



Microstructure and Wear Resistance of FeCoNiCu Medium-Entropy Alloys and AlFeCoNiCu High-Entropy Alloys Coating Produced by Electro-deposition

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ABSTRACT

9370

Increasing utilization of high entropy alloys (HEAs) in different engineering applications, especially in the automotive industry because of their unique properties as they combine two contradictory properties, namely, high ductility and high strength had led to the need for deep knowledge about the manufacture and properties of those alloys. In this study, microstructure, hardness, adhesion, and wear resistance of low alloy steel AISI (4140) by electro-deposition of medium and high entropy alloys thin films were study. All of the elements were completely co-depositing, according to the energy dispersive spectrometry examination (EDS). The film made up of compact and homogenous particles, according to field emission scanning electron microscopy (FESEM) investigation. In comparison to medium entropy alloys (MEA) coatings, as-deposited HEA coatings had a granular morphology that grew finer and more compact. The existence of a combination of BCC and FCC phases, with a proportion of the FCC phase, discovered during structural characterization. In comparison with MEAs sample coated, HEA deposit has higher in both wear resistance and adhesion strength.

Key words: High Entropy Alloy, Medium-Entropy Alloys, Electrodeposition, Coating, Wear Resistance

DOI Number: 10.14704/2022/nq.20.8.NQ44957

NeuroQuantology 2022; 20(8): 9370-9378

INTRODUCTION:

In today's world, metallic materials are extremely essential. They are necessary for life and growth, and they can help to advance human civilization [1, 2]. Because of the innovative mechanical and physical characteristics demonstrated by the created alloys, a novel idea in designing of alloy

depending on the existence of multi-principal constituents has fascinated attention recently. [3-5].

HEAs are new categories of metallic materials that have been developing using a novel approach to materials research. These alloys, unlike conventional alloys, do not contain a primary component and instead rely on



equiatomic mixes of five or many components. The morphology of these alloys must contain a variety of intermetallic phases according to traditional metallurgy concepts. HEAs, on the other hand, create simple solid-solution structures and single-phase crystalline structures because of their higher mixing entropy. HEAs characterized by sluggish diffusion and severe lattice distortions that have a meaningful effect on their morphologies and features [6, 7].

MEAs are comprised of three or more basic components with nearly identical atomic percentages and configurationally entropies ranging from 1 to 1.5R ($R = 8.314 \text{ mol}^{-1}\text{K}^{-1}$). The ΔS_{conf} of HEAs is greater than 1.5R, and they made up of five or more main elements with about equal atomic percentages. Both MEAs and HEAs may generate stable single-phase solid solutions in perfect situations due to the high mixing entropy related to a dis-ordered solution of many components[8].

HEAs and MEAs are attractive alternatives for coating techniques (e.g., electro-deposition) to provide a practical separation between substrate and surface due to their superior strength and wear resistance. Because HEAs and MEAs include rare and expensive alloying metals like cobalt, this strategy can help reduce time and costs [9, 10].

The MEAs and HEAs structures have been extensively studding, and they display extraordinary characteristics like high hardness,

high strength, excellent stiffness, high corrosion and wear resistance, and good magnetic properties, making them especially suitable for use as functional and structural materials. The capacity of MEAs and HEAs to preserve their characteristics at increased temperatures is their most notable property. [11-15].

The study focus is the manufacture of resistant of wear FeCoNiCu MEAs and AlFeCoNiCu HEAs coatings by applying chlorides for electro-deposition method. The behavior of wear was studies under dissimilar wear conditions and compared with a substrate of 4140 low alloy steel sample to overcome the problem of gearbox friction.

The AlFeCoNiCu system chosen as the model matrix because the atomic-size differences () are in the range of 1 to 5% and (ΔH_{mix}) is in the range of 15 to 5 kJ/mol, which matches the Hume-Rothery requirement for the creation of HEAs[6, 11, 16].

9371

Experimental

The FeNiCoCu MEA and AlFeNiCoCu HEA coating was electro-deposited from chlorides bath by a two terminuses DC power supply. A polishing was mechanically of 4140 low alloy steel sample (20 mm × 10 mm) and graphite electrode of the same dimensions were used as the cathode and anode respectively. Table 1 listed the deposition conditions and electrolyte bath composition that employed in this research.



Table 1 : Deposition conditions and electrolyte bath composition.

Bath Composition/ Sample	MEA (g/100ml)	HEA (g/100ml)	Conditions
<i>AlCl₃ · 6H₂O</i>	---	2.4	<i>PH=1.5</i>
<i>FeCl₂ · 4H₂O</i>	0.795	0.7	<i>T=30C^o</i>
<i>CoCl₂ · 6H₂O</i>	0.95	0.95	<i>Time=15min</i>
<i>NiCl₂ · 6H₂O</i>	1.67	1.9	<i>Current=0.16A</i>
<i>CuCl₂ · 2H₂O</i>	0.51	0.51	<i>Stirring=600rpm</i>
<i>Gelatin</i>	---	0.7	
<i>Sodium dodecyl sulfate (SDS)</i>	0.25	0.25	
<i>(C₆H₈O₆)</i>	---	0.5	
<i>(NH₄Cl)</i>	---	11.98	
<i>(KCl)</i>	---	12	
<i>(H₃BO₃)</i>	4.94	4.94	
<i>(C₆H₇NO₃S)</i>	---	0.52	
<i>(CH₂O₂)</i>	---	0.5	

Samples processed in an industry surface grinder procedure after the surface coating. Metallography processes used to create cross-sections of the coatings, which were then, examined using a FESEM. EDS was using to evaluate the chemical composition, while XRD used to establish the phase. Additionally, the micro-hardness measured in metallographic cross-sections according to ASTM E92-17 using digital Vickers hardness tester (HVS-1000) (Babylon University-Iraq). The average value and standard deviation was calculating from five single indents. A digital coating thickness gage Type (TT260), is uses to determine the coating thickness with accuracy of $\pm 0.1 \mu\text{m}$ and measurement is takes in the three places to give averaged thickness for coating sample.

The wear behavior was evaluating in ball-on-disk, oscillation wearing, and scratching testing after micro-structural studies. All tests performed under laboratory circumstances in atmosphere at a temperature of 24-30 °C, moisture of 50-40%, and a load of 5N and 10N, respectively. Velocity of sliding is (0.1 m/s), and distance of sliding was (500m). Using adhesion, oscillatory, and abrasion wear circumstances;

several wear experiments were conducting to evaluate the wear behavior.

Adhesion test are essential in coatings testing, if the operator is attempting to meet quality standards, maintain quality assurance, or meet client requirements. This test done using the PosiTest AT Adhesion Tester using 14-millimeter loading fixture and equal amounts of the included epoxy applied as an adhesive according to ASTM D4541.

Results and discussion

Sample Characterization Results

MEAs have recently gained a lot of interest due to their superior mechanical characteristics when compared to other HEAs. Because of their greater yield strength and work hardening rate, ternary MEAs offer better mechanical characteristics than HEAs at both cryogenic and room temperatures. The twinning stress of MEAs was reach sooner at lower strains, and Nano twinning occurs across a wider strain range [17].

MEA and HEA coating have unique properties and thus leads to an improvement in the properties of the substrate, as shown in Figure



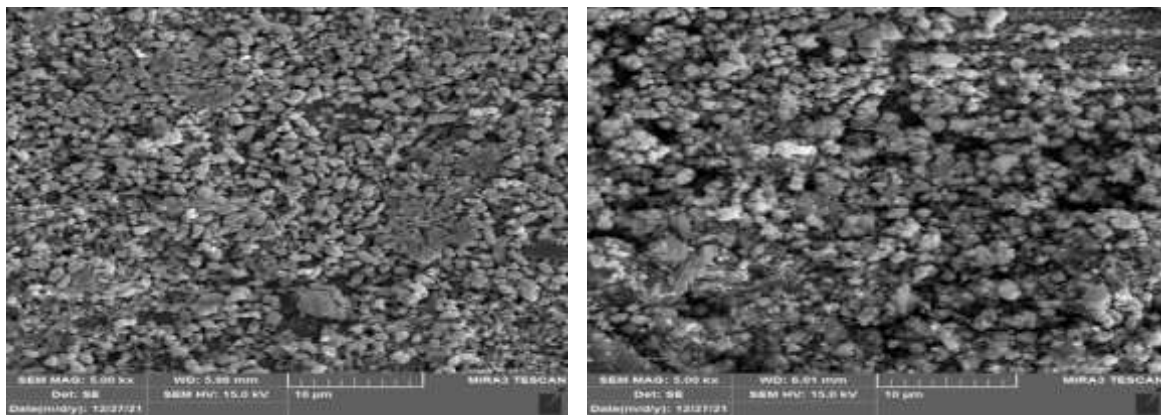
1 that represents the FESEM microstructure images of MEAs and HEAs.

The particle size of HEAs was finer than the MEAs as a result of the 5 element that constitutes the HEAs that leads to increase the number of nucleation sites, therefore the surface roughness decreased similar to an increase in the compressibility of the coating which essential for obtaining superior resistance of wear as shown in figure 1.

The coating composition was examining by the FESEM and EDS procedure. Generally, for MEAs and HEAs, the main components are estimated to be amid (5-35 at. %) [11, 18]. So that coatings surface containing all the

constituent components in atomic-percentage (at.%) that listed in Table 2 and the map shown in the Figure 2. The thickness of all coating determined from prepared samples as cross section was nearly in the variety of 10–14 μm s shown in Figure 3.

Incorporating with the mapping of EDS, the dendrite is a Fe-Cu rich phase whereas the inter-dendrite is a Ni-Co rich phase. The seed-like grains are Cu-rich as agreed with Yang et al. [19]. The morphology of the (FeNiCoCu) MEA coating contains two different phases, one comprising Ni, Co, and Fe, and another with a large concentration of Cu, as shown in Figure 1.



9373

Fig. 1. SEM microstructure of MEA and HEA coatings

Table 2: SEM-EDS Elemental Composition of HEAs and HEAs-CNTs Coating

Sample/Components	Al at%	Fe at%	Co at%	Ni at%	Cu at%
MEA	29.3	0.2	1.5	69
HEA	19.9	35.62	11.265	7.805	25.335

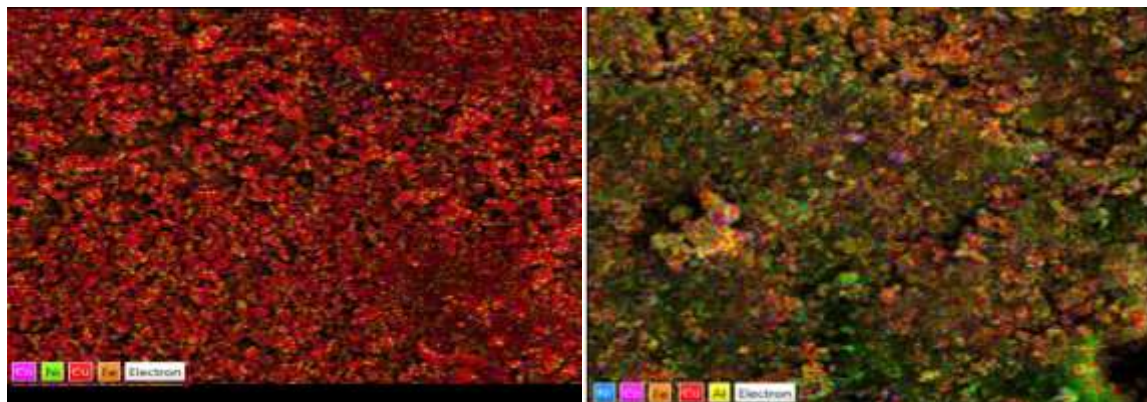


Fig 2. EDS Map of (a) MEAs and b) HEAs Coatings

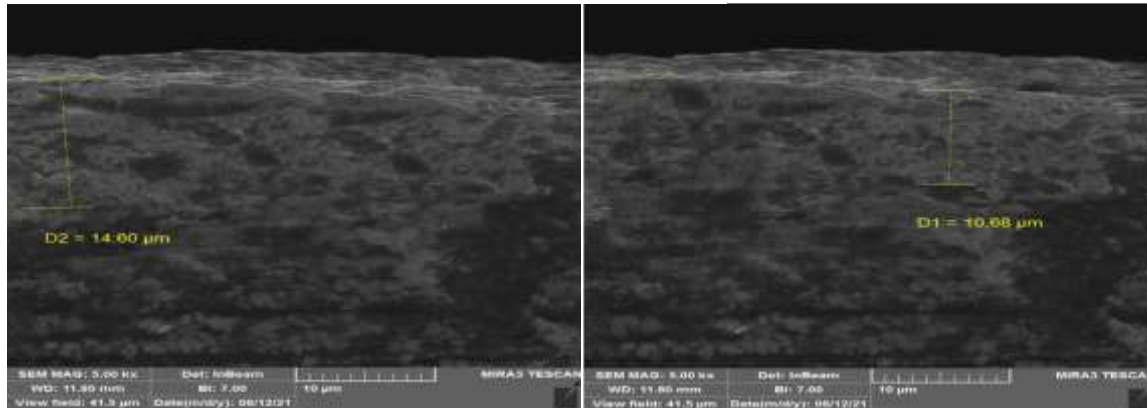


Fig. 3. FESEM image that show the thickness of coating layer of specimen a) MEA , and b) HEA.

HEA and MEA coatings XRD forms at 0.03° step-size are displays in Figure 4. XRD patterns of all coating analyzed show a mixture of FCC and BCC phases.

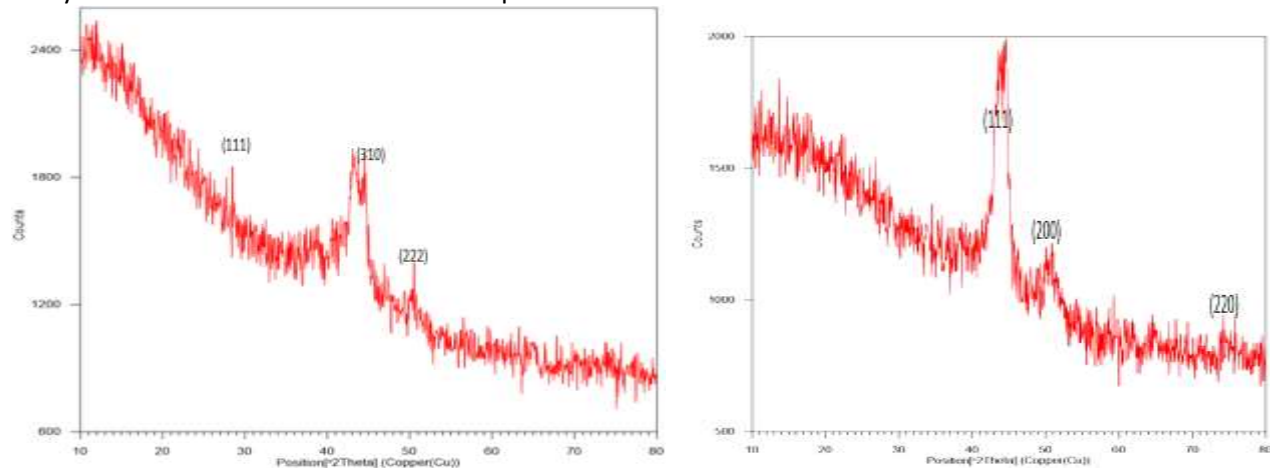


Fig 4. XRD Slow Scan Patterns of (a) MEAs and b) HEAs Coatings

Liu et al., [16] stated that the presence of Al in HEAs promotes the BCC phase to evolve. Implementation of the BCC lattice, which has a smaller packing fraction as well as a more open structure, could relieve the permanent deformation generated in the FCC phase due to the insertion of large atoms the size of Al . The existence of the BCC phase in this situation can sometimes be attributing to the fact that Al's electron configuration favors bonding with transition metals that have an incompletely filled d-shell.

Peaks of FCC structure ((111), (220)) and small peaks of bcc structure ((310), (220)) were seeing in the MEA coating. The Cu-rich phase is the most dominant FCC phase in the sample of MEA coating, but the disorder bcc phase contains Fe, Ni, and Co, because these components (Fe, Ni, and Co) may produce a solid solution because of their lower mixing enthalpy than Cu and other components as agreed with Ulianitsky et al [20] . The HEA XRD patterns indicated that almost all of the



coatings included a combination of BCC and FCC phases.

Wear Test Results

The coefficient of friction and wear tests results of the substrate, MEAs, and HEAs electro deposition coatings are summarize in Figure 5 and Table 3. As shown in the table, HEA has a better influence on the tribological characteristics of electro-deposition coatings than MEA. This sample coating has a reduced friction coefficient as well as stronger wear

resistance. The coefficient of friction the substrate hardly changed before and after HEA coating, while the other MEA electro-deposition coatings decrease to some extent. As a result, it could be infer that HEA may considerably increase electro-deposition coating tribological behavior. The positive effects of HEA on mechanical properties are due to their superior properties and distinct topological structure as compatible to the Gary et al. [21] and Cui et al [22].

Table 3: The coefficient of friction and wear tests for substrate, MEAs, and HEAs electro-deposition coatings

Sample	5 N		10 N	
	Friction Coefficient	Wear Rate *10 ⁻⁴	Friction Coefficient	Wear Rate *10 ⁻⁴
Substrate	0.77	7.5	0.77	10
MEA	0.75	5	0.45	7.8
HEA	0.39	4.9	0.34	6.3

9375

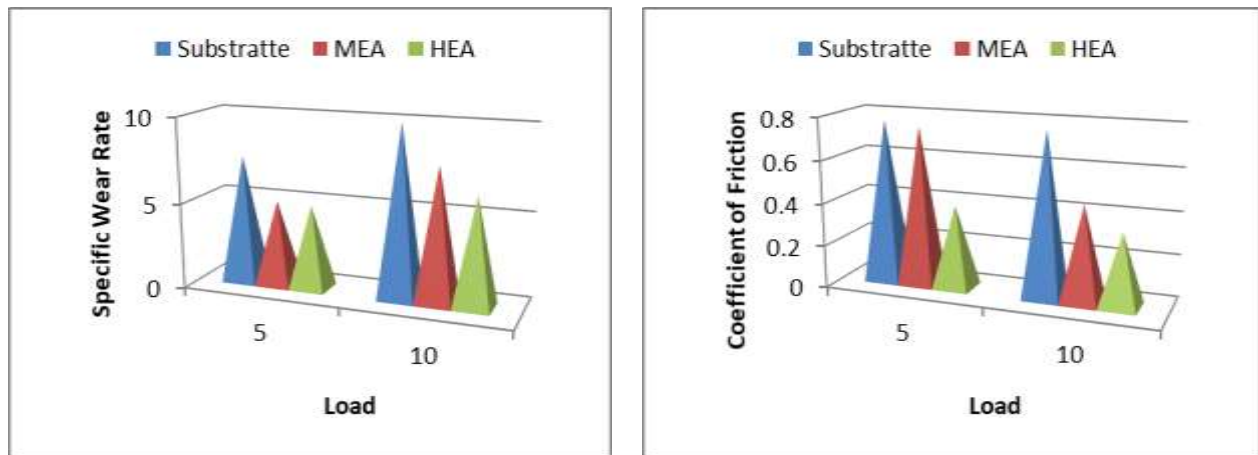


Fig. 5: the comparison between coating samples at 5N, and 10N of a) specific wear rate and b) coefficient of friction



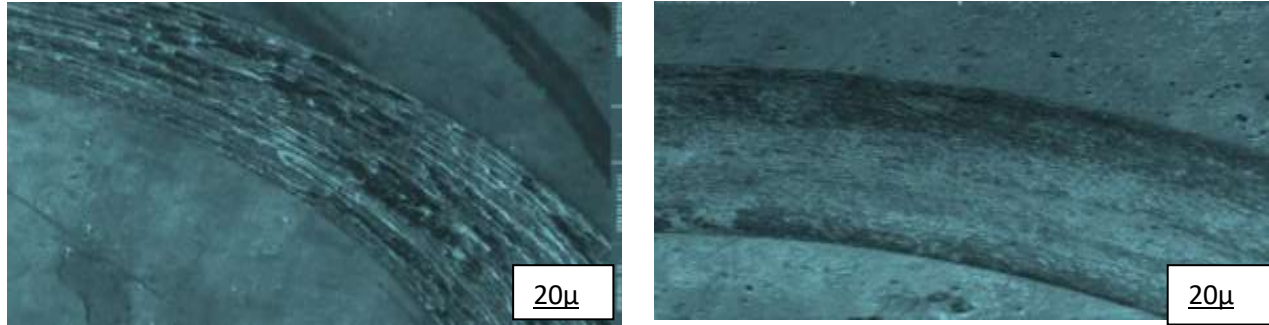


Fig 6: Optical image of wear track the of MEA and HEA

Furthermore, there are hard disinterests of the fragment of wear on the MEA electro-deposition coating. It well known that a MEAs electro-deposition coating is highly wear as compared with HEA coating.

The basic causes for this behavior include the following: Firstly, The hardness of the HEA is higher than MEA. The pin surface was scratch throughout the wear test due to the coating's high hardness value, resulting in increased pin/coating contact surface and grain refinement. As a result, the coating's friction coefficient was increase up to the sliding distance. Secondly, the HEA was less in the micro-holes of the surface during the electro-deposition process, which activates the sites for the stress of tensile. Therefore, HEA can prevent rapid plastic deformation. Thirdly, the coating's slow wear rate can operate as insulators, limiting close contact between matching metal surfaces [24]. The lamellar debris of MEA indicates that delamination happens through wear tests, as shown in Figure 6.

Adhesion Test Results

The epoxy strength value that used in this test equal to 34.6 MPa that obtained from epoxy testing on the substrate sample. The samples of HEAs coating were higher than sample of MEAs coating (10.8 and 11.7 MPa respectively) because of high hardness of HEAs as compared with MEAs. The improvements in

eISSN1303-5150

the adhesion strength can be attributing to uniform dispersion within HEAs coating that agreed with Ref [24]. The thickness of coating layer was effect on the adhesion strength where the strength increased as the thickness of coating layer decreased because of reducing the hardness towards the increment of thickness. In addition, the lattice distortion that happens in HEAs coating led to increase the adhesion strength as a result to hardness increment.

Microhardness Results

Figure 7 shows the surface micro hardness of the samples. As noted, HEA possess the ability to enhance the micro hardness of a surface. The hardness of HEAs samples is large when compared with the MEA as a result of the MEA has the fine grain size which leads to increase the hardness. Also, the HEAs samples as compared with the substrate sample is higher due to the HEAs properties which has high hardness due to a high solid solution hardening has been attributed to substantial lattice distortion and tighter bonding. The higher hardness of HEAs may well be due to a better contact between dislocations and solute atoms than in conventional alloys.

Conclusions

From the obtained results and their discussion, some conclusions can be list as follows:

1. The coating specimen of (AlFeCoNiCu) HEAs is the stronger as compared with

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- MEA which thickness equal to (10.6) μm .
2. The FeNiCoCu MEA coating microstructure contains two different phases, one with Ni, Co, and Fe and the other with a high concentration of Cu.
 3. A mixture of BCC and FCC phases observed in the XRD pattern for the sample coated.
 4. High entropy alloy of (AlFeCoNiCu) coating show the best result of adhesion and wear tests as compared with the MEA.
 5. The pin surface was scratch throughout the wear test due to the coating's high hardness value, resulting in increased pin/coating contact surface and grain refinement.
 6. The hardness of HEAs samples is large when compared with the MEA.
 7. The samples of HEAs coating were higher adhesion strength than sample of MEAs coating (10.8 and 11.7 MPa respectively).

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