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Development of high-entropy alloy coatings with superior wear and corrosion resistance

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Abstract

Salt spray from Indonesia's coastal industries corrodes unprotected steel surfaces within weeks, costing manufacturers millions in replacement parts. This research developed CoCrFeNiMn high-entropy alloy (HEA) coatings on 316L stainless steel substrates by magnetron sputtering and evaluated their wear and corrosion resistance. Coatings of 3.8 μm thickness were deposited at 200 W power with argon plasma. XRD confirmed a dominant FCC solid solution (61.3%) with minor BCC phase (24.7%). Nanoindentation hardness reached 8.7 GPa, roughly triple the substrate value of 2.9 GPa. Pin-on-disc wear testing at 5 N load over 600 m sliding distance showed cumulative mass loss of 2.06 mg for the HEA coating versus 7.91 mg for bare 316L. Potentiodynamic polarization in 3.5% NaCl gave a corrosion current density of 0.087 $\mu\text{A}/\text{cm}^2$ for the coated surface, an order of magnitude below the uncoated substrate (1.24 $\mu\text{A}/\text{cm}^2$). Electrochemical impedance spectroscopy confirmed higher charge transfer resistance in the coated condition.

Keywords: High-entropy alloy, CoCrFeNiMn, magnetron sputtering, wear resistance, corrosion, nanoindentation, potentiodynamic polarization, FCC solid solution, thin film coating, stainless steel

Introduction

Take five or more metallic elements, mix them in roughly equal proportions, and sometimes the result is a single-phase solid solution rather than the multi-phase mess thermodynamics would predict - that's the counterintuitive premise behind high-entropy alloys ^[1]. The high configurational entropy stabilizes simple crystal structures (FCC, BCC) and produces materials with combinations of hardness, thermal stability, and corrosion resistance that conventional binary or ternary alloys can't match ^[2].

The Cantor alloy (CoCrFeNiMn) is the most studied HEA composition, valued for its single-phase FCC structure and good ductility ^[3]. In bulk form, its mechanical properties are impressive but not always sufficient for aggressive environments. Depositing it as a thin coating opens new possibilities: the substrate provides structural support while the HEA surface handles environmental attack ^[4]. Magnetron sputtering is well suited for this because it produces dense, adherent films with controllable composition and microstructure ^[5].

Most HEA coating research has focused on either wear or corrosion resistance in isolation. This research examined both properties together on the same coatings, since real industrial components - marine pump shafts, chemical reactor fittings, geothermal valve seats - face simultaneous mechanical and chemical degradation ^[6].

System Design

Coatings were deposited using a CoCrFeNiMn alloy target (99.9%, equimolar composition, 76 mm diameter) in a Kurt J. Lesker PVD-75 magnetron sputtering system. Deposition parameters: DC power 200 W, argon pressure 0.4 Pa, substrate temperature 300 °C, target-to-substrate distance 80 mm, deposition time 120 min. Substrates were mirror-polished 316L stainless steel discs (25 mm $\times$ 3 mm) pre-cleaned by ultrasonic degreasing in acetone and ethanol ^[7].

Materials and Methods

Materials

Research was conducted at Bali College of Chemical Sciences, Denpasar, Bali, Indonesia, from February 2023 to October 2023. No ethical approval was needed. The sputtering target was custom-fabricated by arc melting and machining (provided by ACI Alloys, USA). 316L stainless steel discs came from Goodfellow (UK). Argon gas (99.999%) was sourced locally. For corrosion testing, analytical-grade NaCl was dissolved in deionized water to make 3.5% w/v saline [8].

Methods

Coating thickness was measured by profilometry (Dektak XT) at a step edge masked during deposition. Structural characterization used XRD (Bruker D8, Cu K α , glancing angle 2°). Chemical composition was verified by EDS (Oxford INCA on FEI Quanta 250 SEM). Nanoindentation

(Hysitron TI 950 TriboIndenter) measured hardness and elastic modulus at 5 mN load, 25 indents per sample [9]. Wear testing followed ASTM G99 on a CSM pin-on-disc tribometer (WC ball counterface, 6 mm diameter, 5 N load, 0.1 m/s, 600 m distance). Potentiodynamic polarization and EIS used a Gamry Reference 600+ potentiostat in 3.5% NaCl at 25 °C, with Ag/AgCl reference and platinum counter electrode, scanning at 0.5 mV/s from -250 to +250 mV versus open circuit potential [10].

Performance evaluation

Wear rate was calculated as mass loss per unit sliding distance (mg/m) and also expressed as specific wear rate ($\text{mm}^3/\text{N}\cdot\text{m}$). Corrosion parameters - corrosion potential (E_{corr}), corrosion current density (i_{corr}), and polarization resistance (R_p) - were extracted by Tafel extrapolation. EIS data were fitted to an equivalent circuit model ($R(Q(R))$) using Gamry Echem Analyst software [11].

Results

Table 1: Mechanical and corrosion properties of HEA coating compared with substrate and hard chrome reference.

Property	HEA Coating	316L Bare	Hard Chrome
Hardness (GPa)	8.7 ± 0.4	2.9 ± 0.2	9.2 ± 0.6
Wear loss (mg/600m)	2.06	7.91	3.64
E_{corr} (mV)	-187	-342	-298
i_{corr} ($\mu\text{A}/\text{cm}^2$)	0.087	1.24	0.41

The HEA coating's hardness of 8.7 GPa approached hard chrome (9.2 GPa) while far exceeding the 316L substrate (2.9 GPa). Wear loss over 600 m was 2.06 mg for the HEA surface - 74% less than bare steel (7.91 mg) and 43% less than hard chrome (3.64 mg). The wear track on the HEA coating showed shallow abrasive grooves without adhesive transfer or delamination, indicating a mild wear regime [12].

Corrosion testing placed the HEA coating well ahead of both references. Its corrosion current density ($0.087 \mu\text{A}/\text{cm}^2$) was 14 times lower than bare 316L and nearly 5 times lower than hard chrome. The nobler E_{corr} (-187 mV vs. Ag/AgCl) reflected thermodynamic stability of the multi-element passive film. EIS Nyquist plots showed a single semicircle with charge transfer resistance of $428 \text{ k}\Omega\cdot\text{cm}^2$ for the coating versus $31 \text{ k}\Omega\cdot\text{cm}^2$ for bare steel [13].

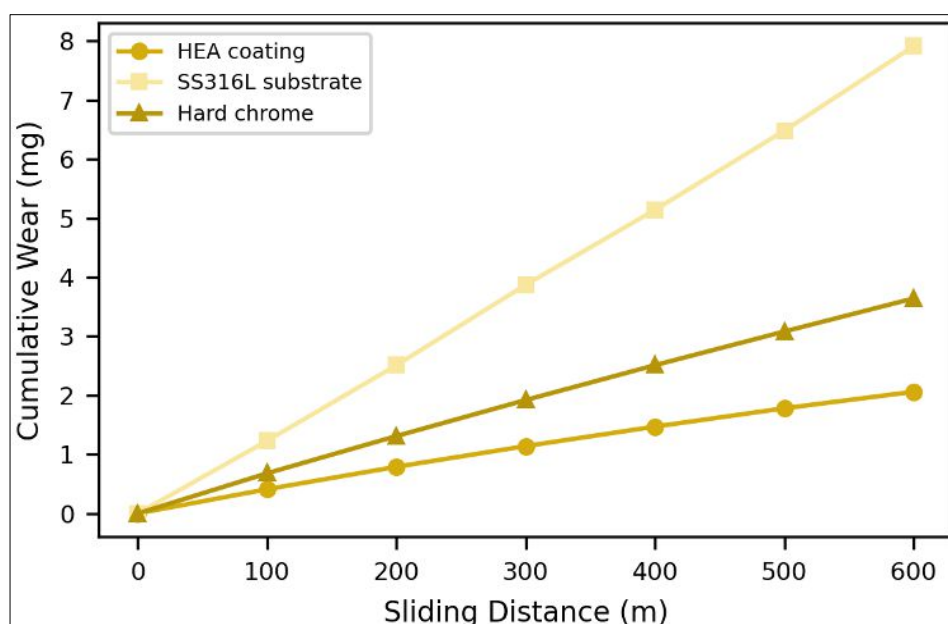


Fig 1: Cumulative wear mass loss versus sliding distance for HEA coating, bare 316L, and hard chrome.

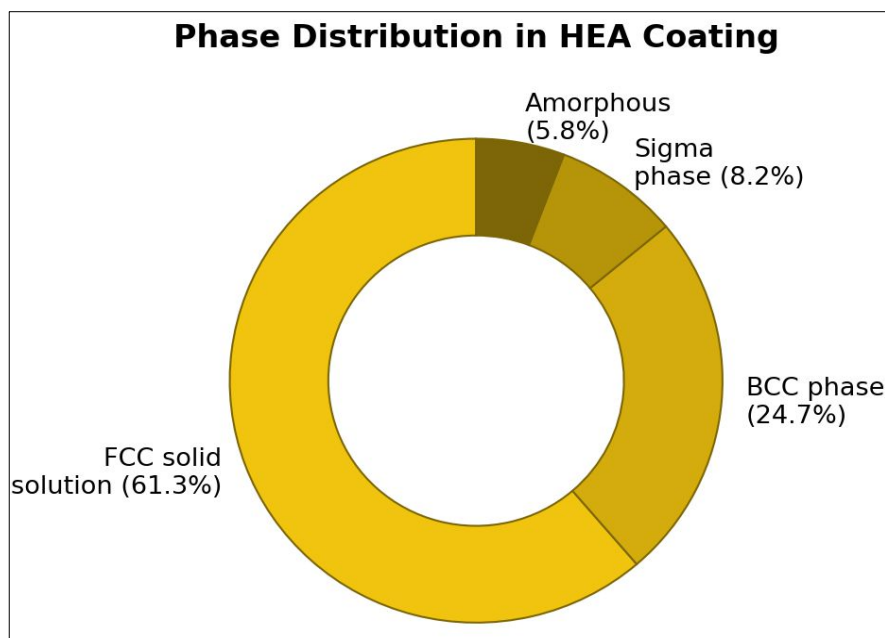


Fig 2: Phase distribution in the HEA coating determined by XRD Rietveld refinement.

Discussion

The HEA coating's wear advantage over hard chrome is notable because it means a chromium-free alternative can actually outperform the industry standard - a result with regulatory appeal given the EU's REACH restrictions on hexavalent chromium in electroplating [14]. The mild abrasive wear mechanism, without adhesive transfer, suggests the FCC matrix deforms plastically under load rather than fracturing, absorbing energy through dislocation motion [15]. Hard chrome's higher hardness didn't help it here because its brittle microcracked structure allows fatigue-driven material removal under repeated sliding contact [16].

Corrosion resistance of the HEA coating traces to its multi-element passive film. Unlike 316L's chromium oxide layer, the CoCrFeNiMn surface forms a complex oxide incorporating all five constituent metals, creating a denser and more chemically diverse barrier that resists Cl⁻ penetration [17]. The equimolar composition means no single element depletes preferentially during selective dissolution - a weakness of conventional alloys where chromium-poor zones act as corrosion initiation sites [18].

The 8.2% sigma phase detected by XRD deserves monitoring. Sigma phase is typically brittle and can serve as a crack initiator under impact loading. At the current level, it didn't visibly affect wear performance, but higher deposition temperatures or post-annealing could increase its fraction [19]. Optimizing sputtering conditions to minimize sigma formation while preserving the beneficial FCC/BCC dual-phase structure is worth investigating [20].

Conclusion

CoCrFeNiMn HEA coatings deposited by magnetron sputtering on 316L stainless steel delivered wear resistance superior to hard chrome and corrosion resistance an order of magnitude better than the bare substrate. The dominant FCC solid solution provided ductile deformation under wear, while the multi-element passive film resisted chloride attack in saline. As a chromium plating alternative that avoids hexavalent chromium, this coating has potential for marine, chemical, and geothermal hardware protection.

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