

Article

Physical Vapor Deposition of Carbon-Doped TiAlTaZrNb High-Entropy Alloy Coatings for Corrosion Protection of H13 Steel

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Abstract

High-entropy alloy (HEA) coatings exhibit enhanced chemical stability when doped with carbon, primarily due to the strong bonding between carbon and transition metals. Typical transition metals used in these coatings include Cr, Fe, Co, Ni, Cu, Ti, V, W, Nb, Ta, and Zr. Owing to their excellent chemical stability, HEA coatings are widely employed to protect component surfaces operating in highly corrosive environments. Against this backdrop, the present study investigates the effect of carbon doping introduced via methane gas flow during the physical vapor deposition of TiAlTaZrNb HEA coatings on corrosion resistance. The morphology and structure of the coatings were analyzed by field emission scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Corrosion protection and coating resistance were assessed through potentiodynamic polarization and electrochemical impedance spectroscopy. While increasing the methane flow resulted in an approximately 34% reduction in coating thickness, the overall coating resistance increased by one order of magnitude, reaching a maximum at a methane flow rate of 9 sccm, corresponding to the carbon solubility limit. This improvement was evidenced by a decrease in the corrosion rate from $8.02 \times 10^{-2} \text{ mm y}^{-1}$ for the uncoated H13 steel to $8.00 \times 10^{-4} \text{ mm y}^{-1}$ for the HEA-coated samples. However, at higher methane flow rates, carbon precipitation and the formation of parallel microcracks contributed to an increase in corrosion rate.

Keywords: high-entropy coating; carbon-doped; H13 steel; corrosion resistance; coating stability



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1. Introduction

The design and fabrication of advanced coatings have become critical for enhancing the properties and performance of materials subjected to extreme environmental and mechanical conditions. Notable progress has been made in the development of thin coatings, such as graphene films produced via stationary atmospheric pressure chemical vapor deposition (SAPCVD), which significantly enhance corrosion resistance and reduce the friction coefficients [1]. Another widely used method for obtaining thin coatings with high chemical stability and corrosion resistance is physical vapor deposition (PVD), whose performance depends on both the chemical composition and deposition parameters.

Multi-principal element alloys have been reported to exhibit higher mixing entropy than pure metals, which can result in simplified structures and microstructures, as well as improved properties [2]. Between 1981 and 1995, Brian Cantor and Jien-Wei Yeh independently explored multicomponent solid-solution alloys in equal molar ratios [2]. However, the first results of their studies on multicomponent crystalline alloys [3] and high-entropy alloys [4] were published only until 2004. The term high-entropy alloys (HEAs) is credited to Professor Yeh, highlighting the exceptionally high entropy of these mixtures, a feature that makes them quite attractive compared to traditional alloys composed of one or two main elements [2]. HEAs are advanced metallic materials characterized by having a multi-element chemical composition. Unlike traditional alloys, in which one or two elements prevail, HEAs are designed to contain at least five main elements, each contributing significantly to the alloy's makeup [5,6]. This compositional design results in a highly disordered atomic structure, which, in turn, gives it unique and promising properties [6]. As such, these chemically complex alloys exhibit remarkable physical characteristics, including high hardness, excellent mechanical strength, good thermal stability, and outstanding resistance to wear and corrosion thanks to their reliable microstructural configuration [7].

Due to these advantages, HEAs have emerged as promising materials for various applications across industries such as aeronautics, biomedicine, and nuclear energy [8,9]. Nevertheless, the use of HEA coatings has faced limitations in some industrial sectors due to their high costs compared to traditional alloys, largely because they incorporate more expensive elements. Consequently, current research on these coatings has predominantly focused on cost-effective alternatives and fields with broader applicability [10].

Considering that the cost of corrosion worldwide is over 3% of the world's gross domestic product, it is important to develop new materials that have excellent corrosion resistance [11]. Two of the first recognized properties of HEAs were their exceptional mechanical behavior and high corrosion resistance [6]. This high corrosion resistance is attributed to the random arrangement of multiple elements within the alloy's structure, which generates a particular locally disordered chemical environment [11]. As a result of their high mixing entropy [11,12], HEA coatings typically form disordered solid-solution phases with Face-Centered Cubic (FCC), Body-Centered Cubic (BCC), or Hexagonal Close-Packed (HCP) structures, in contrast to traditional alloys, which form intermetallic compounds [13].

Several chemical elements present in HEA coatings contribute to the formation of passive oxide layers, thereby enhancing corrosion resistance. This, for instance, was reported by Nascimento et al. [14], who investigated the electronic properties of passive films formed on CoCrFeNi and CoCrFeNiAl systems in NaCl solution. Using Electrochemical Impedance Spectroscopy (EIS), the authors evaluated the corrosion behavior of HEA coatings and found that aluminum altered the crystal structure, leading to the formation of a deficient passive layer and thus increased susceptibility to pitting corrosion.

Similarly, Sim et al. [15] investigated the microstructure, mechanical properties, and corrosion resistance of a medium-entropy alloy (MEA) containing four elements (AlCoCrFe) and compared it to a HEA containing five elements (AlCoCrFeNi). The MEA demonstrated better mechanical properties and higher corrosion resistance than its five-element counterpart. These improvements were attributed to the nanostructure of the MEA, which consisted of a disordered BCC phase rich in Cr-Fe and an ordered BCC phase rich in Al-Ni. The addition of Ni was found to promote the growth of the latter, resulting in a thicker microstructure. An additional annealing process was carried out in the Ti-Al-C system to promote the formation of highly chemically stable alloys to obtain Ti₂AlC phase [16].

Studies have shown that carbon doping (using methane or other gases) during physical vapor deposition (PVD) of TiZrNbTaMoC_xNy HEA coatings promotes carbide formation without carbon precipitation, thereby improving tribo-corrosion resistance [17]. Other

studies involving carbon doping of CrNbSiTaZr HEA coatings under high methane flux rates revealed carbon precipitation in both graphitic and amorphous forms [18].

Thanks to their outstanding mechanical properties and exceptional corrosion resistance, FeCoCrNiAl HEA coatings have been extensively studied and are considered highly promising structural materials for marine applications [19]. A recent study [20] explored the microhardness, friction, and corrosion behavior of FeCoCrNiAl-based HEA coatings deposited on 304 stainless steel using laser shock peening (LSP) and PVD techniques. Samples treated with both methods demonstrated enhanced microhardness and improved wear resistance due to grain refinement. Moreover, the coefficient of friction decreased from 0.51 to 0.32 for the PVD-treated samples and to 0.13 for the LSP-treated samples. Regarding corrosion resistance, the PVD-treated samples exhibited I_{corr} and E_{corr} values comparable to those of the as-cast alloy. The LSP-treated samples, for their part, showed a 43.9% increase in these values, indicating enhanced corrosion resistance, likely due to a greater tendency to passivation compared to the PVD-treated samples [18].

In the work of Zhang et al. [21], the corrosion resistance of FeCoNiCrMnAl_x HEA coatings, deposited on 316L stainless steel via plasma spraying, was evaluated in an alkaline NaOH solution [19]. The FeCoNiCrMnAl_{0.5} and FeCoNiCrMnAl_{1.0} coatings exhibited higher passivation and corrosion potentials (−0.5277 V and −0.5116 V, respectively) than those of 316L stainless steel (−0.6572 V). These results aligned with the estimated corrosion rates: 0.529 mg/(cm²·h) for FeCoNiCrMnAl_{0.5} and 0.671 mg/(cm²·h) for FeCoNiCrMnAl_{1.0}, both of which were lower than the 0.878 mg/(cm²·h) recorded for 316L stainless steel. Collectively, these findings confirm the superior corrosion resistance of HEA coatings when compared to 316L stainless steel [21].

Wei et al. [22] investigated the effect of carbon doping on the corrosion resistance of CoCrFeNi HEAs and reported that the interstitial incorporation of carbon atoms can optimize both mechanical properties and phase configuration. However, its impact on corrosion resistance remains insufficiently explored. Interestingly, the study revealed that alloys doped with moderate carbon content exhibited better corrosion behavior in a 3.5% NaCl solution than those containing carbide phases (M₇C₃), thereby providing valuable insights for the design and application of carbon-doped HEAs.

Given their exceptional corrosion resistance and mechanical performance, HEAs have garnered increasing scientific attention. This is particularly relevant as conventional iron- or nickel-based alloys face significant limitations in advanced industrial applications operating under extreme environments, where high structural load-bearing capacity is also required [21].

Indeed, carbon doping in HEA coatings has demonstrated potential in promoting coating densification and grain refinement [23,24]. Carbon atoms can form strong covalent bonds with transition metals, thereby increasing the overall entropy and favoring the formation of binary carbides, which, in turn, improve the chemical properties of these coatings [25].

This work systematically investigates the effect of carbon content on corrosion resistance and chemical stability of TiAlTaZrNb high-entropy alloy (HEA) coatings by precisely controlling the carbon doping level via methane flow during PVD deposition. It is hypothesized that the relationship between carbon content and coating performance is non-linear, with an optimal carbon concentration that maximizes lattice incorporation while suppressing carbon precipitation. Achieving this balance is expected to enhance coating density and structural integrity, thereby significantly improving the corrosion resistance of the coatings deposited on H13 steel substrates.

2. Experimental Conditions

2.1. Substrate Preparation

The substrate used in this study was annealed H13 steel, with a hardness range of 50–55 HRC and diameter and thickness of 2.5 and 0.5 cm, respectively. The chemical composition of the H13 steel was 0.37 at.% C, 0.40 at.% Si, 0.40 at.% Mn, 5.00 at.% Cr, 3.05 at.% Mo, 0.50 at.% V, and Fe as the balance. The H13 steel substrates were polished sequentially with SiC sandpapers (#360, #600, #1000, #1500, and #2000), finally polished with cloth and alumina with a particle size of 0.3 μm until a mirror finish was obtained. After polishing, they were cleaned in an acetone–ethanol (50:50 *v/v*) solution, dried with a hot air jet, and stored in a desiccator.

2.2. PVD Coating

PVD coatings were deposited in a custom-built vacuum chamber with internal dimensions of 0.55 m $\times$ 0.6 m $\times$ 0.8 m (depth $\times$ width $\times$ height). HEA coatings were applied to the H13 steel substrates via Direct Current (DC) magnetron sputtering, using an equimolar TiAlTaZrNb alloy target. The target, measuring 500 mm in height, 100 mm in width, and 5 mm in thickness, was positioned 90 mm from the steel samples (rotation speed: 12 rpm).

The deposition parameters included a bias voltage of -90 V , a target power of 1700 W, a pressure of 0.45 Pa, an argon (Ar) flow rate of 65 sccm, and a temperature of $180\text{ }^{\circ}\text{C}$. Carbon doping was introduced through the addition of methane at flow rates of 6, 9, and 12 sccm during PVD. For clarity, the samples were designated as follows: the untreated substrate was labeled H13; the HEA-coated substrate deposited without methane flow was labeled 0 sccm; and the HEA-coated substrates deposited with methane flow rates of 6, 9, and 12 sccm were labeled accordingly.

2.3. Electrochemical Testing

Electrochemical tests were performed in three-electrode cells, where coated and uncoated H13 steel served as the working electrode (with an exposed area of 0.7854 cm²). Ag/AgCl was employed as the reference electrode, and a graphite bar as the counter electrode. The electrolyte consisted of 1.75 g of NaCl dissolved in 50 mL of distilled water, with a distance between electrodes of 5 mm. All tests were carried out using a Zahner[®] IM6 potentiostat/galvanostat (Zahner Elektrik GmbH & Co. KG, Kronach, Germany).

First, the Open Circuit Potential (OCP) was measured for one hour. Following this, EIS was conducted at the OCP using a 10 mV AC signal, with scanning frequencies from 100 kHz to 10 mHz. Ten points were collected per decade, with six repetitions at high frequencies and three at low. EIS data were fitted using an equivalent circuit model with Gamry's Echem Analyst software (version 6.25). After EIS, cathodic polarization was performed from OCP to an overpotential of -600 mV , and anodic polarization from OCP to an overpotential of 1000 mV, both at a scan rate of 1 mVs^{-1} . Three experiments were conducted for each around for sample to calculate the average and associated errors. The corrosion rate was calculated under the assumption of homogeneous corrosion. It was determined for the H13 substrate, with the average molecular weight calculated from the substrate composition, assuming a two-electron transfer during the corrosion reaction. The polarization and EIS measurements were conducted in triplicate to ensure reproducibility.

2.4. Physical Characterization

Raman measurements were obtained with a Horiba Jobin Yvon micro-Raman spectrometer (HORIBA Jobin Yvon S.A.S., Longjumeau, France), integrated with a Nikon BX41 microscope (Nikon Corporation, Tokyo, Japan) featuring a 632 nm laser source, a 50 $\times$ objective, and a 0.6D filter. X-Ray Diffraction (XRD) was carried out on 5 $\times$ 5 mm samples using

a Rigaku Miniflex600 diffractometer (Rigaku Corporation, Tokyo, Japan) with an X-ray source of Cu ($K \alpha_1/\alpha_2 = 1.54178 \text{ \AA}$), employing a step size of 0.025° , a 2θ scan range from 10° to 90° , a scan speed of $5^\circ/\text{min}$, and operating at 40 kV and 15 mA. Diffraction patterns were analyzed through High-Score Plus software (version 3.0e) with the PDF-2 database.

The morphologies of the coatings were examined with a Thermo Fisher Scientific Scios 2 LoVac DualBeam Field Emission Scanning Electron Microscope (FESEM) (Thermo Scientific, Waltham, MA, USA), which included a Focused Ion Beam (FIB) source. This system was further coupled with an UltraDry SDBX-30PM-B Energy Dispersive Spectroscopy (EDS) detector and a Quasor II Electron Backscatter Diffraction (EBSD) detector featuring a Complementary Metal-Oxide-Semiconductor (CMOS) sensor.

3. Results and Discussion

3.1. Structural and Morphological Characterization of the TiAlTaZrNb HEA Coatings

Figure 1 shows the FESEM cross-sectional images of the HEA coatings deposited by PVD on H13 steel substrates. The distribution of Ti, Ta, Nb, Zr, Al, and carbon is provided in the Supporting Information (Figures S2–S5), with the carbon mapping included solely for semi-quantitative analysis. All coatings exhibited a dense and homogeneous morphology, with no indications of porosity or microcracks between the coating and the substrate. This behavior is consistent with previous studies on PVD-deposited high-entropy alloy coatings, where the high configurational entropy and enhanced adatom mobility promote uniform microstructures. However, coatings deposited using a methane flow rate of 12 sccm exhibited around four parallel microcracks extended throughout the coating thickness, achieving a length greater than $3 \mu\text{m}$, with a uniform spacing of about $0.3 \mu\text{m}$, which may indicate potential delamination within the coating structure. Similar cracking behavior has been reported in carbon-containing hard coatings, where excessive carbon incorporation leads to the formation of brittle carbide phases and increased residual stresses [4,26]. In reactive PVD systems, the incorporation of interstitial elements such as carbon significantly modifies the stress state of the coating, promoting crack initiation and propagation [27]. Teixeira et al. [28] demonstrated that stress accumulation during deposition is a critical factor governing microcrack formation and coating delamination. The average roughness (R_a) was 0.061, 0.059, 0.008, and $0.072 \mu\text{m}$ for coatings deposited with methane flows of 0, 6, 9, and 12 sccm, respectively. The measured thicknesses of the coatings were $3.74(4)$, $2.45(2)$, $2.46(1)$, and $1.94(2) \mu\text{m}$ for depositions at a methane flow rate of 0, 6, 9, and 12 sccm, respectively. A reduction in coating thickness was observed with increasing methane flow, a result that is consistent with the findings of Kao et al. [18], who reported that methane reduces the deposition rate, leading to lower coating thickness. Additionally, carbon doping promotes further coating densification via carbide formation [16]. Titanium mapping in Figure 1 and Figures S2–S4 in the Supporting Information shows a homogeneous distribution of Ti, Ta, Nb, Zr, and Al. Nevertheless, at a methane flow rate of 12 sccm, an aluminum- and carbon-rich region was observed on the coating surface (see Figure S5 in the Supporting Information). Moreover, the presence of microcracks suggests the precipitation of additional phases in the coating deposited with a high methane flow. This phase variation can lead to delamination due to residual stress, as previously described by Teixeira [28].

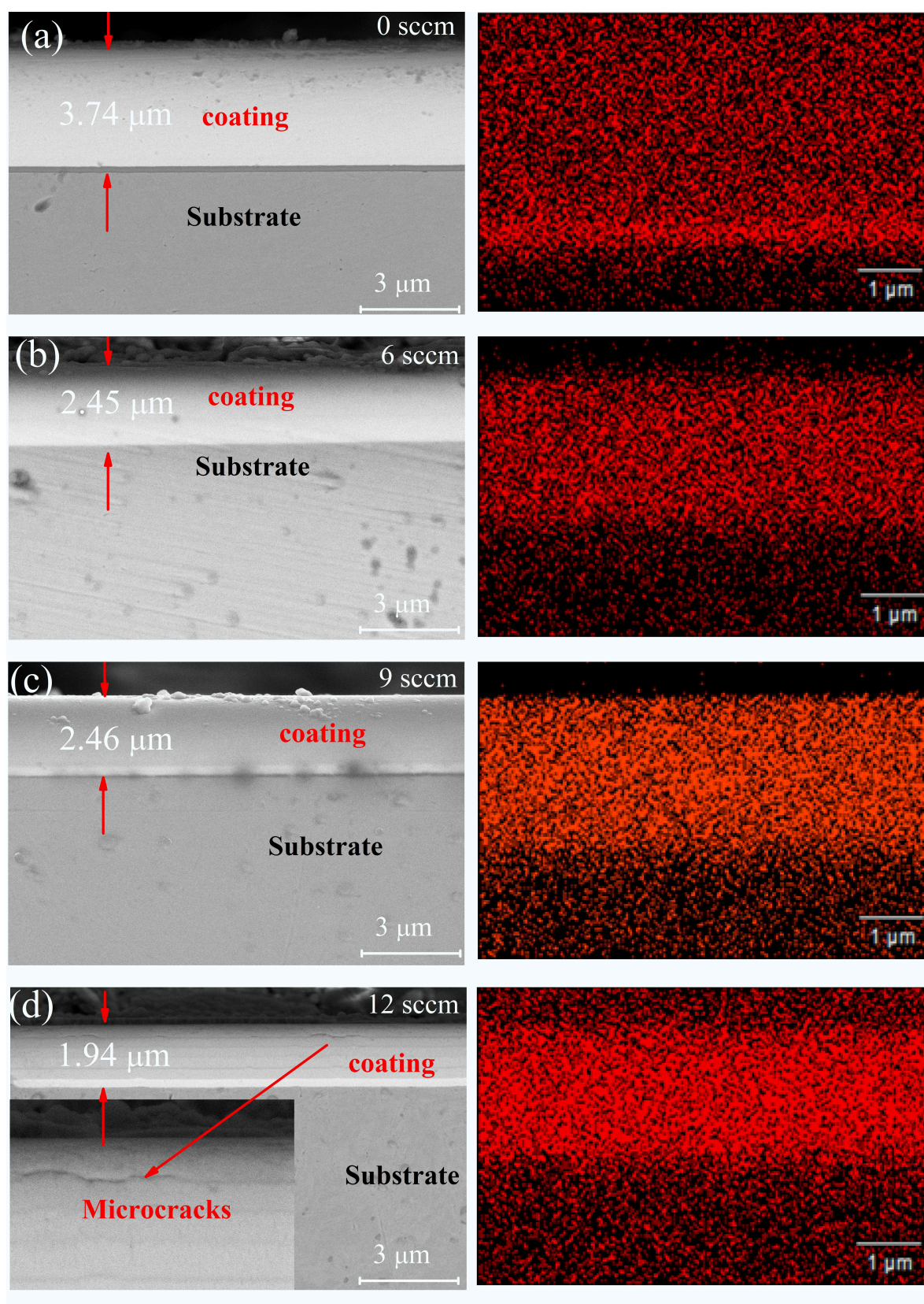


Figure 1. FESEM cross-sectional images of the TiAlTaZrNb HEA coatings deposited at methane flow rates of (a) 0 sccm, (b) 6 sccm, (c) 9 sccm, and (d) 12 sccm. The images on the right show the titanium distribution, represented by red dots. The mapping of the other elements are provided in the Supporting Information (Figures S2–S5).

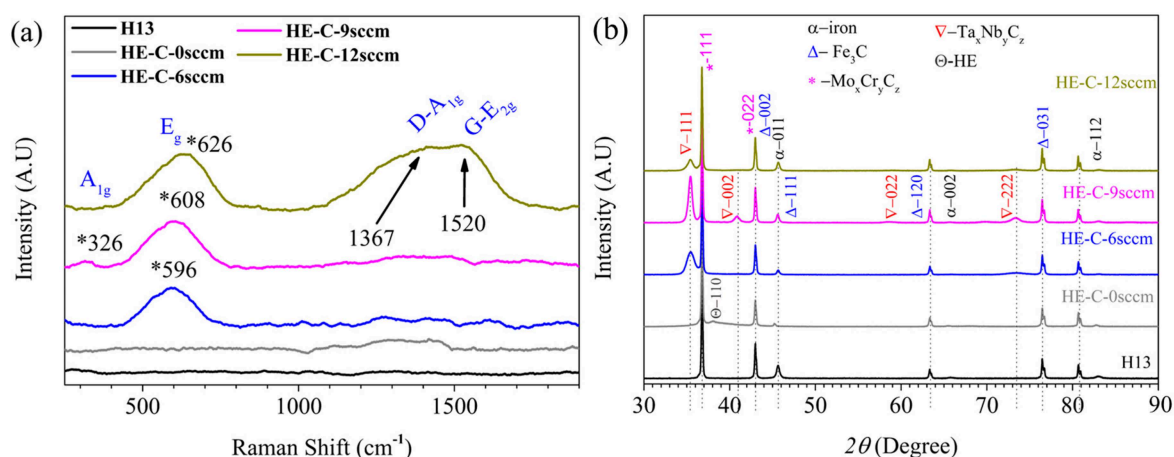
The anomalous increase in aluminum content the anomalous increase in Al and C concentration (42.48 at.%) detected at 12 sccm of CH₄ can be explained in terms of the energy delivered by ion bombardment (E_{bi}) and its impact on the film stoichiometry, as well as by preferential resputtering phenomena and phase formation thermodynamics. According to Musil [29], the total energy (E_T) supplied to the coating is a key factor in determining not only its structure, but also its elemental composition and phase. In the reactive system under study, the methane flow reduces the deposition rate (aD) due to target poisoning. Musil shows that the energy (E_{bi}) is inversely proportional to (aD) ($E_{bi} \approx (U_s \cdot i_s)/aD$), so a lower deposition rate at 12 sccm results in a drastic increase in the energy transferred per unit volume to the atoms arriving at the substrate. This excess energy produces an “atomic-scale heating” effect, providing extraordinary mobility to both incident and deposited species. Under these non-equilibrium conditions, intensified ion bombardment promotes preferential resputtering and compositional redistribution aimed at minimizing the system’s energy. Aluminum, which has a lower cohesive energy and a smaller ionic radius compared to heavier elements such as Ta, Nb, or Zr, is more susceptible to displacement. As a result, Al atoms are preferentially driven toward the growth zone (surface) through atomic migration and resputtering processes, contributing to the observed surface enrichment. Additionally, from a thermodynamic perspective, the formation of nanocomposites is constrained by the solubility limit of the added elements. Excess Al cannot be fully incorporated into the solid solution of the high-entropy alloy, leading to phase segregation. Consequently, the system stabilizes through the formation of an Al- and C-rich surface region, demonstrating that precise control of ion bombardment energy is critical to avoid undesired deviations in coating stoichiometry. Additionally, the high chemical affinity of aluminum for carbon (i.e., the low Gibbs free energy associated with the formation of Al carbides) promotes the segregation of an Al–C-rich phase during the final stages of coating growth. The precipitation of these phases embrittles the structure, which correlates directly with the observed microcrack formation and increased risk of delamination, in agreement with Teixeira’s description of failure driven by residual stress accumulation at hardened interfaces. Teixeira demonstrates that such failure is not a manufacturing defect, but rather a well-documented physical phenomenon (critical stress-induced collapse) associated with the excessive hardening of the aluminum carbide phase [30].

Chemical composition analyses were performed by EDS to evaluate changes in the chemical variation during the coating deposition. Table 1 presents the changes in the chemical composition of the coatings deposited under varying methane flow rates. As can be seen, Ti content decreased with increasing methane flow, whereas the concentration of other elements remained constant at methane flows of 6 and 9 sccm and dropped suddenly at a methane flow of 12 sccm. Slightly lower aluminum deposition was observed with a methane flow of 6 sccm. In contrast, aluminum content increased significantly at a methane flow of 12 sccm, accompanied by reductions in Ti, Zr, Nb, and Ta. The addition of CH₄ during PVD deposition affects the deposition rates of the constituent elements as a consequence of sputtering yield dependence. In particular, Ta, followed by Zr and Ti, is more strongly influenced due to its lower sputtering yield and higher affinity for carbide formation, whereas Al is comparatively less affected [31,32]. This imbalance may induce compositional deviations and contribute to the formation of microstructural defects at higher methane flow rates. These results suggest that the coating deposited at a methane flow of 12 sccm promotes a high carbon content, undergoes significant aluminum evaporation, which may lead a non-uniform chemical composition and aluminum precipitation through the formation of an immiscible hexagonal phase [33]. In addition, the formation of microcracks may be related to phase precipitation in the coatings.

Table 1. Changes in atomic percentage of elements in the coatings deposited under varying methane flow rates.

Element	0 sccm	6 sccm	9 sccm	12 sccm
Al (at.%)	18.72	12.46	18.65	42.48
Ti (at.%)	23.52	22.35	20.34	15.10
Zr (at.%)	16.68	16.55	17.48	12.56
Nb (at.%)	21.23	20.76	21.25	14.93
Ta (at.%)	19.85	27.88	22.29	14.93
ΔS_{mix} (J mol ^{−1} K ^{−1})	−13.33	−13.09	−13.35	−12.28

Figure 2a displays the Raman spectra of the H13 steel substrate and the substrates with a HEA coating deposited at varying methane flow rates. At the methane flow rates of 6 and 9 sccm, peaks were observed at Raman shifts of 326 cm^{−1} and in the 596–626 cm^{−1} range, which correspond to the A_{1g} and E_g vibrational modes of the tantalum, niobium, aluminum, zirconium, and titanium carbides, respectively. Importantly, the peak positions vary depending on the presence of metals such as niobium, aluminum, or zirconium [25,34].

**Figure 2.** (a) Raman spectra. (b) XRD patterns of the H13 steel substrate and the substrates with a HEA coating (TiAlTaZrNb) deposited under varying methane flow rates (0, 6, 9, and 12 sccm), * (Ti, Al, Ta, Zr, Nb)C.

At a methane flow of 12 sccm, additional peaks appeared at Raman shifts of 1367 and 1520 cm^{−1}, which are attributed to the A_{1g} symmetric vibration of amorphous carbon (D-band) and the E_{2g} symmetric vibration of graphitic carbon (G-band), respectively [35,36]. At lower methane flow rates, carbon precipitation was not observed. The coating deposited without methane flow, for its part, exhibited no peaks. Figure 2b illustrates the XRD patterns of the H13 steel substrate and the substrates with a HEA coating deposited at varying methane flow rates. As observed, the H13 steel substrate showed peaks at 2θ values of 45.6°, 65.6°, and 83.0°, corresponding to the (011), (002), and (112) planes of the α-Fe phase, respectively, which have a cubic structure and Im-3m space group (ICSD 98-015-9354) [37]. Also, peaks appeared at 2θ values of 43.1°, 45.8°, 63.3°, and 76.5°, attributed to the (002), (111), (120), (031) planes of the FeC₃ phase, respectively, which has a hexagonal structure and space group P6222 (ICSD 98-016-3151) [38]. Finally, peaks at 2θ values of 36.9° and 42.8° were linked to the (111) and (022) planes of the chromium carbide phase, respectively, which has a cubic structure and Fm-3m space group (ICSD 98-007-6803) [39].

The substrate with a HEA coating deposited without methane flow exhibited a peak at a 2θ value of 38.0°, related to the (110) of hexagonal structure with ICSD 98-010-5527 [40,41]. With methane addition, this peak disappeared, and new peaks appeared at 2θ values of

35.2°, 40.8°, 58.5°, and 73.4°, corresponding to the (111), (002), (022), and (222) planes of the tantalum–niobium carbide, which has a cubic structure and Fm-3m space group (ICSD 98-007-7218) [42]. These peaks were more intense at a methane flow rate of 9 sccm and decreased in intensity at a methane flow rate of 12 sccm. The semiquantitative analyses of tantalum–niobium carbide show values of 13%, 26%, and 5% for methane flow rates of 6, 9, and 12 sccm, respectively. According to these results, at 12 sccm, carbon tends to precipitate as confirmed by the Raman analysis and a lower amount of tantalum–niobium carbide is formed in the coating [43]. The characteristic peaks in the Raman spectrum of the HEA deposited at a methane flow of 12 sccm, associated with carbon, indicate that microcrack formation may be related to carbon precipitation during PVD deposition, as shown in Figure 1d.

3.2. Electrochemical Measurements

3.2.1. Potentiodynamic Polarization

Figure 3 shows the OCP of the H13 steel substrate and the substrates with a HEA coating deposited under varying methane flow rates. Both the H13 steel substrate and the coated sample deposited without methane flow exhibited more cathodic potentials, likely due to an increase in anodic activity. After 2600 s, a steady-state potential was reached.

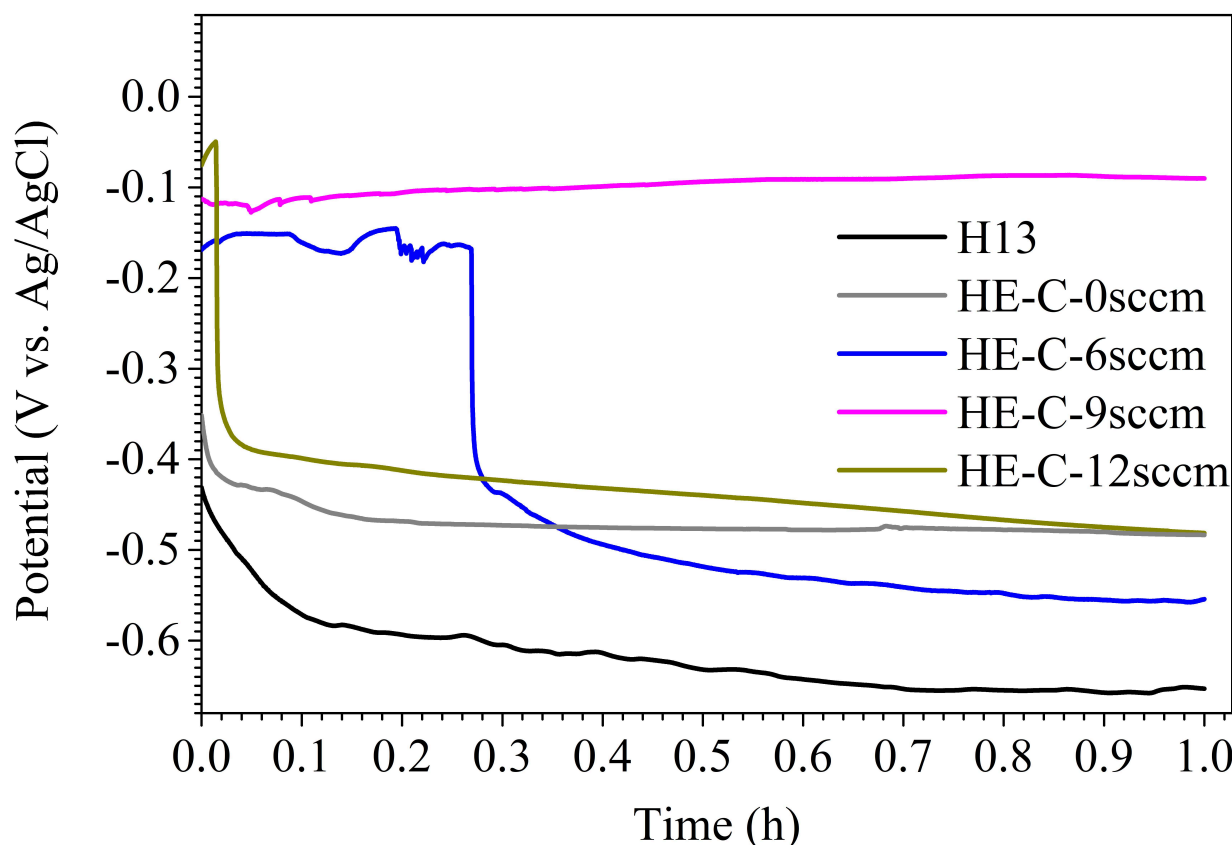


Figure 3. OCP stabilization in the uncoated and coated H13 steel (influence of methane flow on potential and coating stability).

A shift of the OCP to more anodic values was observed for the coatings deposited at the methane flow rates of 6 and 9 sccm, suggesting a decrease in anodic activity. The coating deposited at a methane flow of 6 sccm exhibited a sudden drop in the OCP after 1000 s (see Figure S6), indicating electrolyte penetration through the coating. In contrast, the coating deposited at a methane flow rate of 9 sccm displayed higher stability, with the OCP remaining stable even after 3600 s. For its part, the coating deposited at a methane flow of 12 sccm

showed a rapid decline in the OCP after 100 s, implying that carbon precipitation—as confirmed by Raman spectroscopy—affects the coating’s resistance to electrolyte penetration. Overall, these results indicate that a methane flow rate of 9 sccm during deposition leads to a controlled electrolyte permeability and improves coating stability.

Figure 4 presents the potentiodynamic polarization curves of the H13 steel substrate and the substrates with a HEA coating (TiTaZrNbAl) deposited at varying methane flow rates. In the cathodic region, two Tafel slopes were identified. The first slope of $299.1 \text{ mV dec}^{-1}$ at lower overpotentials is attributed to oxygen reduction, while the second, occurring between 69.36 and $151.5 \text{ mV dec}^{-1}$ at higher overpotentials, corresponds to hydrogen reduction [44]. At intermediate overpotentials between these two slopes, a diffusion-controlled region for the oxygen reduction reaction was observed, where the current remained almost constant [45].

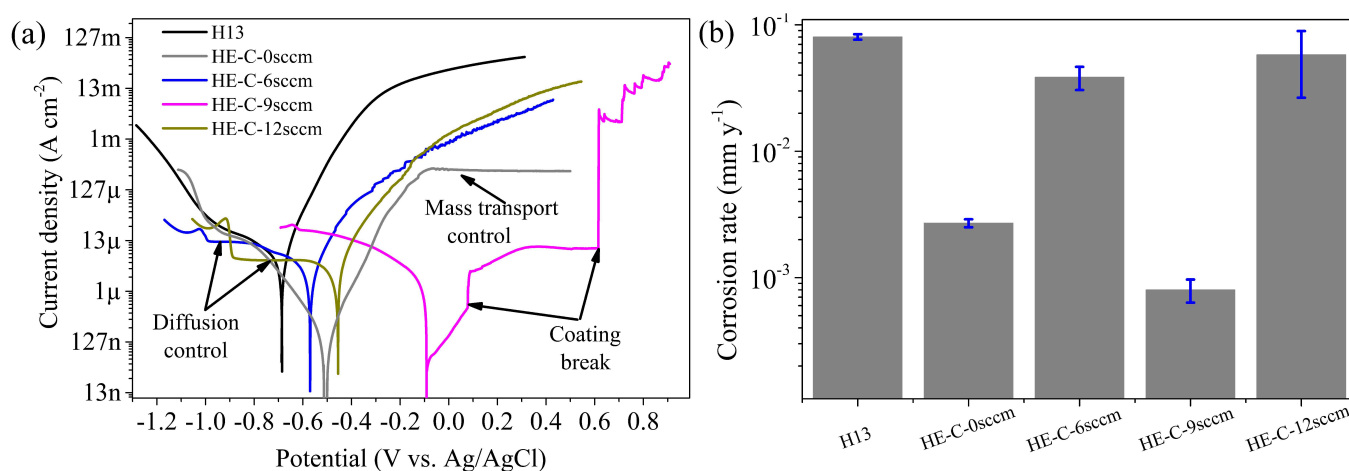


Figure 4. (a) Potentiodynamic polarization curves at 20°C in a 3.5% *w/w* NaCl electrolyte. (b) Corrosion rates.

A broad diffusion-controlled region was identified in the HEA coatings deposited at the methane flow rates of 6 and 12 sccm. In the second Tafel slope, a sudden rise in current was recorded, which may be associated with the breakdown of the coating caused by gas generated during the reduction process, as evidenced in the Supporting Information (Figure S1). These findings suggest that the hydrogen gas trapped at the coating–substrate interface can break the coating. In the anodic region, the uncoated steel exhibited a single Tafel slope of 84.3 mV dec^{-1} , whereas the coated samples showed slopes ranging from 121 to 204 mV dec^{-1} . For the HEA coating deposited at a methane flow rate of 9 sccm (HEA-C-9 sccm), a sudden increase in current occurred at anodic overpotentials between 200 and 700 mV, indicating a breakdown of the protective layer. Interestingly, both the coating deposited without methane flow and the one deposited with a methane flow rate of 9 sccm demonstrated an anodic overpotential region where the current remained nearly stable, suggesting mass-transport control.

Overall, the polarization curves reveal that as methane flow increases during coating deposition, the corrosion current becomes limited by the anodic reaction. In particular, in the coating deposited at a methane flow rate of 9 sccm, the anodic current was lower than the cathodic current, which could be associated with the formation of a more compact layer. The corrosion rate of the substrate with a HEA coating deposited at a methane flow of 9 sccm was $8.00 \times 10^{-4} \text{ mm/year}$, representing a one-order-of-magnitude reduction compared to the HEA coating deposited without methane flow (0 sccm). However, at higher methane flow rates, the corrosion rate increased, likely due to the precipitation of carbon in the PVD coating, as evidenced in the Raman spectra in Figure 2.

In contrast, the corrosion rate was reduced to one-third in the coating deposited without methane flow, an effect that is in agreement with the greater coating thickness observed in Figure 1. Despite the coatings deposited with methane flow being thinner than those without, the corrosion data in Figure 4b show that a methane flow rate of 9 sccm provides the highest corrosion resistance among all the PVD coatings. The superior corrosion resistance of carbon-doped high-entropy ceramic coatings is attributed to the formation of dense and chemically stable carbide phases, as evidenced by semiquantitative XRD analysis of Nb–Ta carbides, which reduce atomic diffusion and facilitate the development of compact passive films that act as effective barriers against corrosive species [46–48].

3.2.2. Electrochemical Impedance Spectroscopy

Figure 5 displays the Nyquist–Bode plots and electrical parameters of EIS measurements at the OCP for the H13 steel substrate and the substrates with HEA coatings. Two capacitive loops and two time-constant process (see Figures S7–S11 in the Supplementary Information and Bode plot) were observed: the first appeared at intermediate frequencies (10–90 Hz), and the second at low frequencies (0.2–2 Hz). The high-frequency intercept on the x-axis corresponds to the electrolyte resistance (R_s).

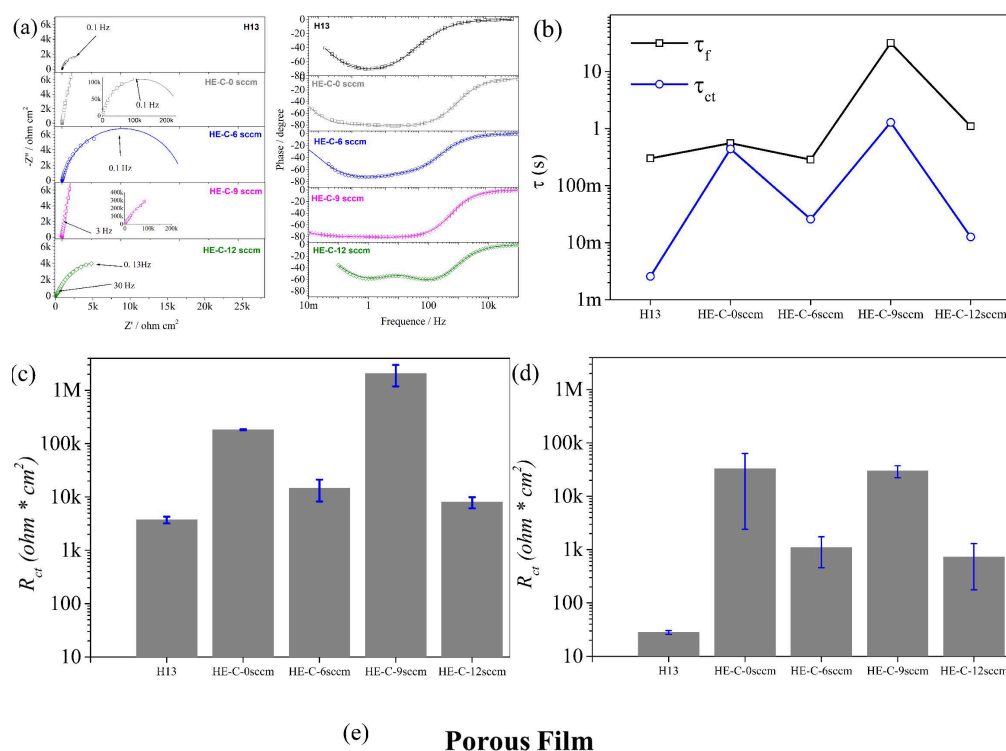


Figure 5. (a) Nyquist plots and Bode plot at the OCP for the H13 steel substrate and the substrates with a HEA coating in 3.5% NaCl at 20 °C. (b) Characteristic times for charge transfer and protective layer processes. (c) Film resistance. (d) Charge transfer resistance. (e) Equivalent circuit model.

The loop observed at intermediate frequencies is attributed to the charge transfer resistance (R_{ct}), in parallel with the double-layer capacitance at the substrate–coating interface (CPE_{dl}). The second loop, seen at low frequencies, is associated with the resistance (R_f) of the corrosion products layer formed on the uncoated H13 steel or with the resistance of the coating itself in the case of PVD-coated substrates—alongside its capacitance (CPE_f) [49]. The equivalent circuit model used to model this behavior is shown in Figure 5e. Effective capacitances were calculated as described by Bisquert et al. [50].

Despite the thin films produced during PVD using methane flow, the addition of methane improves the coating resistance (R_f) and increases the charge transfer resistance (R_{ct}). This implies that the permeability of the ions involved in the corrosion reactions decreases with carbon doping (using methane flow). Interestingly, although the coating deposited without methane flow exhibited better corrosion resistance than the one deposited with a methane flow of 6 sccm, the resistance of the coating deposited with a methane flow rate of 9 sccm was one-order-of-magnitude higher. At a methane flow of 12 sccm, the coating resistance decreased, which may be due to carbon precipitation, as observed in the Raman spectra in Figure 2. Carbon precipitation reduces the formation of carbides, which provide chemical stability to the coating [25]. Additionally, it could lead to local phase variations, potentially increasing the kinetics of the oxidation–reduction reactions due to the presence of galvanic couples.

Table 2 summarizes the structural characteristics and corrosion performance of the coatings deposited at varying methane flow rates. Semi-quantitative analyses of tantalum and niobium carbides were conducted to evaluate the effect of carbide formation on coating resistance and corrosion behavior. The observed coating resistance in H13 steel is mainly associated with the passive layer. The thickest coatings were found in the samples deposited without methane flow, suggesting that methane addition may affect both the deposition rate and densification of the coatings. Moreover, the presence of carbides as was described in XRD (Figure 2b) contributes to enhance the coating’s resistance as evidenced by Figure 5c and Table S2 in the Supporting Information, thereby reducing corrosion rates (see Table 2).

Table 2. Summary of the effect of methane flow on coating resistance and comparison with previous studies.

Sample	Coating Thickness (μm)	TaNbC Amount (%)	Coating Resistance (ohm cm^2)	Corrosion Rate (mm y^{-1})	Ref.
H13 steel		--	3.74×10^3	8.02×10^{-2}	This study
HEAC-0sccm	3.74 (4)	--	1.84×10^5	2.70×10^{-3}	This study
HEAC-6sccm	2.45 (2)	13	1.47×10^4	3.85×10^{-2}	This study
HEAC-9sccm	2.46 (1)	26	2.09×10^6	8.00×10^{-4}	This study
HEAC-12sccm	1.92 (2)	5	8.04×10^3	5.79×10^{-2}	This study
AlCoCrFeNi (electrospark)	20	--	--	4.56×10^{-5}	[51]
CrNbSiTaZr-22 sccm (PVD)	1.75	--	--	1.14×10^{-2}	[18]
FeCoCrNiAl0.1 (PVD)	1.5	--	--	7.32×10^{-2}	[20]

Comparative analyses with previous studies indicate that thick coatings deposited by electrospark alloying generally exhibit superior corrosion resistance. Nevertheless, the PVD coatings developed in the present study achieved corrosion rates two orders of magnitude

lower than those reported in the literature, both with and without methane incorporation (see Table 2).

4. Conclusions

The thickness of the HEA coatings developed in this study was found to decrease with increasing methane flow from 3.74 μm in the absence of methane to 1.92 μm at a methane flow rate of 12 sccm. However, coatings deposited at a methane flow of 12 sccm showed microcrack formation, which compromised the coating's mechanical integrity. In contrast, an intermediate methane flow of 9 sccm resulted in a more compact coating, free of carbon precipitation, thereby enhancing structural stability and lowering corrosion rates.

Although the coating deposited at a methane flow rate of 9 sccm was thinner than that produced without methane flow, it exhibited higher resistance, as confirmed by EIS. Raman spectroscopy and XRD analyses revealed the formation of tantalum, niobium, and titanium carbides, which contributed to increased coating densification.

The highest corrosion resistance was achieved at a methane flow of 9 sccm. In comparison, coatings deposited at higher methane flows (12 sccm) exhibited carbon precipitation in both amorphous and graphitic forms, which reduced the coating's durability and corrosion protection. The obtained polarization curves further indicated that mass-transport control through the coating influences both cathodic and anodic reactions in carbon-doped coatings.

Overall, the corrosion rates of the coatings developed in the present study were two orders of magnitude lower than those reported for other PVD coatings, with a measured value of $8.00 \times 10^{-4} \text{ mm y}^{-1}$.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met16060681/s1>, Figure S1. HE-6sccm Coating after cathodic polarization. Figure S2. Distribution of elements in the coating deposited with 0 sccm of methane Flow. Figure S3. Distribution of elements in the coating deposited with 6 sccm of methane Flow. Figure S4. Distribution of elements in the coating deposited with 9 sccm of methane Flow. Figure S5. Distribution of elements in the coating deposited with 12 sccm of methane Flow. Figure S6. OCP reproducibility of HEC deposited with a methane flow of 6 sccm. Figure S7. Bode plot H13 substrate. Figure S8. Bode plot HE-C-0sccm. Figure S9. Bode plot HE-C-6sccm. Figure S10. Bode plot HE-C-9sccm. Figure S11. Bode plot HE-C-12sccm. Table S1. Carbide quantification by XRD. Table S2. Electrochemical parameters calculated from EIS spectrum and corrosion rate. Table S3. Chemical composition.

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