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The feasibility of Producing CoCrFeMnNi High Entropy Alloy Coatings by Electrochemical Deposition Method and its Characterization

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1. Introduction

High entropy alloys (HEAs) are new types of metallic materials, which unlike traditional alloys, are not based on the main element, but present a multi-component feature. HEAs comprise five or more elements in either equi-molar or near-equi-molar proportion. Solid solutions composed of many elements will be more stable because of 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. Recently, intensive research efforts have been dedicated to developing HEA systems with simple crystal structures. The main aim of these investigations has been 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 studies have produced high entropy alloys 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. Electrodeposition is one of the most efficient and affordable techniques for obtaining new materials with tailored properties.

Types of electrolytes used in electrochemical sedimentation processes include liquid solutions, fused salts, ionic liquids, and ionically conducting solids. Non-aqueous solvents, because of their features such as high electrical conductivity, good chemical and thermal stability, wide operating temperature range and the wide electrochemical window that prevents the regeneration of H_2 gas and hydroxide, are the best alternatives to deposit the metallic coatings such as HEAs. In a study, BiFeCoNiMn, MgMnFeCoNiGd and TmFeCoNiMn HEA thin films were synthesized using electrochemical deposition in DMF (or DMSO) and CH_3CN.

To investigate the corrosion behavior of these alloys, researchers have synthesized various HEAs containing elements like as Al, Co, Cr, Cu, Fe, Ni, Ti, and V, which have shown significant oxidation and corrosion resistance. Also, the Corrosion resistance of high entropy alloys of CoCrFeMnNi was studied.

For the first time, the CoCrFeMnNi HEA coating was synthesized by electrochemical deposition by this group. Because of its good corrosion resistance, the alloy produced is a pleasant choice for coating applications in corrosion protection.

2. Experimental

Before the plating process, the Cu substrates were pre-treated by polishing with abrasive emery papers, followed by electrochemical etching in a H_3PO_4 (30%) solution and rinsing with double-distilled water.

The electrodeposition of the high entropy alloys and the electrochemical studies were carried out at 298 K via a DC Power Supply generator. The HEA thin films were deposited on copper substrates by potentiostatic electro-deposition in an electrolyte based on a DMF–CH_3CN organic system, which contained $FeCl_2$, $CrCl_3$, $MnCl_2$, $NiCl_2$, $CoCl_2$, and $LiClO_4$. The electrolyte composition is given in Table 1.

Table 1. Chemical composition of the electrolyte

$CoCl_2$ (mol/L)	$CrCl_3$ (mol/L)	$FeCl_2$ (mol/L)	$MnCl_2$ (mol/L)	$NiCl_2$ (mol/L)
0/01	0/013	0/01	0/0103	0/001

The electrochemical cell comprises two electrodes, platinum as an anode and substrate as a cathode. Electrodeposition was performed at 1 to 6 volts for 60 min. The morphology and the chemical composition of the high entropy alloy thin films were analyzed via a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX). The crystal structure of the samples was determined by grazing incidence X-ray diffractometry (GXRD). The tests were performed according to the ASTM G8 standard and were repeated 3 times. The results presented are the average of the three tests.

3. Results and Discussion

The EDS results of the films reported in Table 3 showed that the chemical composition of the films synthesized at a potential of 1 to 4 volts included only nickel and iron elements. However, EDX results showed that the films at a potential of 4-6 v contained all five elements present in the solution and were successfully coated. The mixing entropy of the coatings was calculated (Table 2). As seen, the entropy of mixing under all conditions is in the range of high entropy alloy formation.

The XRD patterns of the deposited films on the Cu substrates were examined within a range of $2\theta = 10–80$ degrees and are given in Figure. 1. 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 High Score Plus software, the lattice constant a = 3.6 Å can be calculated from the XRD results via Bragg's law (Figure 1).

The EDS results confirm that the deposits are composed of five elements. Figure 2 shows the changes in the chemical composition of the coating with the change in

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applied potential according to the results of the EDX analysis.

Table 2. The compositions and the molar entropies of mixing of the CosCrFeMnNi flms, depending on the diferent parameters of the electrodeposition, for 1 h.

Condition	Elements (% at)					Δsmix (J/Kmol)
	Co	Cr	Fe	Mn	Ni	
4 v	19/88	10/31	26/10	36/42	7/30	12/179
5 v	24/44	11/96	19/73	37/04	6/83	12/22
6 v	19/30	9/07	26/58	37/65	7/40	12/037

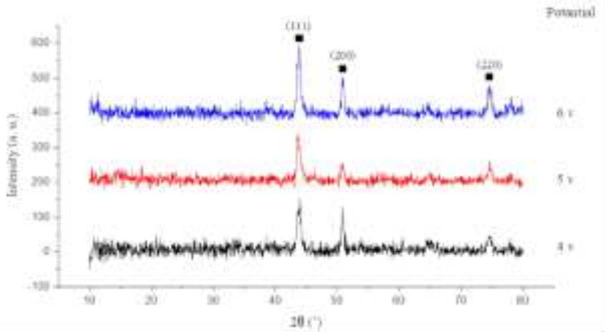

Figure 1. XRD patterns of the CoCrFeMnNi flms deposited at different potentials

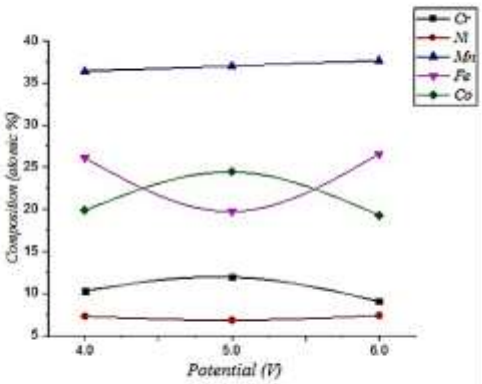

Figure 2.Variation of the chemical composition of the coating

Figures 3 to 5 present the SEM micrographs of the CoCrFeMnNi thin film samples that synthesized in 4, 5, and 6 v, respectively. As seen in Figure 4, the samples have a smooth and non-cracked surface. The average crystallite size was about 109 to 163 nm. There are some hydrogen blisters on the coating surface that can be caused by low overvoltage at this potential and the production of H_2 after the decomposition of chromium hydride. Based on the results of EDX analysis, the manganese amount in this sample is less than the others. Because of the large atomic radius of the manganese, which can lead to internal stresses in the coating, the low and non-cracking properties of this coating can be justified.

As seen in Figure 5, the coating is layered and has an uneven surface. There are blisters on the coating surface, and in some places, the effects of blistering are also observed. The surface consists of several cracks that in some places the cracks are branched to greater width and depth. The size of the crystals was calculated to be about 143 to 210 nm. According to EDX results, this coating contains the maximum amount of cobalt and chromium and the minimum amount of iron and nickel compared to other samples. Therefore, the presence of cracks on the coating surface can be attributed to low nickel and high cobalt values.

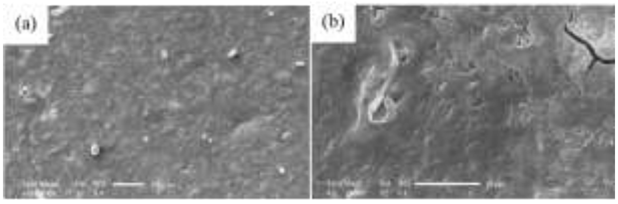

Figure 3. Scanning electron micrographs of the CoCrFeMnNi flm deposited at a potential of 5v.

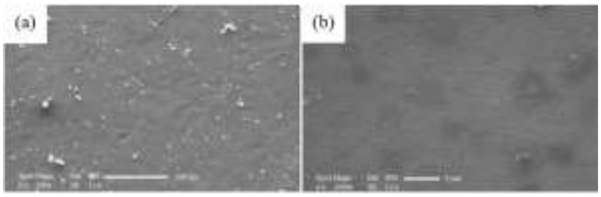

Figure 4. Scanning electron micrographs of the CoCrFeMnNi flm deposited at a potential of 4v.

Figure 6 presents a crack-free coating with small hydrogen blister effects on its surface. Based on the results of XRD analysis, the size of the sample crystals was calculated to be about 119 to 140 nm. The results of EDX analysis showed that in this coating there is a minimum amount of chromium and cobalt and the maximum amount of manganese and nickel, which according to the values of cobalt and nickel can be justified without cracking the coating.

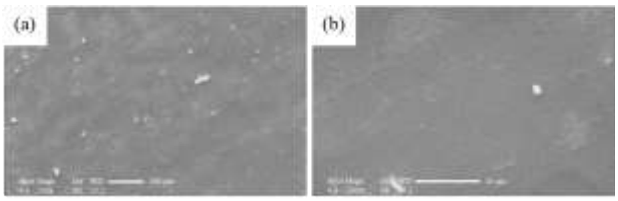

Figure 5. Scanning electron micrographs of the CoCrFeMnNi flm deposited at a potential of 6v.

5. Conclusion

The CoCrFeMnNi high-entropy alloy coating film was successfully synthesized by the potentiostat electrochemical deposition at 4 to 6 v of a DMF-CH_3CN organic system.

EDX analysis showed that at a potential greater than 4 v, all five elements were deposited and the chemical composition changed by the applied potential. In all cases, the mixing entropy was about 12 J/Kmol, within the range of high entropy alloy formation. The results of GXRD analysis proved the formation of single FCC phase solid-solution structure. The coatings morphology was observed to be smooth, cracked, and compacted.