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Comprehensive Characterization of Annealed Coatings: Investigating Roughness and Wear Performance through Wear Testing and Analysis

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Abstract. Surface coatings play a pivotal role in enhancing mechanical and functional properties of various materials. High Entropy Alloy (HEA) annealed coatings have garnered significant interest due to their potential to improve wear resistance and overall durability. This research presents a comprehensive study focused on the characterization of HEA annealed coatings. It focuses on evaluating their roughness and wear performance. In this research, a systematic approach is adopted to assess the effects of annealing on coating surface properties. The investigation begins with the deposition of the $Al_{0.1\text{-}0.5}CoCrCuFeNi$ and MnCoCrCuFeNi coatings using a well-established cold spray (CS) technique, followed by a controlled annealing process. The coating surface roughness is analyzed using profilometry and microscopy techniques. This offers insights into the changes induced by annealing. The wear performance of the annealed coatings is evaluated through tribological tests. The data obtained from wear tests are correlated with surface roughness measurements. This provides a deeper understanding of the interplay between roughness and wear resistance.

1. Introduction

The development of metallurgical science has enabled alloys to demonstrate better and more tailored properties than single metals. However, traditional alloys are composed of a single main element, which limits the degree of freedom in the composition of an alloy. A new alloy concept proposed by J. W. Yeh, and B. Cantoris called "HEA" (High Entropy Alloy), which contains at least five major elements in an atomic percentage of 5-35% [1,2]. Secondary alloying elements are therefore characterized by atomic percentages of less than 5% [1–11]. Currently, the majority of knowledge is focused on alloys containing Al, Co, Cr, Cu, Fe, and Ni, and alloys derived from those alloys, obtained by adding other elements or substituting some of them. Many other alloys are still to be explored [3]. In terms of structural and functional applications, HEAs have a great deal of potential.

A high mixing entropy is found to promote the formation of solid solutions with simple microstructures [1,3]. High strains and stresses are associated with crystal lattices, as well as increasing strength and hardness, and a reduced sensitivity to temperature variations [1,2,3,10,11]. In many cases, HEAs can demonstrate excellent properties due to their characteristic chemical composition, which consists of several main elements: high strength and hardness, considerable wear resistance, exceptional resistance to high temperatures, good structural stability, and excellent corrosion and oxidation resistance. HEAs do not require any special production techniques or facilities, so they can be manufactured using current technologies.

Due to the presence of multiple main elements within HEAs, there are "core effects" that are responsible for determining the microstructural characteristics and exceptional properties of the materials. As a result of these effects, there is a high mixing entropy, a severe distortion of the crystal lattice, sluggish diffusion, and a cocktail effect [1,2,3,6,7,10,11]. It was reported in [13] that samples of Al0.5CoCrCuFeNi alloy quenched in water and cold rolled showed better performance than many conventional alloys, with fatigue strength limit values ranging from 540 to 945 MPa. It is evident from these results that the HEA of this system is potentially useful in future applications in which fatigue strength is an important consideration. The chemical composition of HEAs determines their tribological properties. By adding elements such as Al, Fe, and Nb, grains become refined and phases with a BCC structure are formed.

In addition, Mn and Cr play a significant role in the formation of hard phases. As C, N, B, and Si concentrations increase, carbides, silicates, and boron compounds are formed, or the phase transition from FCC to BCC/B2 occurs. A similar heat treatment to AISI 304 stainless steel increases the hardness of Mo better than those of AISI 304 stainless steel. In HEAs, wear resistance is determined by the type of phase present. The wear resistance of alloys made exclusively of simple and disordered phases ("SDPs") is generally not greater than that of conventional alloys with similar hardness. In contrast, if the prevailing phase is complex and ordered ("COPs"), the wear resistance of the alloy is often much greater than that of conventional alloys of similar hardness [3,13]. As a result, one of the major applications of HEAs is the creation of coatings with high wear resistance, which can be deposited using a variety of techniques. Coatings containing particles of ceramic materials dispersed in the metal matrix can increase the coating's overall hardness and, consequently, reduce the coating's wear rate [1,2,4,7-9,13-19].

The purpose of this paper is to describe annealed HEA coatings that have been cold sprayed and have been characterized with regards to dimensions and profiles as well as surface and microstructural characteristics, including roughness measurements and mechanical property determination of Cold Spray HEA coatings on Mg substrates. The wear performance of the annealed coatings is further evaluated by means of tribological tests. Annealing heat treatment is a practical way for adjusting the microstructures/properties and improvements in wear/corrosion/oxidation resistance of some light weight HEAs has been reported [3]. Compressively stressed cold sprayed (CS) HEA coatings can be recrystallized by annealing heat treatment to restore HEA coatings ductility and workability. The deformation via MA+CS and annealing behavior of a ductile HEA alloy, such as Al0.5CoCrCuFeNi, with favorable properties like high work hardening, elevated temperature strength, wear/oxidation resistance were investigated to elucidate the phenomena exhibited in HEAs. The formation of two HEAs is investigated using $Al_{0.1-0.5}CoCrCuFeNi$ and MnCoCrCuFeNi, as well as three deposition temperatures: 650°C, 750°C, and 850°C.

2.Experimental procedure

2.1. Materials and post-MA+CS vacuum annealing

Several pure elemental powders were used in this study, including Al, (Mn), Co, Cr, Cu, Fe, and Ni, all of which had high purity levels above 99.9%. A process known as mechanical alloying (MA) was used to create octonary high-entropy alloys (HEA): $Al_{0.1-0.5}CoCrCuFeNi$ and MnCoCrCuFeNi. Refer to reference [20] for additional information regarding the steps involved in mechanical mixing (MM) and mechanical alloying (MA). According to Table I, calculations were performed using pure elemental powders of Al, Cu, Co, Cr, Fe, and Ni to achieve the desired compositions of $Al_{0.1-0.5}CoCrCuFeNi$ and MnCoCrCuFeNi.

After mixing and homogenizing the materials, they were subjected to MA for 5.5 hours. In order to prevent contamination from the surrounding atmosphere, the MA powders were stored in airtight containers filled with argon gas until they were processed by Cold Spray (CS). Reference [20] provides a more detailed explanation of the impact of MA on powders.

During the cold spray deposition process, a magnesium (Mg) substrate was coated with High Entropy Alloys (HEAs) of Al$_{0.1-0.5}$CoCrCuFeNi and MnCoCrCuFeNi using various nitrogen gas temperatures, specifically at 650°C, 750°C, and 850°C. For this purpose, Trinity College, Dublin, Ireland, has made use of the Cold Spray deposition system as described in references [20], [21]. In both the MA and CS Al0.5HEA coatings, varying microstructures and properties were obtained by meticulously controlling the parameters of the cold spray process and the coating. In the cold spray process, nitrogen was used at a pressure of 30 bar, a type NZ1 nozzle with a standoff distance of 47mm, a powder feed rate of 9%, a nozzle speed of 15 millimeters per second, a beam distance of 2 millimeters, and four layers of coating were applied in a circular pattern. It was a 50mm x 50mm Mg substrate plate, and the powder feedstocks for the CS were -63 mm size fractions of MA Al0.5HEA powder. Furthermore, at 600oC for 1.0 hr under 0.05 bar pressure, vacuum annealing was carried out in a batch furnace at the National Heat Treatment Center, Kildare, Ireland. Tables 1 and 2 show the nominal chemical composition of coatings and samples denomination.

Table 1. Composition of HEA powders in nominal unit.

Samples Designation	Nominal chemical composition						
		Al	Cu	Cr	Co	Fe	Ni
Al$_{0.1}$CoCrCuFeNi	At%	4.22	17.38	21.2	18.67	19.74	18.79
	Wt%	1.96	19.61	19.61	19.61	19.61	19.61
Al$_{0.2}$CoCrCuFeNi	At%	8.13	16.65	20.33	17.91	18.95	18.02
	Wt%	3.85	19.23	19.23	19.23	19.23	19.23
Al$_{0.5}$CoCrCuFeNi	At%	18.3	14.8	18.09	15.96	16.84	16.0
	Wt%	9.15	18.1	18.1	18.1	18.1	18.1
	At%	-	15.62	16.81	13.6	13.6	16.86
	Wt%	-	16.7	16.7	16.7	16.7	16.7

Table 2. $Al_{0.1-0.5}$CoCrCuFeNi and $Al_{0.1}$CoCrCuFeNi chemical composition samples prepared by cold spray.

Al0.1CoCrCuFeNi	Cold spray-Temperature [°C]	650	750	850
	Denomination	A	B	C
Al0.2CoCrCuFeNi	Cold spray-Temperature [°C]	650	750	850
	Denomination	D	E	F
Al0.5CoCrCuFeNi	Cold spray-Temperature[°C]	650	750	850
	Denomination	G	H	I
MnCoCrCuFeNi	Cold spray-Temperature[°C]	650	750	850

2.2 Microstructure characterization

The details of sample preparation and microstructural characterization are provided in Ref. [22]. HEA coating and Mg substrate were intentionally removed (partially and entirely) in order to observe directly their interface from a plane-on perspective. An assessment of the coating microstructure was conducted by preparing cross-sectional samples according to standard metallographic procedures and polishing them with 0.06 mm colloidal silica. Using an energy-dispersive X-ray spectrometer (EDS) equipped with a scanning electron microscope (SEM), the coating elements were analyzed. In Figure 1, macro photos of annealed MA+CS Al0.1-0.5(Mn)CoCrCuFeNi HEA coatings have been taken at three process gas (N2) temperatures, including 650, 750, and 850 degrees Celsius.

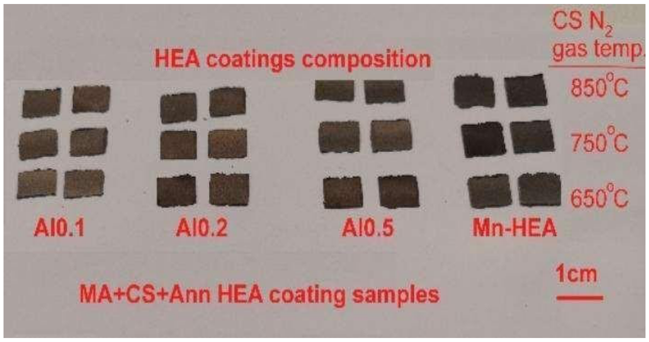

Figure 1. A macrophotograph of MA+CS Al0.1-0.5 and Mn-HEA annealed coatings on magnesium.

2.3 Surface characterization measurement

The roughness was measured using an RTP80 roughness tester by SM-Instruments. Table 3 summarizes the measurement specifications. All specimen coatings were measured for surface roughness. Measurements were made in directions parallel to and perpendicular to the direction of deposition. The cut-off dimension was 0.25 mm, and the measuring length was 1.5 mm. Each coating sample was subjected to 5 roughness measurements. Each coating sample was subjected to three roughness measurements. Particularly: Ra, Rq, Rt. Standard definitions (UNI EN ISO 4287 (2011)) indicate that they are all parameters related to the amplitude of roughness, which is the distance between peaks and valleys. In terms of the assessed profile, Ra represents the arithmetical mean deviation; Rq represents the root square of the mean deviation and is an average amplitude measurement along the height direction. In relation to the total height of the profile, Rt represents the height of the profile at its maximum height, which is the distance between its maximum peak and its minimum valley.

Table 3. Detailed specifications for the RTP80 roughness tester.

Characteristic	Description/value
Measuring range [µm]	±500
Resolution [µm]	0.001
Cut-off length [mm]	0.25
Measuring length [mm]	1.5

2.4 Microhardness measurement

Innovatest Vickers microdurometers were used to measure the HV30 microhardness profiles of the coating samples with a 3 N preload and a 15 s indentation time. Firstly, annealed coatings were stuck onto Mg substrates with glue. Each specimen's microhardness was calculated by averaging the results of 3 indentations made on the polished side cross-section.

2.5 Tribological analysis

Wear tests are conducted under ambient conditions using a pin-on-disk tribometer (Anton Paar TriTec, TRB) at the Polytechnic University of Turin. A dedicated pin was developed to ensure a tight clamping of the samples during testing. The counterparts used during the wear tests are made of quenched 100Cr6 steel with a grinding surface. Figure 2 illustrates the experimental setup used during the wear tests. Table 4 illustrates the wear testing parameters.

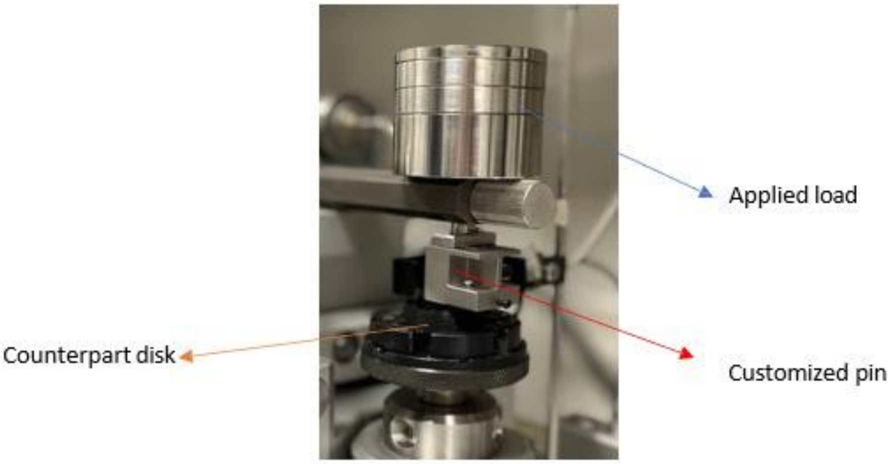

Figure 2. Experimental setup.

Table 4. Parameters of wear testing.

Wear testing parameters	
Rotational speed [rpm]	250
Normal load [N]	10
Sliding length [m]	200
Linear speed [mm/s]	235.6

3. Result and discussion

3.1 *Result and discussion*

Fig. 3a illustrates SEM-SE imaging of Al0.5 CS850oC annealed at 600˚ C. There is a similar level of roughness on the surface of the coating as in the MA+CS sample [23]. According to [23, the level of porosity is very low compared to the MA+CS sample. Surface roughness at the interface between the HEA coating and the Applied load Customized pin Counterpart disk magnesium substrate indicates a good level of bonding and adhesion. Figure 3b shows the same results for a 600oC annealed Mn-HEA CS850oC sample. The top surface roughness is also similar to that of the MA+CS counterpart. Porosity levels are also very low, interfaces are rough, and the first direct and plane on surface imaging (viewing) of the interface following mechanical removal of the Mg substrate from the HEA coating following annealing processes indicates the roughness of the interface that is responsible for its excellent bonding with the Mg substrate by the HEA coating

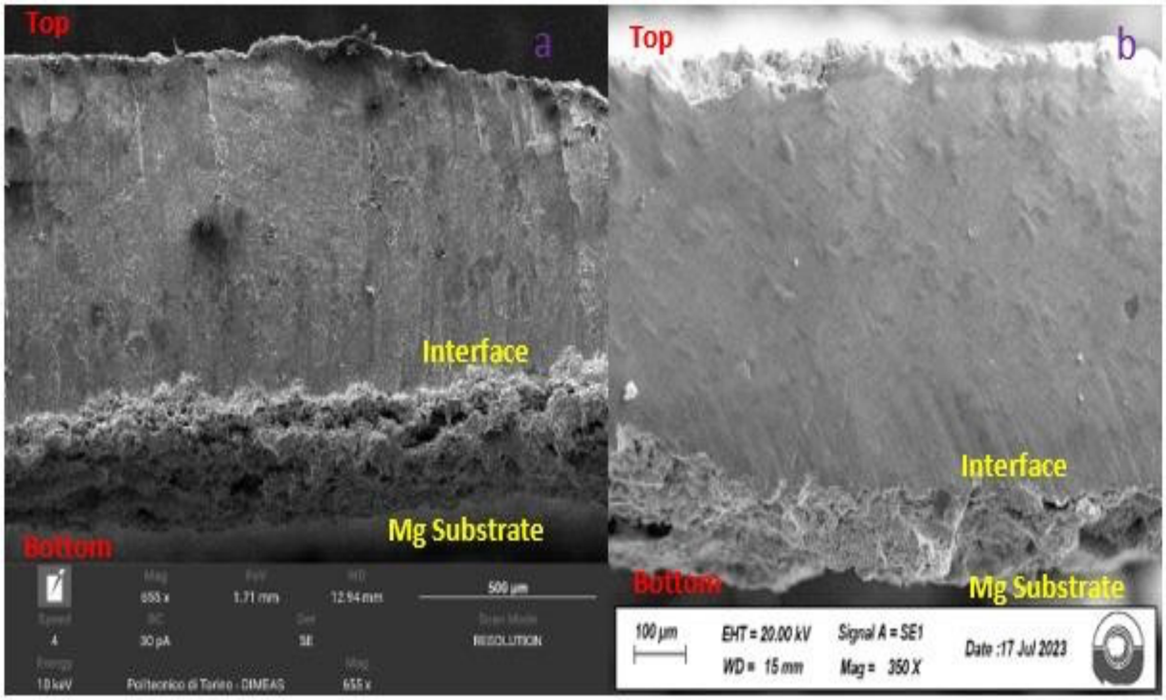

Figure 3. SEM micrograph: a) Al0.5 HEA CS 850˚C b) Mn-HEA CS 850˚C.

3.2 Surface characterization

3.2.1 Roughness measurements

An analysis of the roughness values obtained for samples with the same chemical composition at different deposition temperatures is presented in Figure 4. In Al0.1CoCrCuFeNi, all roughness parameters decrease with increasing deposition temperature. As a result of experimental scattering, a monotonic relationship between roughness parameters and deposition temperature cannot be established for other specimens.

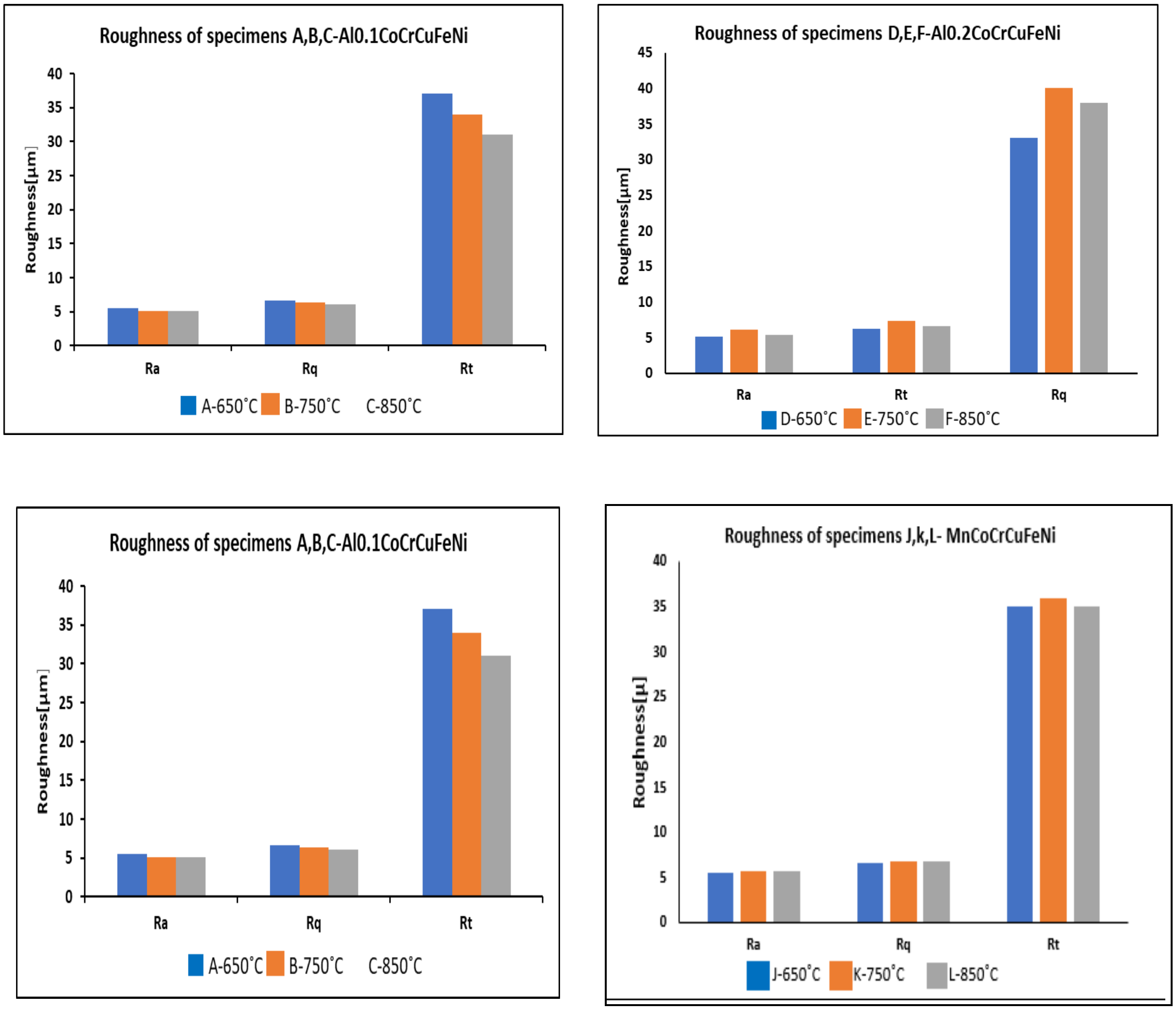

Figure 4. Roughness values.

3.3 Microhardness test

After careful polishing of the lateral surfaces of the samples, indentations were made at the interface close to the substrate. Based on three measurements, a mean value was calculated for each position. Table 5 indicates that the microhardness of a coating is highly dependent on its chemical composition. Microhardness averages for samples with Al0.1CoCrCuFeNi composition (A-C) are the lowest, whereas mean microhardness averages for samples with Al0.5CoCrCuFeNi (G-I) composition are the highest.

Table 5. Vickers microhardness measurements for all compositions.

Coating			
Al$_{0.1}$CoCrCuFeNi	A (650 °C)	Average	**113.26**
		Std dev	**4.55**
	B (750 °C)	Average	**79.48**
		Std dev	**7.76**
	C (850°C)	Average	**95.22**
		Std dev	**9.42**
Al$_{0.2}$CoCrCuFeNi	D (650 °C)	Average	**151.57**
		Std dev	**15.33**
	E (750 °C)	Average	**80.427**
		Std dev	**14.73**
	F (850 °C)	Average	**91.21**
		Std dev	**19.96**
Al$_{0.5}$CoCrCuFeNi	G (650 °C)	Average	**92.34**
		Std dev	**4.76**
	H (750 °C)	Average	**171.49**
		Std dev	**14.17**
	I (850 ◦C)	Average	**131.96**
		Std dev	**25.78**
MnCoCrCuFeNi	J (650 ◦C)	Average	**91.8**
		Std dev	**18.56**
	K (750 ◦C)	Average	**84.123**
		Std dev	**3.70**
	L (850 ◦C)	Average	**152.03**
		Std dev	**13.09**

3.4 Wear test

Figure 5 depicts the average friction coefficient observed in each test. In the case of the Al 0.1-0.5 CoCrCuFeNi composition at 750°C, the friction coefficient is at its maximum. Conversely, for the MnCoCrCuFeNi composition, an increase in the cold spray temperature leads to a decrease in the friction coefficient.

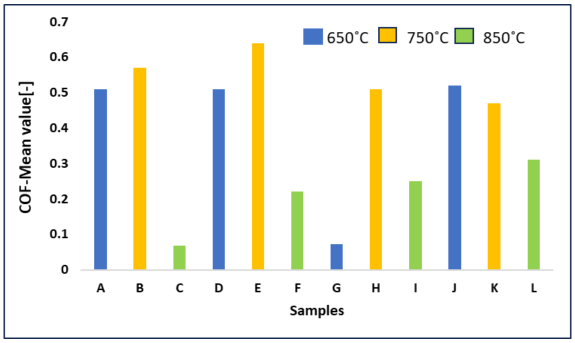

Figure 5. Coefficients of Friction (mean value) of coating samples.

4. Conclusion

The microstructure, roughness, hardness properties, and wear results of Al0.1-0.5(Mn) CoCuCrFeNi High Entropy Alloy (HEA) coatings deposited on a magnesium substrate using nitrogen as the process gas at three different temperatures were examined. Vacuum annealing was conducted in a batch furnace at a pressure of 0.05 bar for a duration of 1.0 hour at a temperature of 600 degrees Celsius. The findings from this study allow for the following conclusions to be made. According to the experimental data collected, it cannot be inferred that the roughness of the coating is affected by the chemical composition of the high entropy alloy. The chemical composition of a coating has a notable impact on its microhardness. There is a clear trend of increasing microhardness as the aluminum content in the samples rises.

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