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To cite this article: R M Florea and I Carcea 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **591** 012014

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# Sustainable anti-corrosive protection technologies for metal products by electrodeposition of HEA layers

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**Abstract.** The purpose of this paper is to study the electrochemical synthesis of thin films of multi-component alloys with improved structures and properties to ensure optimal protection of metallic materials used in extreme environments against various types of corrosion, oxidation and wear. Electrochemical deposition is an inexpensive alternative to thin film synthesis because it does not require complex or costly equipment and uses readily available raw materials. This simple method offers the possibility of depositing thin layers on substrates of complex geometry and can be achieved at low process temperatures with reduced energy consumption. Electrodeposition allows easy control of chemical composition, morphology and thickness of coatings by varying deposition parameters. HEA alloys are usually developed by physical methods, most commonly by casting-melting. Mechanical alloying and rapid solidification are other synthesis processes used to obtain structural materials. HEA coatings have also been obtained by various deposition methods, such as magnetron-sputtering and laser deposition. In this paper is investigated the microstructure, mechanical properties and oxidation behaviour of HEA coating obtained by electrochemical deposition.

## 1. Introduction

Corrosion is a destructive attack of the material due to the reaction with the environment. Severe consequences of corrosion process are an important issue worldwide. With only a few exceptions, such as gold, most metals are not stable in metallic form but in the form of oxides or compounds are (i.e. ores) [1- 5]. As soon as they are used in the environment, where there is oxygen (typically air) and an electrolyte (usually water and/or soil), the metals tend to deteriorate and revert to their oxidized elementary form. In a spontaneous and electrochemical process, the metals behave like some anodes, fact that goes to different types of corrosion.

Corrosion and wear are often associated with the degradation processes of metals and their alloys and contributes to economic losses and environmental pollution [2, 4]. These phenomena can occur both in natural environments and anthropic. Corrosion control methods and abrasion resistance are becoming very important as human society grows more concerned with the conservation of the natural environment [5].

Deposited electrochemical coatings are a widely used method for protection of metallic surfaces. These coatings can consist of simple metals, but also of binary and ternary alloys, enhancing protection to corrosion, oxidation or wear. Electrochemical deposition is a cheap alternative for the synthesis of thin films because it does not require a complex or expensive equipment and uses



traditional raw materials [4, 5]. This simple method provides the possibility to deposit thin layers on substrates with complex geometry and can be performed at low temperatures and with a minimum power consumption. Electrodeposition allows an easy control of chemical composition, morphology and thickness of coatings deposition by variation of the process parameters [5].

The subject of this work is represented by electrochemical synthesis and investigation of thin films from multi-alloy components with improved structures and properties, to ensure optimum protection of metallic materials used in extreme environments, against various types of corrosion, oxidation and wear. Thus, it is studied the process of electrochemical deposition of Al-Cu-Fe-Cr-Mn-Ni alloys with high entropy.

## 2. Investigation on high entropy alloys (HEA)

### 2.1. High entropy effect

It has been reported in scientific literature that HEA presents a multitude of attractive features, such as high hardness, very good resistance to wear, fatigue resistance, a very good tensile strength at elevated temperatures, good thermal stability and enhanced resistance to oxidation and corrosion.

To HEA has been granted special attention in recent years, developing more than 300 kinds of alloys in this category. Most scientific studies of the literature focused on investigating the correlation between microstructure, phase composition and mechanical properties [6 - 9].

Thermodynamic entropy represents the ratio between the amount of heat available in a system and the temperature of the system, being defined by the equation (1):

$$dS = \Delta Q / T \quad (1)$$

where  $S$  is the entropy,  $Q$  is the quantity of heat, and  $T$  is the absolute temperature.

For estimating the entropy of a metal alloy, Boltzmann hypothesis asserts that this entropy has the maximum value at echiatomic compositions, as a result of the following formula, equation (2):

$$\Delta S = -k \ln w = -R \left( \frac{1}{n \ln 1/n} + \frac{1}{n \ln 1/n} + \dots + \frac{1}{n \ln 1/n} \right) = -R \ln \frac{1}{n} = R \ln n \quad (2)$$

where  $R$  is the ideal gas constant and  $n$  is the number of elements in the system.

Starting with  $n = 5$ ,  $\Delta S$  becomes higher than the majority of intermetallic compounds leading to preferential formation of solid solutions. When  $5 \leq n \leq 13$ , alloys have entropies with values between  $1.61R$  and  $2.56R$  and belong to the domain of high-entropy.

### 2.2. Resistance to corrosion

The possibility of variation of the elements and the ability to form amorphous phases are the key advantages of alloys with high entropy, entropies which helps the alloys to have outstanding mechanical and electrochemical properties. In the case of HEA, a high resistance corrosion resistance can be achieved by choosing the proper chemical composition.

Study of electrochemical characteristics at elevated temperatures showed that the resistance to corrosion of alloys diminishes with increasing the temperature, the decrease being more pronounced in 1 M  $H_2SO_4$  solution than the 1 M NaCl solution. It should be noted that HEA are characterized by a higher corrosion resistance than 304 stainless steel in medium acid in the entire temperature range. The 1 M NaCl solution the high-entropy alloy is less resistant than stainless steel at elevated temperatures because of lower activation energy [10].

## 3. Metals and alloys electrodeposition

An alloy electrodeposition requires, by definition, submission of two or more metals. In other words, it is necessary that their ions to be present in an electrolyte which forms a film at the cathode, where

individual potentials of filing may be close or similar; cathodic deposition of alloys (or metals) is made up of the following stages [3, 4, 11, 12]:

- Ions migration: ions moisturized from electrolyte migrate to the cathode by the influence of the applied potential and by diffusion and/or convection;
- The transfer of electrons: from the cathode surface, moisturised metallic ions enter in the double diffusion layer in which the water molecules of the hydrated ion are aligned by the electric field present in this layer. Subsequently, metallic ions enter into the double layer created where, because of stronger electric field, the hydrated part is lost. Then, the individually ion can be neutralized on the cathode surface and is adsorbed;
- Incorporation: the atom adsorbed is moving toward a point of growth on the cathode and is incorporated into the growing network.

### 3.1. Electrochemical deposition of alloys with high entropy

Currently, non-aqueous electrolyte represents the best alternative for electrodeposition of metals and alloys, due to their characteristics: chemical and thermal stability, high electrical conductivity, a large range of working temperatures and, most importantly, wide electrochemical window, the lack of hydrogen generation and formation of hydroxides [10, 11, 13, 14]. Electrochemical deposition process scheme of thin films is presented in figure 1.

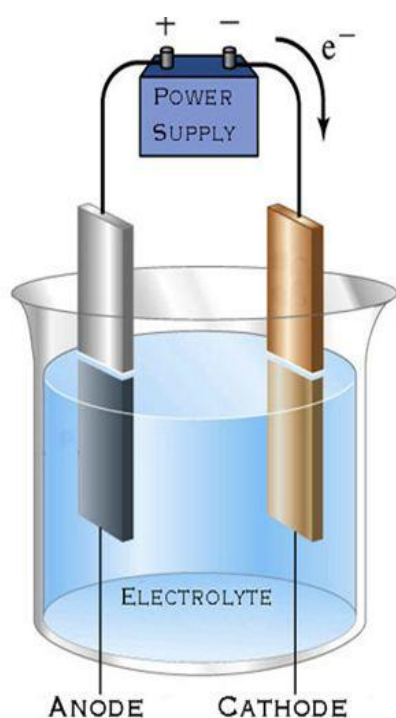


**Figure 1.** Thin films electrochemical deposition process scheme.

So far, there are very few references in the literature about obtaining of HEA by electrodeposition [7, 10, 11]. One research team has reported the obtaining of HEA thin films with various compositions using electrochemical methods. The aim of the research work was getting thin films with magnetic properties for various applications. Thus, the group of researchers from the “Sun Yat-Sen” Chinese University of Guangzhou, headed by Yeh Xiang Tong, developed HEA thin films by electrochemical deposition on various substrates, using electrolytes based on organic compounds type dimetilformamida-acetonitrile ( $\text{CH}_3\text{CN}$ -DMF) or dimetilsulfoxida-acetonitrile (DMSO- $\text{CH}_3\text{CN}$ ). The deposited films were amorphous and after heat treatment, they have presented solid solution-type structures of FCC [6, 7, 11, 13].

### 3.2. Electrochemical deposition of FeCoNiCrMn thin films

With the electrodeposition method have been obtained multi-component alloys thin films with different compositions, structures and properties [14 - 18]. Experimental model includes the following steps:

- Preparation of deposition solutions;
- Pretreatment of metallic surfaces in preparation for coating;
- Thin film deposition.

The HEA coating was deposited on a flat 6082 Al alloy substrate. 10mm thick A36 steel was chosen as substrate, and the chemical composition was presented in table 1.

**Table 1.** Chemical composition (wt %) of substrate material.

| Element | Fe   | Ni   | Cr   | Mn      | C     | Mo    | Cu    | Si   |
|---------|------|------|------|---------|-------|-------|-------|------|
| wt.%    | Bal. | ≤0.4 | ≤0.2 | 0.9-1.6 | ≤0.18 | ≤0.08 | ≤0.35 | ≤0.5 |

Solutions used for depositing thin films were prepared by using double-distilled water and chemicals substances with >99% purity. The pH will be brought to the appropriate value by the addition of NaOH for autocatalytic deposition and H<sub>2</sub>SO<sub>4</sub> for electrodeposition.

The nominal composition of the HEA coating is provided in table 2.

**Table 2.** Nominal composition (wt %) of the FeCoNiCrMn HEA used in this work.

| Element | Fe    | Co    | Ni    | Cr    | Mn   |
|---------|-------|-------|-------|-------|------|
| wt.%    | 20.09 | 20.96 | 21.01 | 18.86 | Bal. |

## 4. Results and discussion

### 4.1. Microstructure and phase composition of HEA coatings

HEA coating was machined into a cubic shape a surface area of 20 x 20mm and coating thickness of 1.5 mm (figure 2(a)). In figure 2(b) is shown the XRD spectra of HEA coating and reveals only FCC single phase. Also, here was detected a peak which occurred from grain refinement in the coating. This fact is detailed in figure 2(c).

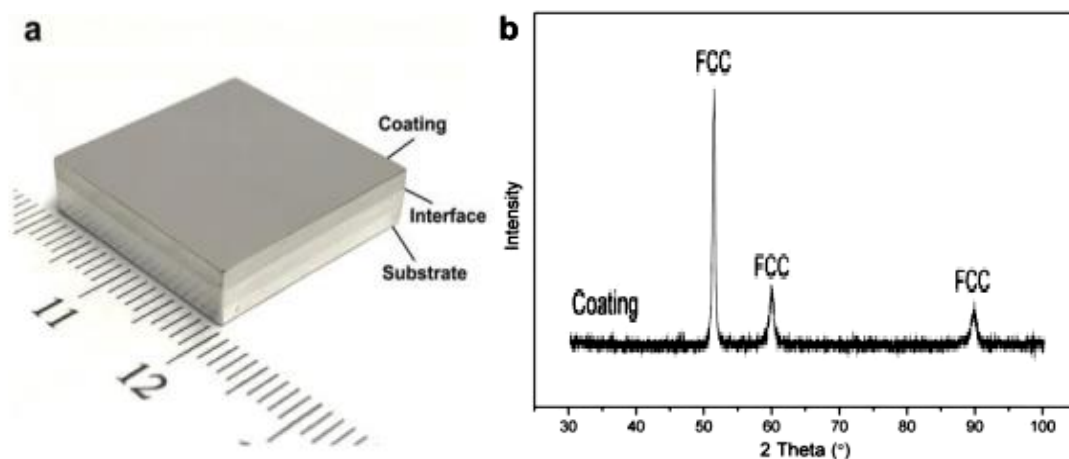
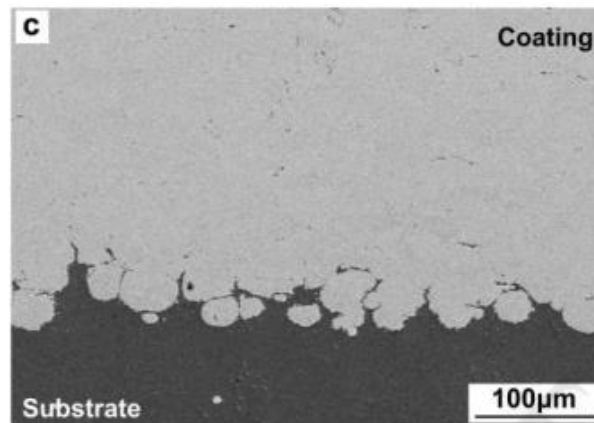


**Figure 2.** HEA coating general characterization: (a) HEA coating Machined; (b) XRD spectra of the HEA coating.



(c) SEM image of the HEA coating.

The HEA coating section illustrated in figure 3(c) is subjected to a higher resolution. So, the figure 3(a) shows a SEM micrograph of HEA coating. Here could be observed inter-particle interfaces marked with black arrows which appear because of the insufficient local plastic deformation. The inter-particle interfaces are not favourable for the coating cohesion strength [14], however this inconvenient can be sublimated through variation of the deposition parameters. In figure 3(b) it is shown the HEA coating EDX mapping on the selected area marked in figure 3(a). It can be easily observed that five elements are uniformly distributed in the coating without obvious segregation and inter-reaction.

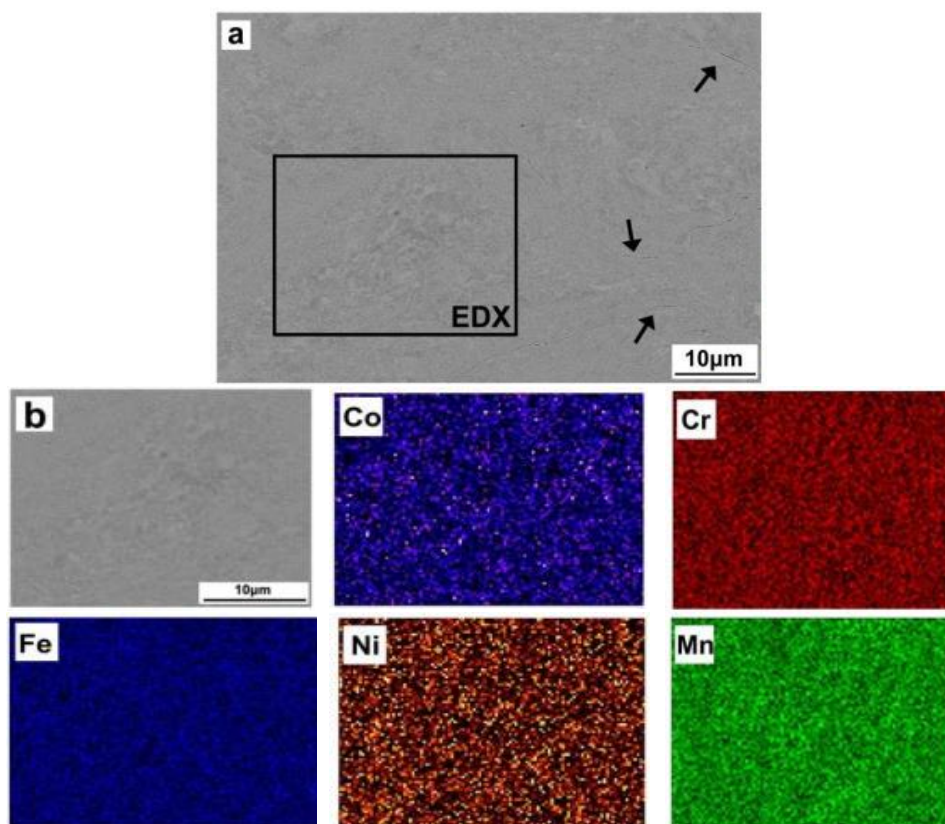


**Figure 3.** (a) High resolution SEM image of the HEA coating;  
(b) EDX map acquired at the selected area marked in previous image.

#### 4.2. HEA coating grain structure

For the characterization of HEA coating grain structure an EBSD mapping was performed. In figure 4 it is shown the inverse pole figures (IPFs) of HEA coating. As it is described in section 4.1, particles of HEA undergo severe plastic deformation upon impact with deposited coating.

Where the particle material experiences the largest plastic deformation (at the localized inter-particle interfacial regions), under the combined action of adiabatic heating and plastic deformation occurs a dynamic recrystallization which leads to a further refinement of sub-grains into ultrafine grains. Therefore, the HEA coating grains were significantly refined. The increased dislocation density and number of grain boundaries contributed together to the hardening effect.

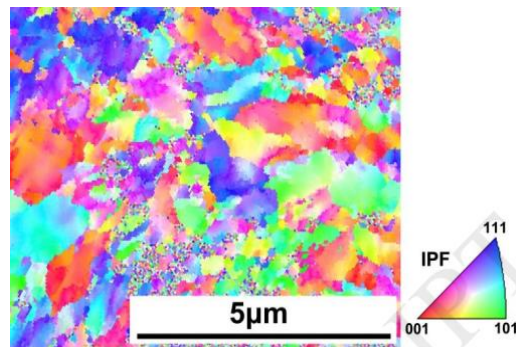


**Figure 4.** EBSD IPF map of HEA coating

#### 4.3. Electrochemical measurements of HEA coating

For electrochemical investigation, the corrosion specimens were sectioned and mounted into one holder with an exposed facet of  $4 \times 10$  mm. It was used a solution of 3.5wt. % NaCl. The experiments were conducted at 25°C under atmospheric pressure. For the potentiodynamic polarization and the electrochemical impedance spectroscopy (EIS) was used a typical three electrode cell. A specimen functioned as working electrode. The reference electrode was a saturated calomel electrode (SCE) with  $E = 0.2415V_{SHE}$  and an Hg/Hg<sub>2</sub>SO<sub>4</sub> (saturated K<sub>2</sub>SO<sub>4</sub>) with  $E = 0.658V_{SHE}$ . Also it was used a platinum sheet as counter electrodes. All potential values are converted into  $V_{SHE}$ . The curves of potentiodynamic polarization were tested and plotted at a scan rate of 1mV/s from  $-0.5V_{SHE}$  to a potential of  $1V_{SHE}$ . The corroded surface was immersed in NaCl solution for 5 days.

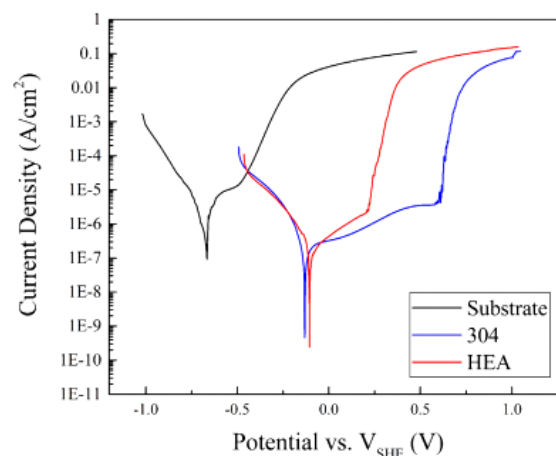


**Figure 5.** Polarization curves in 3.5wt.% NaCl solution.

Figure 5 shows the potentiodynamic polarization curves of HEA coating. For comparison, in the figure also appear the curves for 304 stainless steel and substrate (A36 steel). As it can be seen from the curves, HEA coating and 304SS shows a significant nobler corrosion resistance than the substrate

material. More than that, the polarization curves reveal the fact that 304SS and CrMnFeCoNi HEA coating have a tendency of being “spontaneously passive” [19].

## 5. Conclusions

CrMnFeCoNi HEA coating on A36 steel substrate was obtained using electrochemical deposition technology. The coating presents a simple FCC phase and has, mainly, columnar dendrites structure. Also, it can easily have observed a good metallurgical bonding with the substrate. The obtained HEA coating shows a very low porosity and presents phase structure without any phase transformation. The electrochemical test indicates that HEA coating can provide an excellent corrosion resistance for the A36 steel substrate. The investigations presented in this work prove that electrochemical deposition technology can be applied for the fabrication of thick and dense HEA coating. Further, more investigations are highly encouraged to fully understand the microstructure and various properties of HEA coating.

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## Acknowledgement

This research received funding through the PN III 3.2 Orizont 2020 M-ERA.NET under project 76/2017 “HEAMODELL-High entropy alloys with predictable mechanical properties by computational modelling”.

The authors want to thank to SC RANCON SRL for support and general HEA discussions.