euspen's 26th International Conference & Exhibition, Krakow, PL, June 2026
www.euspen.eu

Electrochemical accretion of high entropy alloy traces from aqueous electrolytes towards modular moulds, tools and integrated sensing applications

Krishna Kumar Saxena[1,2,*], Adnan Al Farisi[1,2], Muhammad Hazak Arshad[1,2], Dominiek Reynaerts[1,2]

[1]*KU Leuven, Department of Mechanical Engineering, Micro -& Precision Engineering Group, Belgium.*
[2]*Member FlandersMake, Belgium*
**krishna.saxena@kuleuven.be*

Abstract
High-entropy alloys (HEAs) exhibit exceptional combinations of strength, wear resistance, and thermal stability due to their multi-element compositions and high configurational entropy. This work investigates the electrochemical accretion of CoCuFeMoWNi HEA traces from an aqueous electrolyte. The influence of key process parameters, including voltage, pulse characteristics, pH, and electrolyte temperature, on deposit morphology and composition was examined. Results demonstrate the feasibility of producing multi-element HEA deposits via controlled electrochemical accretion, indicating a promising route for integrating HEA features into manufacturing process chains.

Keywords: Electrochemical manufacturing, electrochemical deposition, electrochemical accretion, high entropy alloy.

1. Introduction

High-entropy alloys (HEAs) are a relatively new class of metallic materials composed of multiple principal elements, typically five or more, in near-equiatomic proportions [1]. Unlike conventional alloys that are based on one dominant element, HEAs derive their stability from high configurational entropy, which lowers the Gibbs free energy of the system ($\Delta G = \Delta H - T\Delta S$). This thermodynamic effect promotes the formation of stable solid-solution phases rather than brittle intermetallic compounds. As a result, HEAs often exhibit a unique combination of mechanical strength, hardness, corrosion resistance, and thermal stability, making them attractive for demanding environments where conventional alloys show performance limitations. Because of these characteristics, HEAs are being actively explored for applications in sectors such as aerospace, energy systems, high-value components, and precision manufacturing [2], [3]. In particular, the ability to introduce HEA layers or localised material features through surface engineering provides opportunities for advanced tooling technologies. Tool and mould materials frequently experience severe thermal cycling, oxidation, and abrasive contact while maintaining strict dimensional tolerances. Materials capable of retaining mechanical and chemical stability under such conditions are therefore of high interest. Beyond structural functionality, HEAs are also promising for high-temperature sensing applications (> 1200 degC) due to their compositional stability and resistance to degradation in harsh environments, enabling durable conductive paths or sensing elements integrated directly within structural components.

Electrochemical accretion or layered deposition offers a promising route for fabricating such material systems on metallic substrates [4], [5]. Compared with conventional synthesis routes such as casting, sputtering, or laser-based deposition, electrochemical manufacturing operates at relatively low temperatures and can be implemented with lower energy consumption. In addition, electrochemical parameters including current density, electrolyte composition, and pulse conditions provide significant control over the composition and morphology of deposited layers. However, the electrodeposition of multi-component HEAs remains challenging because the constituent elements often exhibit substantially different reduction potentials and deposition kinetics, complicating controlled co-deposition from aqueous electrolytes [5].

This work presents an initial investigation into the electrochemical deposition of a six-component high-entropy alloy (HEA), CoCuFeMoWNi, on steel substrates representative of mould base materials. The selected alloy system is known for its favorable combination of hardness, wear resistance, and corrosion stability at elevated temperatures, and typically forms a dual-phase microstructure consisting of FCC and BCC phases. Electrodeposition experiments are carried out using aqueous electrolyte systems [6], focusing on how key process parameters including current density, pulse duty cycle, pulse frequency, electrolyte pH, and bath temperature affect the formation of localised HEA deposits. By systematically studying these variables, the work explores the conditions required to achieve stable co-deposition of the multiple alloying elements. The objective of this study is to assess the feasibility of producing localised, multi-element HEA traces through electrochemical accretion, with potential relevance for modular mould and tooling concepts as well as for the fabrication of conductive paths suitable for high-temperature sensing applications.

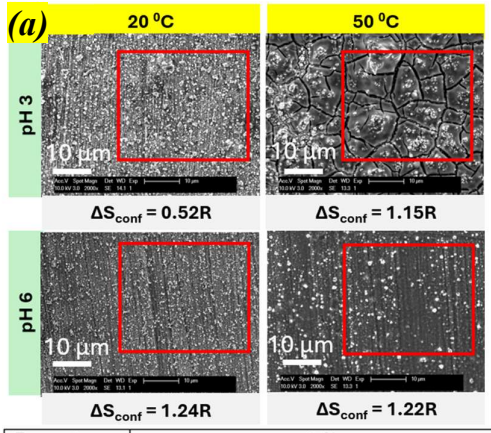
2. Experimentation

A multi-element aqueous electrolyte was formulated to enable the electrodeposition of CoCuFeMoWNi high-entropy alloy (HEA) system. The electrolyte consisted of $NiSO_4.7H_2O$ (0.15 mol/l), $CoCl_2.6H_2O$ (0.02 mol/l), $Na_2WO_4.2H_2O$ (0.2 mol/l), $FeSO_4.7H_2O$ (0.02 mol/l), $Na_2MoO_4.2H_2O$ (0.007 mol/l), $CuSO_4.5H_2O$ (0.007 mol/l). Hydrated metal salts were selected due to their high solubility and stable ion release in water, ensuring consistent metal ion availability during deposition. The electrolyte composition was designed considering electrochemical first principles i.e. elements with more negative reduction potentials were introduced at higher concentrations to promote incorporation into the deposit. Interactions such as induced co-deposition (e.g., Fe facilitating Mo and W reduction) and competitive deposition (e.g., Ni competing with Mo and W)

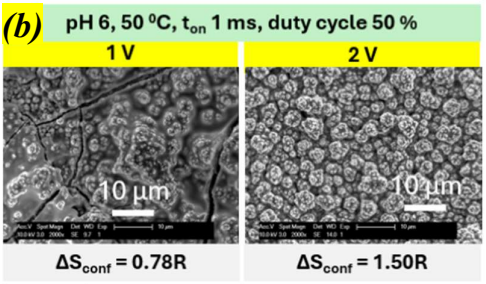
were also considered. Citric acid (0.4 mol/l) was used as a complexing agent to stabilise ions and moderate potential differences, while boric acid (0.4 mol/l) acted as a buffer to maintain stable pH conditions. Experiments were conducted in a lab-scale beaker setup using a gold-coated rod as the anode and W-EDM cut steel strips (5 mm width) as cathodes. Process parameters included voltages of 1-2 V, pulse-on times of 50-1000 µs, duty cycle of 50%, electrolyte temperatures of 20-50 °C, and pH values of 3, 6 under constant charge conditions (Q = 12.69 C).

3. Results and discussion

Figure 1 summarises the results of the electrochemically accreted HEA traces where voltage was used as a key parameter instead of current density to achieve better control over the process. The configurational entropy (ΔS_{conf}) of the deposits was estimated from the atomic fractions obtained by EDX analysis (oxygen excluded) using the Boltzmann expression $\Delta S_{conf} = -R\Sigma c \ln c$, where c denotes the atomic fraction of each element.



Parameters		wt. %					
pH	T (°C)	W	Mo	Cu	Ni	Co	Fe
3	20	2.85	1.73	85.67	2.85	0.00	6.89
	50	29.05	7.32	49.83	3.63	0.00	10.16
6	20	7.63	3.64	55.33	9.11	5.32	18.96
	50	17.76	10.45	52.98	10.28	0.51	8.02



	wt. %					
Voltage	W	Mo	Cu	Ni	Co	Fe
1 V	15.14	7.11	70.37	2.03	0.00	5.34
2 V	27.33	7.35	38.80	12.04	4.64	9.84

Figure 1. (a) HEA traces deposited under varying pH and temperature conditions using a constant direct voltage of 1 V. (b) SEM micrographs and corresponding EDX-derived compositions (excluding oxygen) of the traces deposited under pulsed voltage conditions at 1 V and 2 V.

Figure 1(a) shows the evolution of surface morphology and composition at different pH values and temperatures under a constant potential of 1 V. At pH 3, the deposits were dominated by copper and cobalt was not detected. In contrast, at pH 6 all six intended elements were incorporated into the deposit. The calculated entropy values at pH 6 were comparable for both investigated temperatures (20 °C and 50 °C). The layer formed at 50 °C exhibited a more homogeneous morphology and contained relatively higher amounts of Mo and Ni. Further experiments were performed under pulsed electrochemical accretion conditions at pH 6 using applied voltages of 1 V and 2 V (Figure 1(b)). At 1 V, cobalt was still absent from the deposits despite the presence of citric acid in the electrolyte, whereas nickel was detected. Increasing the voltage to 2 V enabled the incorporation of all six elements, although cobalt remained the least abundant, while tungsten and copper showed preferential deposition. Morphologically, the deposit formed at 1 V displayed cracks and isolated granular features, possibly associated with differences in grain growth. In contrast, the layer deposited at 2 V showed a more uniform granular surface without visible cracking. The maximum configurational entropy reached 1.5R at 2 V (Figure 1(b)), approaching the typical HEA range of 1.61–1.76R expected for equiatomic six-element alloys. Figure 2 presents the elemental distribution map for the deposit obtained at 2 V (Fig. 1(b)), confirming the spatial presence of all six elements across the surface. The granular surface texture together with the measured roughness (Sa = 0.39 µm, Sensofar®) further indicates the formation of a successful deposit.

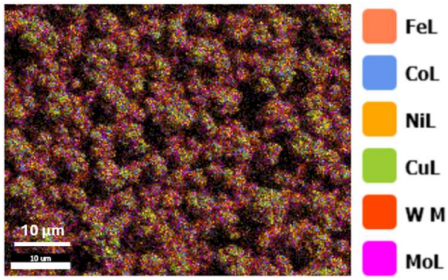


Figure 2. Elemental distribution map (oxygen excluded) of the surface deposited at 2 V (Fig. 1(b)), confirming the presence of all six HEA constituents across the workpiece coupon.

4. Concluding remarks

This study investigated the electrochemical synthesis of a six-component HEA (CoCuFeMoWNi) using an aqueous electrolyte system. The preliminary experiments resulted in a maximum configurational entropy of approximately 1.5R, which approaches the theoretical entropy range of 1.61-1.76R expected for six-element HEAs with atomic fractions between 5–35%. Under suitable conditions pH 6, electrolyte temperature of 50 °C, applied voltage of 2 V, pulse-on time of 1 ms, and a duty cycle of 50%, the deposited layer exhibited a uniform granular morphology without visible surface cracking. Elemental analysis further confirmed the successful incorporation of all six alloying elements. Future work will focus on refining the electrolyte composition and optimising electrochemical process parameters to achieve improved control over elemental distribution and phase formation.

Acknowldegement

The authors would like to acknowledge funding support from FWO senior postdoctoral project #1235425N, KU Leuven IOF C3 funds #C3/23/060 VLAIO IM # HBC.2025.0277.

References

[1] Choi W M, Jo Y H, Sohn SS, Lee S, Lee BJ 2018, *npj Comput. Mater.*, **4**, no. 1, pp. 1-9.

[2] Klink A, Harst S, Olivier M, Tombul U, and Bergs T 2020, *Procedia CIRP*, **95**, pp. 178-182.

[3] Martin A, Pfaffendorf F, and Schubert A 2021, *proc. of. INSECT 2021*, p. 93.

[4] Wittenburg J, et al. 2024, Procedia CIRP, **123**, pp. 197-202.

[5] Shojaei Z, Khayati G R, et. al. 2022, *Int. J. Miner. Metall. Mater.*, **29**, no. 9, pp. 1683-1696.

[6] Ahmadkhaniha D, Kruemmling J, and Zanella C 2022, *J. Electrochem. Soc.*, **169**, no. 8, p. 082515.