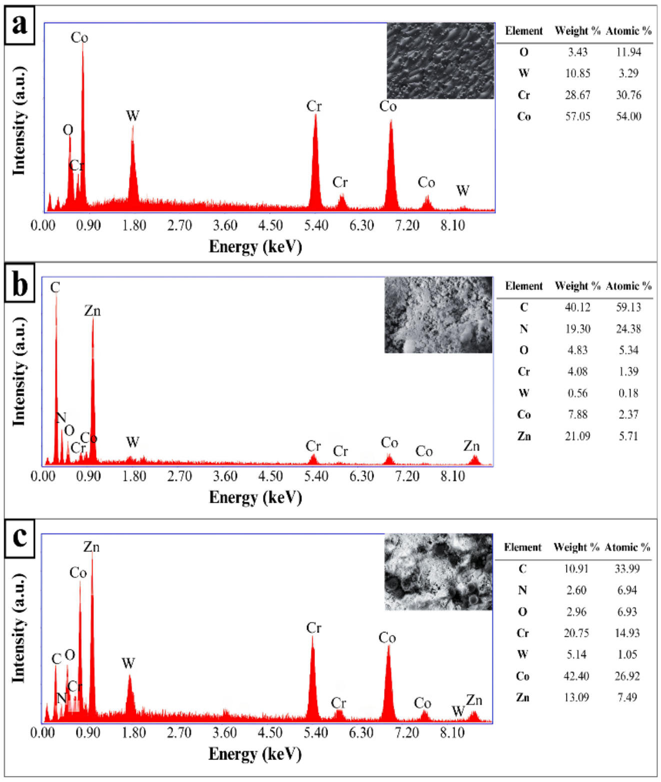

Fig. 7 EDX analyzes of CoCrW samples: (a) untreated, ZIF-8 coated with EPD method applying for (b) 20 V-15 min, and (c) 40 V-15 min

IV. DISCUSSION

When the XRD graph obtained as a result of ZIF-8 synthesis was evaluated, similar results were encountered with the literature. In addition, morphological analysis of ZIF-8 particles synthesized by SEM analysis was performed and compared with the literature. As a result of the study, XRD and SEM analyses confirm that the synthesis of ZIF-8 at 50 °C was successfully synthesized at a smaller grain size than the ZIF-8 particles synthesized at room temperature.

After synthesis, ZIF-8 particles were coated on CoCrW samples produced with SLM by EPD method at different stress parameters. The surface and cross-sectional morphological analysis after the coating process confirms that the coating was successful.

V. CONCLUSION

The results of the study are summarized as follows:

- ✓ ZIF-8 particles with a size of about 50 nm were homogeneously synthesized at 50 °C compared to ZIF-8 particles synthesized at room temperature.
- ✓ CoCrW samples can be easily produced in 10 x 10 x 2 m^3 dimensions with the additive manufacturing method SLM.
- ✓ The synthesized nano-sized ZIF-8 particles were successfully coated on CoCrW samples by electrophoretic deposition method by applying different voltage parameters.
- ✓ 20 V - 15 minutes coating parameter was evaluated as the optimum parameter as a result of SEM analysis.

This study is a preliminary study and will be subjected to corrosion and abrasion tests for in-vitro analysis after the coating parameters are made more suitable. As a result of this study, the coating of ZIF-8 particles on CoCrW alloy by EPD method was confirmed.

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Authors' Contributions

The authors' contributions to the paper are equal.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The authors declare that this study complies with Research and Publication Ethics

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