



# Synthesis of CoCrFeMnNi High Entropy Alloy Thin Films by Pulse Electrodeposition: Part 1: Effect of Pulse Electrodeposition Parameters

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## Abstract

CoCrFeMnNi high entropy alloy (HEAs) thin films were prepared using the pulse electrodeposition method. The films were co-deposited in an electrolyte based on an N,N-dimethylformamide—acetonitrile (CH<sub>3</sub>CN) organic system containing Co, Cr, Fe, Mn, and Ni chloride cations using the pulse electrodeposition method at frequencies of 2500 and 5000 Hz as well as duty cycles of 50% and 60%. The composition and morphology of the resulting thin films were studied. The energy-dispersive X-ray spectroscopy analysis revealed that all five elements were successfully co-deposited. The calculated entropy of mixing in different conditions ranged between 11.86 and 12.46 J K<sup>-1</sup> mol<sup>-1</sup> for a duty cycle of 60% in frequencies of 2500 and 5000 Hz, respectively, this indicates that the resulting materials are HEAs. The scanning electron microscopy investigations revealed that the prepared films at a duty cycle of 50% in frequencies of 2500 and 5000 Hz exhibit an inhomogeneous morphology with crystal clusters measuring between 330 and 399 nm. The grazing incidence X-ray diffraction patterns indicated that the as-deposited CoCrFeMnNi thin films consisted of a single face-centered-cubic structure.

**Keywords** High entropy alloys · Solid solution · Organic system · Pulse electrodeposition · Grazing incidence X-ray diffraction

## 1 Introduction

High entropy alloys (HEAs) are new types of metallic materials, which unlike traditional alloys, are not based on the main element, but instead, present a multi-component feature. HEAs consist of five or more elements in either equimolar or near-equimolar proportion [1–3]. Solid solutions composed of many elements will tend to be more stable due to their large mixing entropies, which can significantly diminish the free energy of the system and make a random solid solution more stable than the ordered phases [4, 5]. Recently, intensive research efforts have been dedicated to developing HEA systems with simple crystal structures. Furthermore, the main aim of these investigations was attaining

properties, such as good corrosion resistance, high strength, high hardness, and good toughness. In this regard, the selection of a suitable HEA system is of great importance.

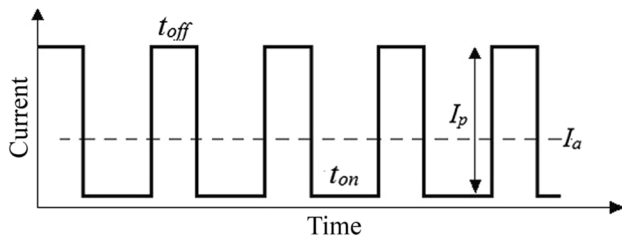
Most studied high entropy alloys were produced through arc melting. Various alloys were investigated as potential functional coatings for different applications that synthesized mainly through physical deposition methods such as magnetron sputtering [6–9]. Electrodeposition is one of the most efficient and affordable techniques for obtaining new materials with tailored properties [10–13].

The electrodeposition of alloy coatings can be carried out through two different conventional methods: direct current (DC) plating (or constant potential) and pulse plating. In pulse plating, in addition to plating current density or voltage, other three additional parameters can be varied independently to control the film quality (peak current density, on- and off-times, and duty cycle) [14]. The variation of these parameters could be used to control the composition and microstructure of the deposits [15]. Understanding the pulse potential is possible by several parameters, such as the reference voltage ( $V_R$ ), the peak voltage ( $V_p$ ), the peak-to-peak voltage ( $V_{p,p}$ ), the on-time ( $t_{on}$ ) and off-time ( $t_{off}$ ), the pulse frequency ( $f$ ), and the

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**Fig. 1** Description of the pulse potential

duty cycle ( $\theta$ ), which are shown in Fig. 1. Such parameters can determine changes in the charge and mass transfer processes; and thus, influence the morphology, composition, and properties of the resulting coating significantly [14–16].

The corrosion behavior of Fe-based alloys, such as Co–Fe, Ni–Co, and Ni–Fe, has been widely studied in recent years. In higher chromium content, it was observed that Fe–Ni–Cr-based deposited alloys are nobler and exhibit a wide passivation range [17, 18]. Fonte et al. [19] and Kwon et al. [20] reported that strength, flexibility, and corrosion resistance of coatings could be significantly improved by the addition of transition metal ions, such as Fe, Ni, Mn, and Co [21, 22]. The main problem with chromium alloy coatings is their proneness to cracking. During the crystallization of chromium on the cathode surface, the hexagonal chromium hydride ( $\text{CrH}_x$ ) is also formed. The alloy's hydrides are not stable and decompose into metal and hydrogen gas during the subsequent precipitation of the alloy. Thus, by changing its lattice structure from hexagonal to BCC, it leads to the apparition of cracks in the structure of the coating. Also,  $\text{H}_2$  trapping in the coating structure would lead to blisters in the coating [23]. Yeh et al. [24] have prepared various HEAs containing Al, Co, Cr, Cu, Fe, Ni, Ti, and V, which exhibit remarkable oxidation and corrosion resistance. Further, Ye et al. [19] have studied corrosion resistant CoCrFeMnNi HEAs.

In the present work, the major goal was to obtain a thin film of a high entropy alloy with the composition of Co–Cr–Fe–Mn–Ni using pulse electrochemical deposition. According to studies, the alloy system is expected to have decent corrosion resistance and promising potential for coating applications in the field of corrosion protection. To the best of our knowledge, no reports were made to this day concerning the synthesis of such alloys via the pulse electrodeposition method. In the first part of this research, the effect of pulse deposition parameters on the morphology of electrodeposited CoCrFeMnNi high entropy alloy thin films was investigated. In the second part, the effect of HEAs different morphologies and compositions on the corrosion resistance of the resulting coatings will be presented.

**Table 1** Chemical composition of the electrolyte

$\text{CoCl}_2$ ( $\text{mol L}^{-1}$ )	$\text{CrCl}_3$ ( $\text{mol L}^{-1}$ )	$\text{FeCl}_2$ ( $\text{mol L}^{-1}$ )	$\text{MnCl}_2$ ( $\text{mol L}^{-1}$ )	$\text{NiCl}_2$ ( $\text{mol L}^{-1}$ )
0.01	0.013	0.01	0.0103	0.001

## 2 Experimental

The pulse electrodeposition of the high entropy alloys and the electrochemical studies were carried out at 298 K via an LFG-1300s function generator. The HEA thin films were deposited on copper substrates (99.98% copper discs, 10 mm in diameter, and 0.4 mm in thickness) by pulse electrodeposition in an electrolyte based on a DMF– $\text{CH}_3\text{CN}$  (with a 4:1 volume fraction) organic system, which contained  $\text{FeCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{LiClO}_4$ . The electrolyte composition is given in Table 1. The given composition was determined as follows: first of all, the equivalent molar ratio of different components was tested; and the composition of the resulting coating was studied via the energy-dispersive X-ray spectroscopy (EDS). Next, according to the EDS results, the composition of the electrolyte was adjusted so that the near-equi-molar composition can be achieved in the coating.

Prior to the plating process, the Cu substrates were pre-treated by polishing with abrasive emery papers of 120–1000 granulations, followed by electrochemical etching in an  $\text{H}_3\text{PO}_4$  (30%) solution and rinsing with double distilled water.

In the pulse electrodeposition, the on and off-potentials were of  $-9$  V and  $1$  V, respectively. Besides, duty cycles of 50 and 60%, as well as frequencies of 2500 and 5000 Hz were applied. The morphology and the chemical composition of the high entropy alloy thin films were analyzed via a Philips-XL30 scanning electron microscope (SEM) equipped with a Seron-AIS2300C energy dispersive X-ray spectrometer. The crystal structure of the samples was determined by grazing incidence X-ray diffractometry (GXR) using an Asenware AW-DX300 X-ray diffractometer (Cu anode, 40 kV, 30 mA, Step Time: 1 s, Step size: 0.05). The obtained data were processed by the X'Pert HighScore Plus software. The Nelson–Riley function [24, 25] was used to calculate the lattice parameter and its strain. The crystallite size was calculated using the width of the (111) peak at their half height through the Scherrer's equation [26, 27].

## 3 Results and Discussion

### 3.1 Effect of Pulse Potential on the Coating Composition

The EDS results confirm that the deposits are composed of five elements. The effect of the frequency and duty cycle

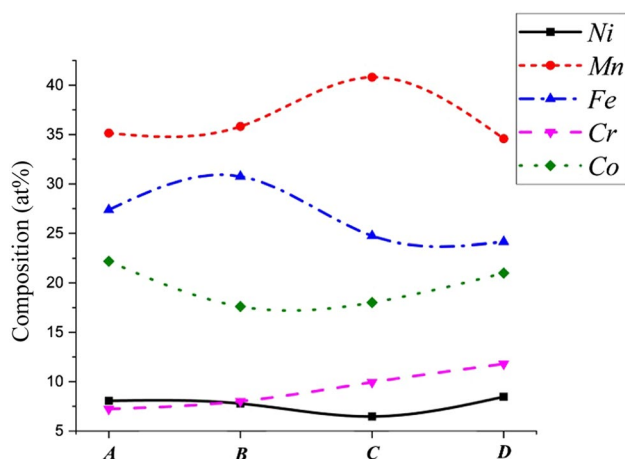
(in values of 2500 and 5000 Hz as well as at two duty cycle values of 50% and 60%) on the composition of the CoCrFeMnNi alloy thin films were studied. It was observed that when the constant frequency of 5000 Hz has been used, decreasing the duty cycle decrease has resulted in increasing the Fe content from 24.15% to 30.76%, and when the frequency of 2500 Hz has been applied, the Fe percentage in the deposit increased from 24.75% to 27.38%. Also, the Cr content has increased from 7.23% to 9.94% (for a frequency of 2500 Hz) and from 8.01% to 11.80% (for a frequency of 5000 Hz) with increasing the duty cycle. The results of the duty cycle variation effect (in the range of 50%–60%), for the two frequency values (2500 Hz and 5000 Hz), on the alloy composition is presented in Table 2 and Fig. 2.

Copper (substrate) was also detected in some samples because of the low coating thickness. It was observed that depending on the percentage of Cu in the EDS results, the thickness of the coatings deposited in a period of 1 h varied as follows:

$$\text{(Maximum thickness) } 2500 \text{ Hz-}\%60 > 5000 \text{ Hz-}\%60 > 2500 \text{ Hz-}\%50 > 5000 \text{ Hz-}\%50 \text{ (Minimum thickness)}$$

In the present study, it is observed that after increasing the duty cycle from 50 to 60% and reducing the frequency from 5000 to 2500 Hz, the thickness of the films increased. According to the results of Saravanan's study, increasing the duty cycle and reducing the frequency during pulse plating leads to an increase of the coating thickness [28]. Jiang also observed that increasing the frequency reduces the thickness of the deposited coatings [29].

The molar entropies of mixing reached a maximum value of  $12.46 \text{ J K}^{-1} \text{ mol}^{-1}$  for the thin films deposited using the frequency of 5000 Hz and the duty cycle of 60%. According to Soare et al. [10] although the elements were present in near-equi-molar ratios in the initial electrolyte solution after the electrochemical deposition at constant potentials of  $-1.5$  to  $-2.7 \text{ V}$ , the composition of the resulting thin films was not equi-molar. The mixing entropy for the AlCrFeMnNi alloy varied from  $8.8 \text{ J K}^{-1} \text{ mol}^{-1}$  (for a potential of  $-1.5 \text{ V}$ ) to  $9.65 \text{ J K}^{-1} \text{ mol}^{-1}$  (for a potential of  $-2.5 \text{ V}$ ), and for the AlCrCuFeMnNi one the values varied from  $7.1 \text{ J K}^{-1} \text{ mol}^{-1}$  (for a potential of  $-1.5 \text{ V}$ )



**Fig. 2** Variation of the chemical composition of the coatings depending on the conditions of pulse electrodeposition

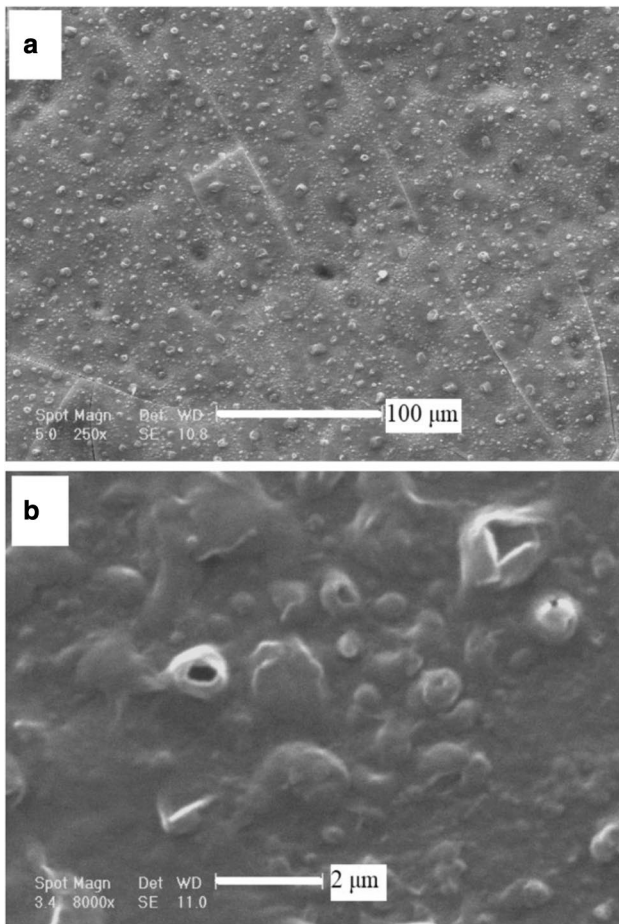
to  $10.24 \text{ J K}^{-1} \text{ mol}^{-1}$  (for a potential of  $-2.5 \text{ V}$ ). These values are higher than the minimum entropy required for the formation of high entropy alloys. Also, Yao et al. [5] investigated the formation of Bi-Fe-Co-Ni-Mn alloys deposited at  $-2 \text{ V}$  and obtained high entropy alloys with near-equi-molar ratios but with entropy in the range of  $11.8$  to  $13.3 \text{ J K}^{-1} \text{ mol}^{-1}$ . According to the determined compositions for the electrodeposited CoCrFeMnNi alloy and the calculations (as shown in Table 2), the entropy of mixing in different coating conditions ranged from  $11.86$  to  $12.46 \text{ J K}^{-1} \text{ mol}^{-1}$ , which indicates the resulting material is a high entropy alloy.

#### 4 Effect of the Pulse Potential on Coating Morphology

Figures 3 and 4 present the SEM micrographs of the CoCrFeMnNi thin films samples A and B in Table 2. The surface of the deposits showed an inhomogeneous morphology with crystal clusters of sizes between 370 and 450 nm. Figures 5 and 6 present the SEM micrographs of samples C and D. The surface of the films is protuberant and homogeneous without obvious cracks. The particles are agglomerated and compact. The average sizes of the inhomogeneities are of approximately 200 and 140 nm, respectively.

**Table 2** The compositions and the molar entropies of mixing of the CoCrFeMnNi films, depending on the different parameters of pulse electrodeposition, for 1 h

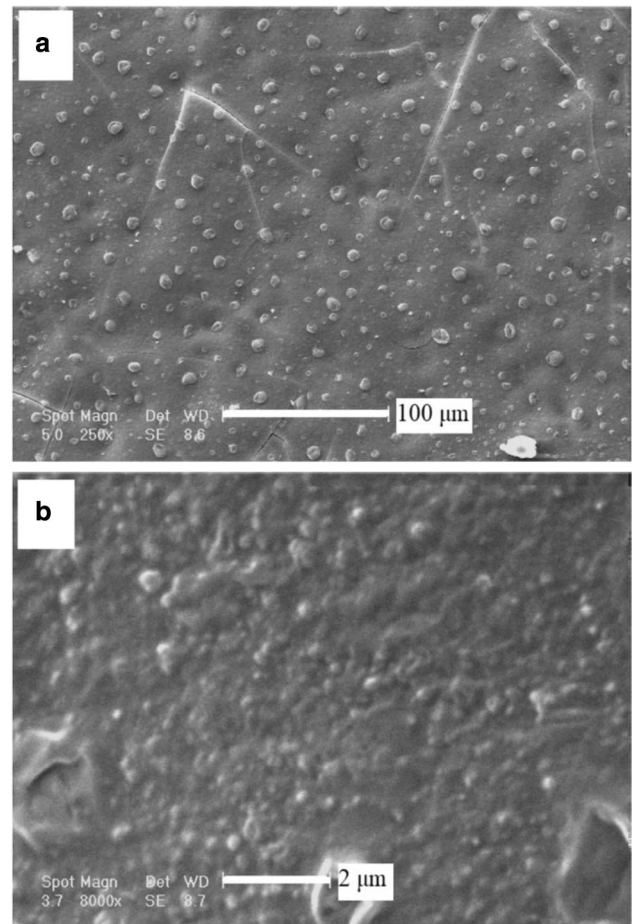
Element (at%)/condition	Co	Cr	Fe	Mn	Ni	$\Delta S_{\text{mix}}$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
A 2500 Hz/50%	22.20	7.23	27.38	35.15	8.06	12.04
B 5000 Hz/50%	17.62	8.01	30.76	35.83	7.78	11.996
C 2500 Hz/60%	18.02	9.94	24.75	40.81	6.47	11.86
D 5000 Hz/60%	21.00	11.80	24.15	34.58	8.47	12.46



**Fig. 3** Scanning electron micrographs of the CoCrFeMnNi film deposited at a 2500 Hz frequency and a 50% duty cycle, **a** at 250 $\times$  and **b** at 8000 $\times$  magnification

## 5 The Effect of Pulse Parameters on Crystallite Size

The crystallite size of the alloys was calculated through Scherrer's equation and is shown in Table 3. According to the results, changes in the crystallite size can be observed with the change in the duty cycle and frequency of pulse electrodeposition (Fig. 7). It can be noticed that with increasing the duty cycle from 50 to 60%, the crystallite size decreased. In a study by Sajadnejad et al. on the preparation of nickel coatings through the pulse method, it was observed that with increasing the duty cycle (10 to 75%), the crystallite size also increased. It was also observed that the crystallite size increased by varying the frequency from 10 to 50 Hz; however, by changing the frequency from 50 to 100 Hz, the crystallite size decreased [30]. In the present study, it can be observed that by frequency increase from 2500 to 5000 Hz in two duty cycles of 50 and 60%, the crystallite sized increases and decreases,



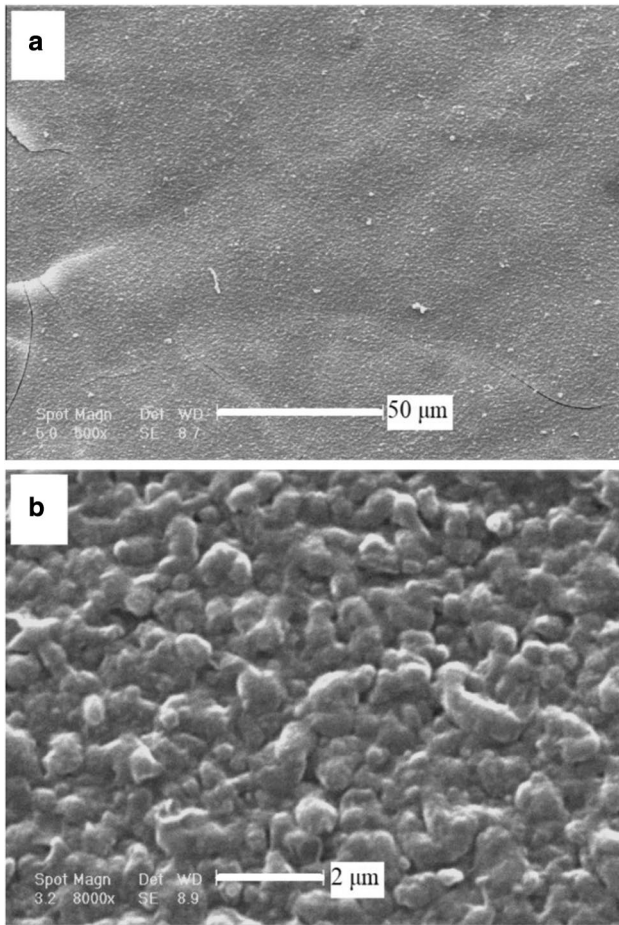
**Fig. 4** Scanning electron micrographs of the CoCrFeMnNi film deposited at a 5000 Hz frequency and a 50% duty cycle, **a** at 250 $\times$  and **b** at 8000 $\times$  magnification

respectively. In another study by Jiang et al. on the preparation of Ni-Co / ZrO<sub>2</sub> composite coatings, it was observed that the average crystallinity obtained at a frequency of 100 kHz was lower than the one achieved at a frequency of 140 kHz [29].

## 6 The Effect of Pulse Parameters on Coating Morphology

According to the results of Bidmeshki et al. [31] and comparison with the results obtained in this study, it is observed that the coating is formed as a single phase, and there is no evidence for the presence of secondary phases and intermediate compounds in the coatings. These results are consistent with the identification of a single-phase FCC structure in the XRD results in Sect. 3.3.

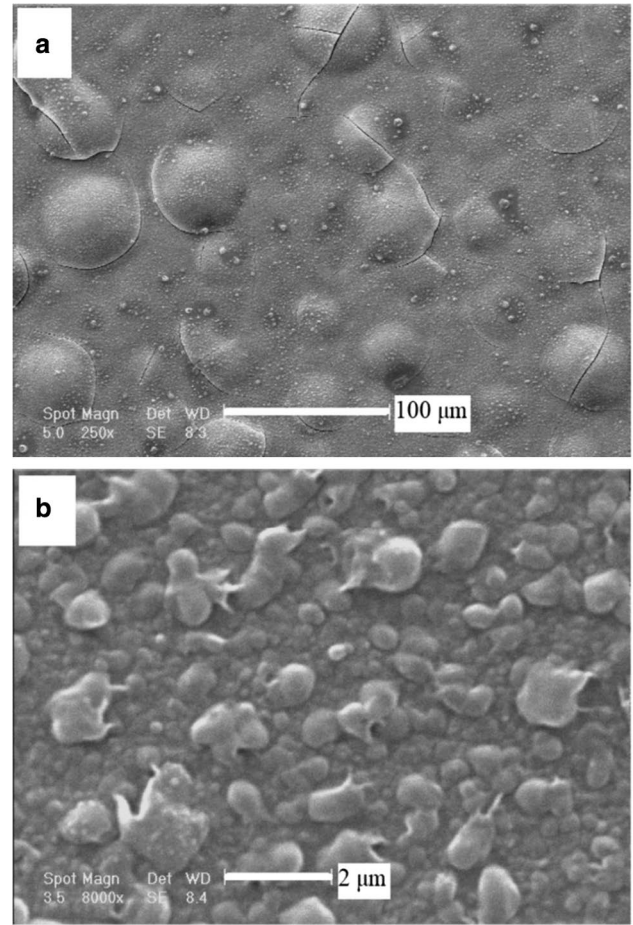
As hinted in the introduction, the main problem with chromium alloy coatings is their proneness to cracking; whereas, the pulse electrodeposition use would lead



**Fig. 5** Scanning electron micrographs of the CoCrFeMnNi film deposited at a 2500 Hz frequency and a 60% duty cycle, **a** at 500 $\times$  and **b** at 8000 $\times$  magnification

to  $\text{CrH}_x$  decomposition in the off-time mode, and finally reduction of cracks due to the presence of chromium in the structure. In other words, chromium hydride decomposes during the off-time; hydrogen is released and reduces the chromium-induced cracks. In a study by Adelkhani et al., it was observed that reducing the duty cycle and increasing the rest time resulted in the reduction of the cracks in the coating surface [23]. In the present study, according to the BSE micrographs of the coating surface, it was observed that reducing the duty cycle from 60 to 50% at both 2500 and 5000 Hz frequencies lead to the mitigation of cracks in the coating.

In a study concerning the effect of the duty cycle on pulse electrodeposition, it has been observed that the overpotential at the lowest duty cycle is theoretically lower than the higher duty cycles and DC plating. This would reduce the hydrogen and oxygen evolution rates [32]. In Figs. 3, 4, 5 and 6, it can be seen that; by decreasing the hydrogen reactivity in higher duty cycles, the formation of chromium hydrides was reduced; this fact eventually leads to a reduction of cracks



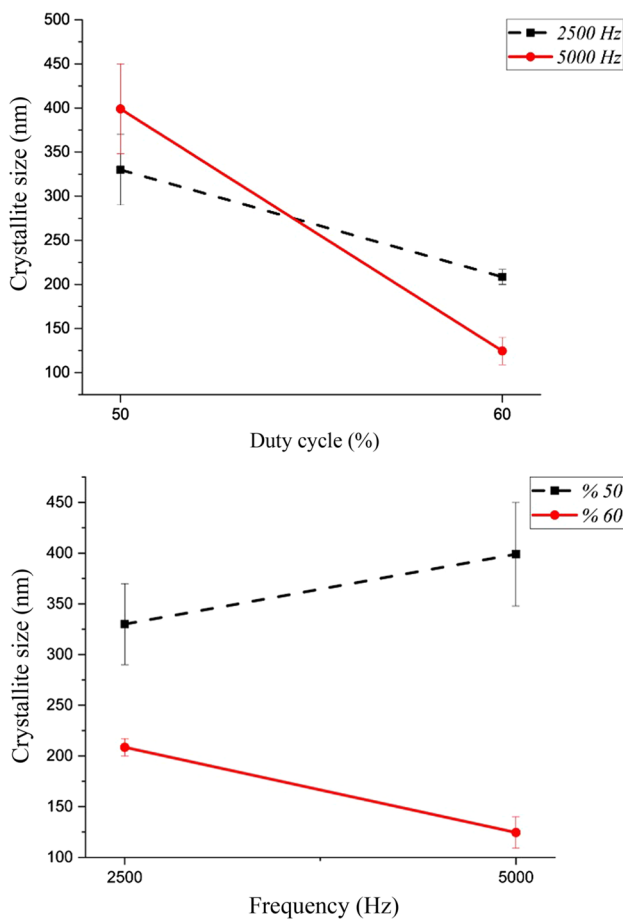
**Fig. 6** Scanning electron micrographs of the CoCrFeMnNi film deposited at a 5000 Hz frequency and a 60% duty cycle, **a** at 250 $\times$  and **b** at 8000 $\times$  magnification

**Table 3** Lattice parameter and lattice strain of samples electrodeposited in different conditions

Condition	A	B	C	D
Lattice parameter [a (Å)]	3.60	3.61	3.61	3.60
Lattice strain [ε (%)]	0.321	0.267	0.428	0.854
Crystallite size (nm)	290–370	348–450	200–217	109–140

and hydrogen blisters in the coating. In addition, the chromium content of the resulting coating alloy was increased as well.

In a further study by Jiang et al. on Ni-Co /  $\text{ZrO}_2$  coatings at frequencies from 20 to 140 kHz, it was observed that the increase in frequency led to a change in the morphology of the coating from rough, rugged, and porous structures to smooth and compact ones [31]. In another study by Chung, it was noted that increasing the frequency due to the increased nucleation rate on the cathode surface led to a decrease in surface roughness and uniformity [33]. In the present study,



**Fig. 7** Variation of crystallite size depending on the duty cycle and applied pulse frequency

it is also observed that with increasing the frequency from 2500 to 5000 Hz in a constant duty cycle, the coating structure is smoother and more compact; and also the particles are finer. Further, the porosity has been decreased on the surface of the coating.

Chung et al., in their research on the generation of NiCo coatings in a frequency range of 10 to 100 Hz, showed that increasing the frequency and reducing the working cycle led to a decrease in surface roughness [28]. By examining and comparing coating micrographs at two constant frequencies of 2500 and 5000 Hz, it can be seen that by reducing the duty cycle from 60 to 50% due to longer rest periods, the nucleation rate has been increased, and the growth of nuclei has been reduced so that a fine-grained, compact, and smooth structure has been produced.

Wu et al., in their research on MnCo coating, showed that increasing the on-time and the duty cycle, have increased the grain size and the porosity in the structure; and also, increasing off-time and reducing the duty cycle have led to fine and spherical grained, as well as more compact and regular structure [15]. In their study, it is also observed that with

increasing grain size in the lower duty cycle, the spherical particles have been produced; and thus, it would lead to a less dense structure with more porosity.

In another study by Tury et al. on producing the Ni-Co film by pulse electroplating method, it was observed that by decreasing the current density, increasing the off-time, and reducing the duty cycle, a smooth, compact, and homogeneous coating with a small particle size would be created. By reducing the off-time and increasing the duty cycle, the surface would be rough with angular particles and a cauliflower-like structure. By increasing the current density at lower off-time, the seeds are fibrous [34]. In the present study, it can be seen that in the duty cycle of 60%, the particles are well-distinguished and angular; however, in a duty cycle of 50%, the coating is more compact.

## 7 The Effect of Pulse Parameters on the Coating Composition

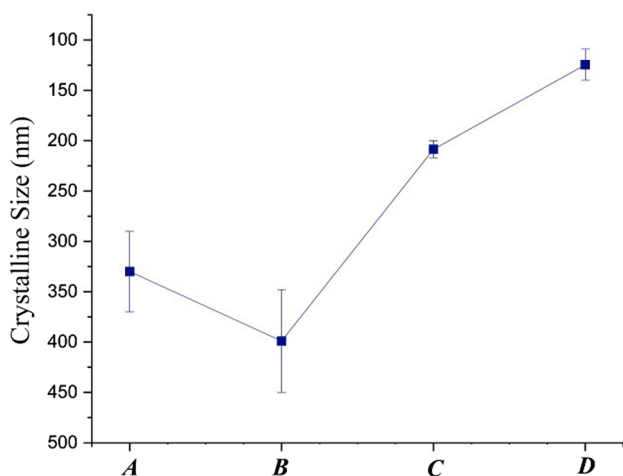
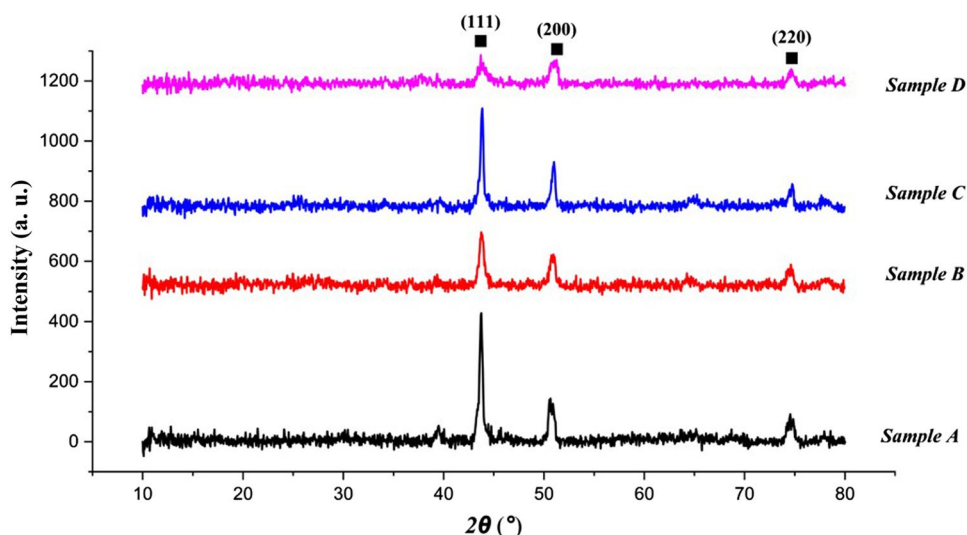
In the sample coated at a frequency of 2500 Hz and a duty cycle of 50%, there is a maximum amount of precipitated cobalt, which resulted in smaller grain size and granulated structure in the coating. In studies on the alloy coatings, it has been shown that during precipitation, nickel and cobalt ions react with  $\text{OH}^-$  and form metal mono-hydroxides, which are absorbed by the surface. Therefore, due to the greater adsorption of  $\text{Co}(\text{OH})^+$ , the amount of cobalt in the alloy increases and leads to the formation of bigger grains and a fibril (Co-like) structure [35]. In a study by Tury et al. on the formation of Ni-Co alloy, it was observed that the cobalt hydroxide creation during off-time, prevented the growth as well as diffusion of nickel and cobalt nuclei, and finally contributed to finding the coating structure [34].

Pereira et al. investigated the development of NiFeCu alloy coating. In their study, the size of the particles in the coating was increased by decreasing the Fe concentration deposited in the coating [36]. In the current study, according to the results of EDS analysis in Table 2, it is noted that the amount of deposited Fe in samples with a duty cycle of 60%, was lower at both frequencies of 2500 and 5000 Hz. Also, according to Figs. 5 and 6, the greater growths of particles are visible.

## 8 The Structure of the as-Deposited Film

The XRD patterns of the deposited films on the Cu substrates were examined within a range of  $2\theta = 10^\circ\text{--}80^\circ$  and are given in Fig. 8. No diffraction peaks can be found for the as-deposited films, except the simple face-centered-cubic (FCC) solid-solution structure. After simulation by X'Pert HighScore Plus software, the lattice constant  $a = 3.6 \text{ \AA}$  can be calculated from the XRD results via Bragg's law (Fig. 8).

**Fig. 8** XRD patterns of the CoCrFeMnNi films deposited at different pulse electrodeposition parameters



**Fig. 9** Variation of the crystallite size depending on the pulse electrodeposition parameters

Variation of the crystallite size depending on the pulse electrodeposition parameters, as presented in Table 3, is given in Fig. 9. The absence of complex, ordered, and intermetallic phases can be attributed to the lower free energy relating to the effect of the mixing high entropy. According to Zhou et al. [3], the high entropy of mixing can reduce the free energy remarkably and make a random solid solution more stable than the ordered phases.

## 9 Conclusions

The use of the pulse electrochemical deposition method has successfully led to the synthesis of CoCrFeMnNi high entropy alloy thin films. It was noted that the surface

morphology of the films and the composition of the HEA alloy depended on the various applied pulse parameters, such as duty cycle and frequency. The structure and surface morphology of the CoCrFeMnNi electrodeposited coatings were reported in this work for the first time. A single solid solution structure of face-centered cubic (FCC) type was identified by the XRD analysis. It can be concluded that applying the strategy of producing high entropy alloys via electrodeposition may provide a promising approach to the design of new metallic materials with remarkable properties.

## Compliance with Ethical Standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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