

Effect of microstructure on corrosion and wear behavior of laser-clad CoCrFeMo_{0.85}Ni compositionally complex alloy coatings

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ARTICLE INFO

Keywords:

Compositionally Complex Alloy
High-Entropy Alloy
Laser Cladding
Corrosion Resistance
Wear Behavior
Mechanical Alloying
Gas Atomization

ABSTRACT

Laser-clad CoCrFeMo_{0.85}Ni compositionally complex alloy (CCA) coatings were fabricated from gas atomized (GA) and mechanically alloyed (MA) powders, forming dense, adherent multilayer structures of FCC, BCC, and intermetallic σ -phases. The MA resulted in a more heterogeneous multiphase microstructure and lower hardness. Both coatings exhibited localized pitting corrosion. The GA produced a more chemically uniform FCC-based microstructure with spatially segregated σ -phase, reducing local electrochemical driving forces for micro-galvanic corrosion and pit initiation, although localized breakdown persisted once passivity was lost. Wear performance in both coatings was governed by abrasive and adhesive mechanisms facilitated by oxide formation, with maximum wear depth below 10 % of the coating thickness.

1. Introduction

Compositionally complex alloys (CCAs), also referred to as multi-principal element alloys (MPEAs) or high-entropy alloys (HEAs), represent a novel class of materials comprising four or more principal elements in near-equiatomic or significant proportions [1]. The expansive compositional space of CCAs offers a unique opportunity to tailor microstructures and properties for specific applications, which has led to growing interest in their mechanical strength [2,3], thermal stability [4,5], and corrosion resistance [6,7].

Among these, the CoCrFeMo_xNi alloy family has attracted considerable attention due to its complementary combination of strength, ductility, and corrosion resistance. Unlike conventional alloys, where strength and ductility are often inversely related, CoCrFeMo_xNi alloys can achieve a favorable strength–ductility synergy through the formation of intermetallic phases [8]. Even small additions of Mo have been shown to significantly enhance strength and hardness via precipitation of σ and μ phases without causing severe embrittlement [8–11]. Higher

Mo contents (e.g., $x = 1$) further increase hardness [12,13]; however, coarsening of intermetallic phases and preferential grain boundary corrosion have been reported at elevated Mo levels [14]. Nevertheless, Mo promotes the formation of dense, protective oxide films, enhancing uniform corrosion resistance in chloride-containing environments and maintaining passivity under harsh conditions such as superheated steam containing HCl and H₂S [15,16]. Dual-phase microstructures comprising hard BCC and soft FCC phases can additionally provide a favorable balance between strength and wear resistance [17].

Despite their excellent properties, the high cost of bulk CoCrFeMo_xNi alloys limits broader application [18–20]. Surface engineering approaches, such as laser cladding, provide a cost-effective alternative by enabling the deposition of thin, high-performance CCA coatings on low-cost substrates. Laser cladding offers strong metallurgical bonding, refined microstructures, and reduced material waste. Previous studies have demonstrated that laser-clad CoCrFeMo_xNi coatings exhibit strong resistance to corrosion and wear in aggressive environments [21–24]. However, coating performance is highly sensitive to powder

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characteristics and processing parameters. For example, coatings derived from gas-atomized (GA) powders generally exhibit better corrosion resistance than those produced from mechanically alloyed (MA) powders, owing to a more uniform distribution of Mo-rich phases [21,25]. Differences in phase constitution (BCC, σ) have also been observed depending on the powder-to-coating transformation route, such as vacuum arc melting (VAM) or electro-spark deposition (ESD) [22–25]. Overall, laser cladding demonstrates significant potential for reducing porosity and improving surface integrity relative to other deposition methods. Laser cladding originates from laser-based additive manufacturing technologies such as selective laser melting (SLM) [26], laser cladding (or laser metal deposition) is particularly suited for surface engineering applications, where localized deposition, controlled dilution, and rapid solidification enable tailored microstructures and functional performance. Laser cladding employs a high-energy laser beam to melt and fuse the cladding material onto a substrate surface. Owing to its concentrated energy input, high cooling rates, and low dilution, laser cladding typically produces dense coatings with fine microstructures, strong metallurgical bonding, and a narrow heat-affected zone compared with conventional coating methods [27,28]. These attributes make laser cladding particularly attractive for fabricating compositionally complex and high-entropy alloy coatings, where microstructural refinement and phase stability are critical. Previous studies [27,29] have shown that processing parameters such as laser power and scanning speed strongly influence melt pool geometry and solidification behavior, thereby affecting coating morphology and phase evolution. However, their direct impact on functional properties such as hardness and wear resistance is not always straightforward. In parallel, increasing attention has been directed toward the corrosion performance of laser-clad HEA coatings, with several reports demonstrating enhanced corrosion resistance in chloride-containing environments. Despite these advances, the coupled effects of powder processing route, laser-induced microstructural development, and corrosion–wear performance relationships remain insufficiently understood.

Wang et al. [28] examined a laser-clad FeCoCrNiAl_{0.5}Ti_{0.5} HEA coating deposited on AISI 1045 steel and reported improved corrosion resistance in a 3.5 wt% NaCl solution, attributed to the formation of a relatively uniform microstructure enriched with passivating elements such as Cr. Similarly, laser-based fabrication of FeNiCoCrMo coatings on 304 stainless steel demonstrated that Cr and Ni promote the development of dense and adherent oxide films, thereby enhancing corrosion protection [27]. The incorporation of Mo further contributes to performance by facilitating the formation of Mo-rich phases due to its high melting point, increasing hardness and suppressing localized corrosion through lattice distortion and reduced pit nucleation susceptibility [10–13]. In other related studies, Zhang et al. [27] showed that coatings produced from GA powders exhibited fine microstructures with a uniform distribution of Mo-rich phases, resulting in enhanced corrosion resistance. In contrast, coatings derived from MA powders displayed greater microstructural heterogeneity, influencing both wear behavior and corrosion resistance. Similarly, HEA coatings prepared from GA powders often exhibit a single FCC phase with refined grain structures and improved corrosion properties [28]. Tian et al. [29] further corroborated these findings, reporting that GA powders produced high-quality CrCoFeNiMn HEA coatings with uniform size and composition, leading to superior mechanical properties and wear resistance. Collectively, these studies underscore the critical role of powder synthesis routes in determining the microstructure and performance of laser-clad HEA coatings.

Despite these advances, a systematic understanding of how powder microstructure influences the characteristics of laser-clad coatings, particularly with respect to wear behavior and acidic corrosion, remains limited. To address this gap, the present study investigates the influence of powder processing routes on the microstructure, phase distribution, and resulting corrosion and wear behavior of laser-clad CoCrFeMo_{0.85}Ni coatings, emphasizing correlations between powder properties, coating

microstructure, and performance. Two powder variants, GA (gas-atomized) and MA (mechanically alloyed), were used to fabricate coatings on a low-cost substrate. By evaluating coatings produced from powders with distinct microstructures, this work aims to elucidate the relationships between feedstock characteristics, coating microstructure, and functional performance, thereby providing guidance for the development of cost-effective, high-performance CCA coatings for structural and engineering applications.

2. Materials and methods

2.1. Materials and spraying process

The mechanically alloyed (MA) powders were produced from pure elemental powders of Co, Cr, Fe, Ni, and Mo (Laboratorium®) using a planetary ball mill (Fritsch – Pulverisette 6® Idar-Oberstein, Germany) for an effective milling time of 210 min. The elemental powders were placed in a stainless-steel vial with stainless steel balls at a ball-to-powder weight ratio of 10:1. Wet milling in 2 % n-heptane was employed to enhance the degree of alloying and reduce powder adhesion to the milling media. From the resulting batch, a particle size fraction of $-56 + 20 \mu\text{m}$ was extracted by mechanical sieving.

The gas atomized (GA) powders were produced under an argon atmosphere using a HERMIGA 75/5 VI EAC unit (Phoenix Scientific Industries Ltd), with an estimated cooling rate of 10^5 – 10^6 °C/s. A final particle size fraction of $-48 + 15 \mu\text{m}$ was obtained via mechanical sieving with vibratory sieve shaker (Fritsch–Analysette 3® SPARTAN, Idar-Oberstein, Germany) equipment.

The chemical composition of the powders (reported as nominal elemental weights for both mechanical alloying and gas atomizing) and the substrate (as provided by the manufacturer) are listed in Table 1. The substrate material is P265GH carbon steel, selected as a cost-effective alternative with good metallurgical compatibility with laser-clad coatings, enabling reliable evaluation of wear and corrosion performance in potential engineering applications.

The laser cladding (LC) process involved precise control over process parameters to ensure metallurgical bonding and microstructural uniformity. Key parameters are summarized below in Table 2. A 5.3 kW disc laser system (Trudisk 8002 Trumpf®, Germany) equipped with a Tru-Control 1000 controller and Trumpf BEO D70 processing optics with motor collimation was used to prepare the LC coatings. Substrates were grit blasted with 60 mesh brown alumina and degreased with acetone prior to deposition.

2.2. Microstructural analyses

A Zeiss® Supra 25, equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector (Oxford Instruments®), was employed as the field emission scanning electron microscope (FE-SEM) for microstructural and chemical analyses. Coating surfaces and cross-sections were examined both before and after corrosion testing. Cross-sections were prepared by mounting specimens in a thermosetting phenol formaldehyde resin (Bakelite) and polishing using silicon carbide abrasive papers followed by diamond paste to achieve a final surface roughness of approximately 0.025 μm Ra.

The phase compositions of the powders and coatings were studied using X-ray diffraction (XRD) with a Bruker® D8 Advance diffractometer operating at 40 kV and 30 mA, employing Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.3. Hardness test

The hardness of the CCAs was obtained on the surface and from 6 different locations in the cross-section with Vickers micro-hardness tester (VH1202 Wilson®, Esslingen, Germany) using 0.1 kg-f load.

Table 1

Nominal composition (wt%) of powders (both MA, and GA) and substrates used in the experiments.

Element	Co	Cr	Fe	Ni	Mo	C	Mn	Si	P	S	N	Cu	Al
CoCrFeMo _{0.85} Ni	19.2	16.9	18.2	19.1	26.6	–	–	–	–	–	–	–	–
P265GH	–	0.03	99.0	0.06	–	0.07	0.76	0.01	0.02	0.01	0.01	0.03	0.04

Table 2

Laser cladding parameters for deposition of powders (both MA, and GA).

Parameter	Value
Laser Power	550 W
Scanning Speed	10 mm/s
Powder Disk Speed	9.3 %
Number of Layers	1
Carrier Gas (Ar) Flow	4 L/min
Shielding Gas (Ar) Flow	6 L/min
Powder Feed Rate	10 g/min

2.4. Wear testing

Dry sliding conditions were selected to establish a controlled baseline for assessing the intrinsic wear behavior of the coatings and to isolate the influence of microstructure, phase constitution and hardness on wear mechanisms, without the additional variables introduced by lubrication. Although lubricated or wet conditions may alter absolute wear rates, the dominant microstructure-controlled wear mechanisms and relative performance trends between the coatings are expected to remain qualitatively consistent. The wear behavior of the as-sprayed coatings was evaluated under dry sliding conditions using a ball-on-disc tribometer (TRB³, Anton Paar®, Graz, Austria) under ambient conditions. The testing setup and procedures followed ASTM G99 standards, including configuration, methodology, and friction/wear measurement criteria. A tungsten carbide (WC) ball with a hardness of 1640 HV was used as the counter body due to its established performance in bearings, seals, and couplings, and its suitability for accelerated laboratory wear testing. The WC ball was pressed under a load of 10 N at a constant rotational speed of 200 rpm for a duration of one hour, corresponding to approximately 12,000 cycles.

The coefficient of friction (CoF) was continuously monitored and recorded using Anton Paar® Instrument X software (version 8.1.5). After testing, worn surfaces were analyzed using an optical profilometer (NC-OP, Solarius®, California, USA). Wear track profiles were extracted at

three or more representative locations, and the average values were used to calculate the wear volume and determine the wear rate.

2.5. Electrochemical corrosion testing

Coating degradation was assessed by means of potentiodynamic polarization test, using an ACM Instruments® Gill 16 electrochemical system. Saturated calomel electrode (SCE) and platinated titanium electrode were used as reference and auxiliary (counter) electrode respectively. Results were analysed using the ACM® Core Running software. A 3.5 wt% NaCl aqueous solution at room temperature (25 °C) and constant pH 4 was employed. Measurements were taken at a scan rate of 1 mV/s with a step size of 1 mV in a ± 2000 mV potential range around the open circuit potential.

3. Results and discussion

3.1. Phase analysis of powders and coatings

Fig. 1a and b show the XRD patterns of the as-prepared powders and the resulting coatings, respectively. Both the MA- and GA-derived powders exhibit dominant FCC peaks, indicative of a single-phase solid solution primarily composed of Ni, Cr, Fe, and Co. However, notable differences are observed. In the MA powder, residual Mo leads to the appearance of a secondary Mo-rich phase, likely with a BCC structure, suggesting incomplete homogenization. In contrast, the GA powder shows no detectable BCC phase but exhibits early signs of σ -phase formation, implying more effective pre-alloying during the gas atomization process.

Following the laser cladding, phase evolution becomes more pronounced. Variations in diffraction intensity suggest phase heterogeneity, likely arising from local compositional differences [30] induced during the cladding process. The MA-derived coating retains the Mo-rich BCC peak and additionally exhibits σ -phase reflections, indicating that rapid solidification promotes the transformation of residual BCC Mo into the thermodynamically stable σ intermetallic phase. In the GA coating, the σ -phase is fully developed, while the BCC phase is largely absent,

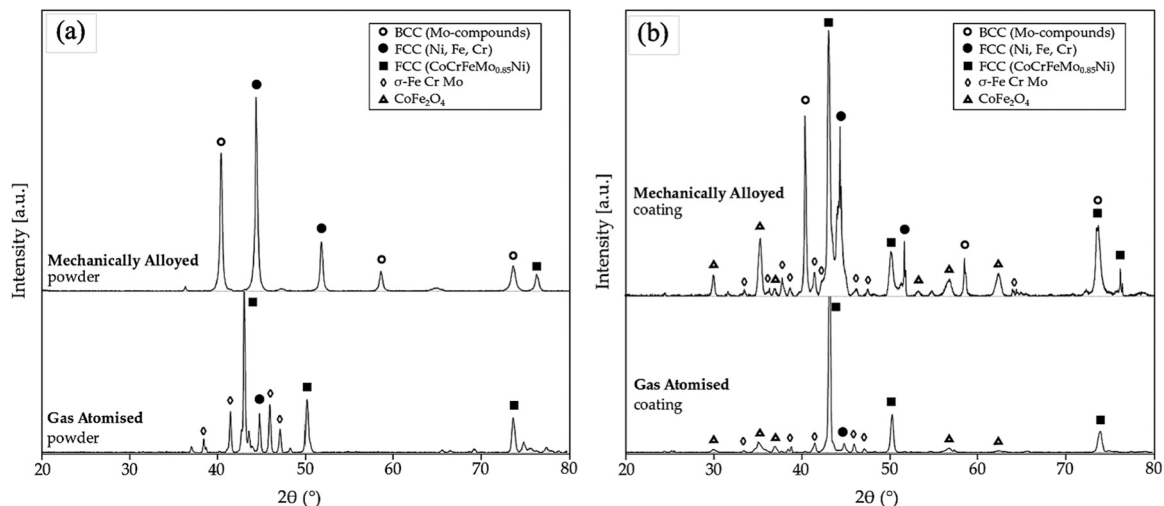


Fig. 1. XRD patterns of (a) precursor powders produced via mechanical alloying exhibit FCC and BCC phases, while gas atomization shows FCC and σ phases (b) coatings derived from mechanically alloyed powders show FCC, BCC and σ -phases, while gas-atomized powders produced FCC and σ phases.

consistent with EBSD observations showing a relatively uniform σ -phase distribution (3.2). This suggests that in the GA precursor powders, elemental Mo had already partially transitioned into intermetallic form prior to, and during, laser cladding.

CoFe_2O_4 spinel is absent in both the MA and GA powders presented in Fig. 1, with only the primary phases (i.e., FCC/BCC CCA matrix and intermetallic phases) detected. However, the high temperatures associated with laser cladding promote the formation of this thermodynamically stable oxide (see Fig. 1), likely due to trace oxygen exposure. When present, the oxide may segregate at the coating surface or within interdendritic regions and becomes detectable by XRD when its volume fraction exceeds approximately 1–5 wt%, depending on crystallinity and phase symmetry [31].

3.2. Microstructure analysis of powders and coatings

The SEM morphologies of the MA and GA powders are presented in Fig. 2. To further assess the technological properties of the powders, a series of measurements was performed and is summarized in Table 3, using a standard Carney funnel and a graduated cylinder with 25 g of material.

The GA powders exhibit homogeneous, spherical particles, whereas the MA powders display a polyhedral morphology with relatively uniform particle size.

The angular and blocky geometry observed in mechanically alloyed (MA) powders results from high-energy mechanical impacts, which generate localized pressure and repeated fracture–welding events that alloy the elemental particles. In contrast, gas atomization (GA) involves in-flight solidification of droplets directly atomized from a molten alloy, producing spherical particles due to the minimization of Gibbs free energy associated with this geometry.

The GA powder demonstrates an improved free-flow rate compared with the MA powder, as well as higher compactibility at lower slope angles. This enhanced densification is attributed to the favorable particle morphology and reduced interparticle friction of the GA powder, which promote more uniform packing during powder deposition and compaction.

Two principal microstructural regions were identified in Figs. 3–5: a continuous FCC matrix (region A) and an interdendritic second-phase morphology (region B) in both coatings. SEM micrographs of the laser-clad $\text{CoCrFeMo}_{0.85}\text{Ni}$ coatings produced from MA and GA powders are shown in Fig. 3. Several non-interconnected gas pores are visible, likely associated with the presence of Mo in the clad layer. Similar porosity has been reported in Mo-containing CCAs [1,2] and attributed to the formation of MoO_2 , which has a relatively low vaporization temperature ($\sim 1155^\circ\text{C}$) [2,3].

Distinct dendritic and interdendritic morphologies were observed in

Table 3

MA and GA metallic powders technological characterization.

Powder	Free Flow	Loose Bulk Density	Tap Density	Packing Ratio	Slope Angle
	(g/s)	(g/cm ³)	(g/cm ³)	(%)	(°)
MA	4.33	3.57	4.41	80.95	19.79
GA	2.67	4.23	5.31	79.66	11.28

the two coatings. The MA-derived coating exhibits an equiaxed dendritic structure with localized directional features, whereas the GA-derived coating displays a cellular/columnar dendritic matrix, appearing as a lighter grey contrast in SEM images. While SEM highlights morphological differences between the coatings, EBSD provides a more definitive classification of the underlying solidification substructures.

EBSD orientation maps (Figs. 4 and 5) further reveal grain anisotropy in the $\langle 001 \rangle$, $\langle 101 \rangle$, and $\langle 111 \rangle$ crystallographic directions, indicating that grain growth and dendritic network formation were strongly influenced by laser-induced solidification dynamics. Back-scattered electron (BSE) images (Figs. 3b and 3d) show contrast variations that correlate with compositional heterogeneity identified by EDS and EBSD phase indexing (Table 4). In the MA-derived coating, EBSD phase mapping (Fig. 4b) confirms the coexistence of FCC and BCC phases, consistent with XRD results. This phase structures is attributed to a relatively slower solidification rate, which allows sufficient time for phase separation and BCC formation alongside the dominant FCC phase [22,32]. In contrast, the GA-derived coating (Fig. 5b) exhibits a more uniform phase distribution, with σ -phase predominantly located at grain boundaries and a stabilized FCC matrix composed of both equiaxed and columnar grains. Although the higher solidification rate in GA-derived coatings restricts extensive phase transformation, localized elemental segregation during rapid solidification still promotes σ -phase formation within interdendritic regions [33].

The comparative phase composition and elemental distribution are summarized in Table 4, based on EDS point analyses at regions A and B in Fig. 3. Both coatings exhibit Fe enrichment (36.1 – 60.7 at%), primarily due to dilution from the steel substrate (Fig. 3a). EBSD phase maps of the MA-derived coating (Fig. 4c–g) show that Co, Cr, and Ni are uniformly distributed within the FCC matrix, whereas Cr and Mo segregate into interdendritic regions, confirming the presence of a Mo-rich BCC phase in agreement with XRD results (Fig. 1b). This segregation is attributed to the sluggish diffusion of Mo during solidification, which preferentially partitions into the interdendritic phase.

XRD analysis further identifies two FCC solid solutions in the MA-derived coating: FCC-(Ni,Fe,Cr) and a fully alloyed FCC– $\text{CoCrFeMo}_{0.85}\text{Ni}$. In contrast, the GA-derived coating consists primarily of an FCC– $\text{CoCrFeMo}_{0.85}\text{Ni}$ solid solution and a σ -(Fe,Cr,Mo) intermetallic

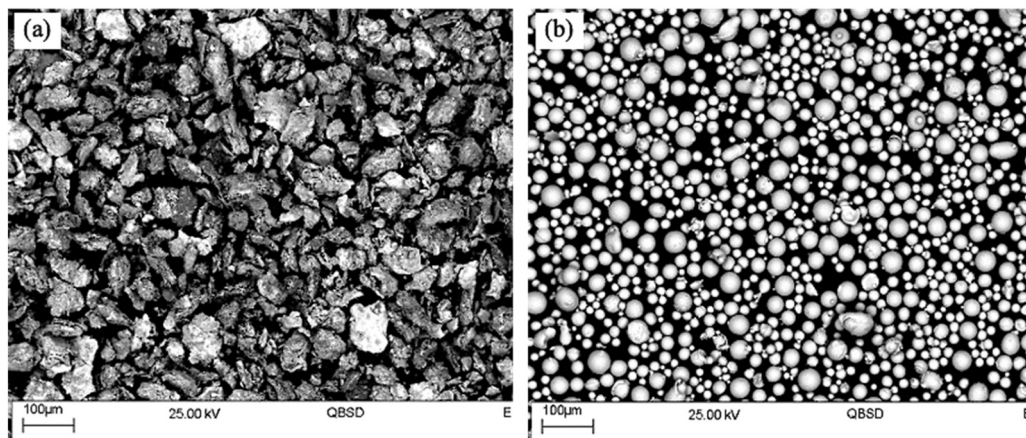


Fig. 2. SEM micrographs of the precursor metallic powders: (a) mechanically alloyed – MA and (b) gas-atomized – GA.

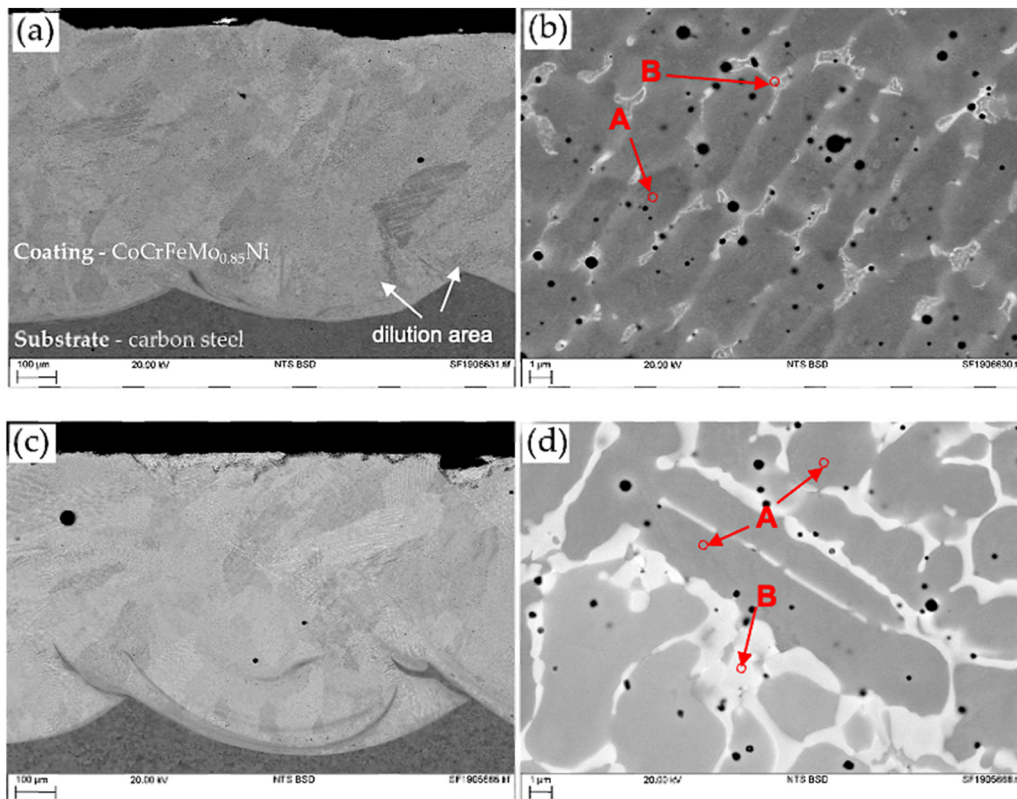


Fig. 3. SEM micrographs of CCA coatings: (a, b) mechanically alloyed (MA) and (c, d) gas-atomized (GA). The red arrows indicate dendritic (A) and interdendritic (B) regions.

phase. EBSD maps (Fig. 5c–g) confirm Mo and Cr enrichment at grain boundaries, consistent with σ -phase formation.

These observations are consistent with previous studies on FeCoCrMoNi-based alloys [9,21,22,34], which report σ -phase formation at grain boundaries where cooling rates are locally reduced. The σ -phase typically exhibits a tetragonal Cr–Fe/Mo-rich structure, whereas other Mo-rich intermetallics, such as Fe_3Mo or CoMo_2Ni (μ phase, rhombohedral structure), have been reported under different cooling conditions or fabrication routes [32,35]. Lower Mo contents in CoCrFeNiMo_x alloys ($x = 0.1\text{--}0.5$) have similarly been shown to promote dispersed σ -phase precipitation within an FCC matrix [36].

Overall, the combined XRD and EBSD analyses demonstrate that the powder processing route plays a critical role in governing phase evolution during laser cladding. The MA-derived coating develops a fine, multiphase microstructure comprising FCC, BCC, and σ phases due to enhanced solid-state mixing during mechanical alloying and non-equilibrium phase retention during rapid solidification. In contrast, the GA-derived coating is characterized by a predominantly FCC matrix with spatially segregated σ -phase, consistent with cellular/columnar solidification and compositional partitioning. These findings are in agreement with prior report [27–29], which show that gas-atomized powders promote chemically uniform FCC matrices while still allowing localized phase segregation during solidification, thereby influencing the mechanical and corrosion behavior of laser-clad coatings.

From Table 4, the MA-derived coating exhibits substantial phase-to-phase variation in elemental composition, reflecting the coexistence of FCC and BCC/ σ phases within a finely intermingled multiphase microstructure. In contrast, the GA-derived coating shows a predominantly FCC matrix, with σ -phase formation occurring in more spatially segregated regions. These results indicate that the powder processing route strongly influences local chemical partitioning and phase distribution during laser cladding.

The Cr content in the MA-derived coating is notably lower than the

nominal 16.9 wt%, with values of only 5.3 wt% in the BCC phase and 8.5 wt% in the FCC region, suggesting elemental redistribution or loss during deposition. A portion of Cr may also be sequestered in fine-scale secondary phases or oxides, such as Cr_2O_3 or Cr-rich spinels at grain boundaries, which are not fully resolved by the present analysis. By comparison, the GA-derived coating exhibits improved Cr retention and clearer phase segregation, with 11.5 wt% Cr in the FCC matrix and 12.1 wt% in the σ -phase, reflecting the greater chemical uniformity of gas-atomized powders. Despite these compositional differences, both coatings exhibit strong metallurgical bonding to the substrate and show no evidence of macrocracking or delamination, indicating effective process control during laser cladding.

3.3. Microstructural evolution in laser cladding

The laser-clad $\text{CoCrFeMo}_{0.85}\text{Ni}$ coatings exhibited a dense microstructure with a well-developed metallurgical bond to the substrate. The rapid solidification rate during laser processing ($10^3\text{--}10^6\text{ K}\cdot\text{s}^{-1}$) [37] promote solute trapping, which, combined with the high mixing entropy characteristic of compositionally complex alloys (CCAs), favors the formation of solid-solution phases. XRD analysis confirms a predominantly FCC structure, with the presence of BCC and σ phases consistent with thermodynamic stabilization driven by high-entropy effects and atomic size mismatch [20].

Microstructural evolution during laser cladding is governed by rapid heating, melting, and solidification, which substantially modify the morphology and phase distribution of the precursor powders, whether gas-atomized (GA) or mechanically alloyed (MA). Successive clad layers fuse cohesively, producing dense coatings with refined multiphase microstructures.

Molybdenum's high melting point and limited wettability slightly influence melt pool behavior and thermal gradients during processing. Rapid melting followed by equally rapid solidification promotes the

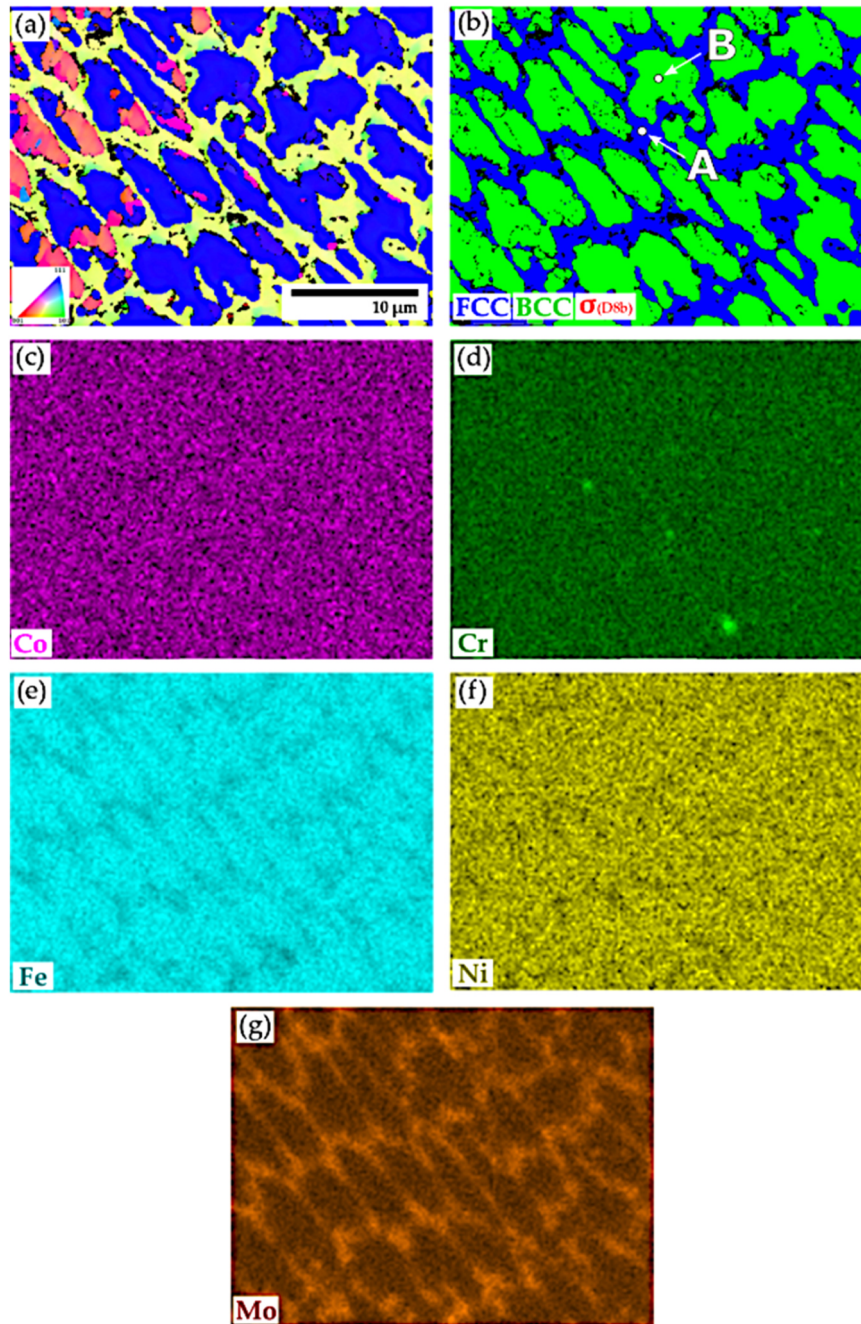


Fig. 4. EBSD orientation maps of the mechanically alloyed (MA) coating deposited by laser cladding. The white arrows indicate interdendritic (A) and dendritic (B) regions.

formation of fine dendritic structures. The resulting solidification morphology is governed by the thermal gradient (G) and solidification rate (R), particularly their ratio (G/R) [38], where lower G/R values favor equiaxed and dendritic structures. As shown in Fig. 6, planar or cellular dendrites form near the fusion boundary due to high G/R , while eutectic-like and equiaxed structures develop toward the center and top of the clad layer where G/R decreases. Equiaxed dendrites are prevalent throughout the coating, likely due to the presence of interdendritic phases that suppress columnar growth [39]. This observation is consistent with measured dendrite sizes of approximately 3–5 μm in both GA- and MA-derived coatings, with the MA coating exhibiting a higher fraction of interdendritic regions due to its additional BCC and σ -phase content, as indicated by XRD.

The MA powders enter the melt pool with incomplete chemical

homogenization, irregular particle morphology, and a higher defect density. During laser cladding, the short thermal cycle is insufficient to fully homogenize these inherited compositional fluctuations, resulting in pronounced elemental partitioning, the coexistence of multiple phases (FCC + BCC + σ), and a finely intermingled but chemically heterogeneous microstructure. Additional Fe dilution from the steel substrate further amplifies local compositional gradients. Consequently, the persistence of Mo-rich BCC phases in the MA-derived coating is attributed to incomplete powder homogenization and Mo's low diffusivity, which limits redistribution during solidification and promotes isolated BCC solidification. These Mo-rich regions, often enriched in Cr and characterized by high local Mo/Cr ratios, provide favorable conditions for subsequent σ -phase formation.

In contrast, GA powders are chemically pre-alloyed and

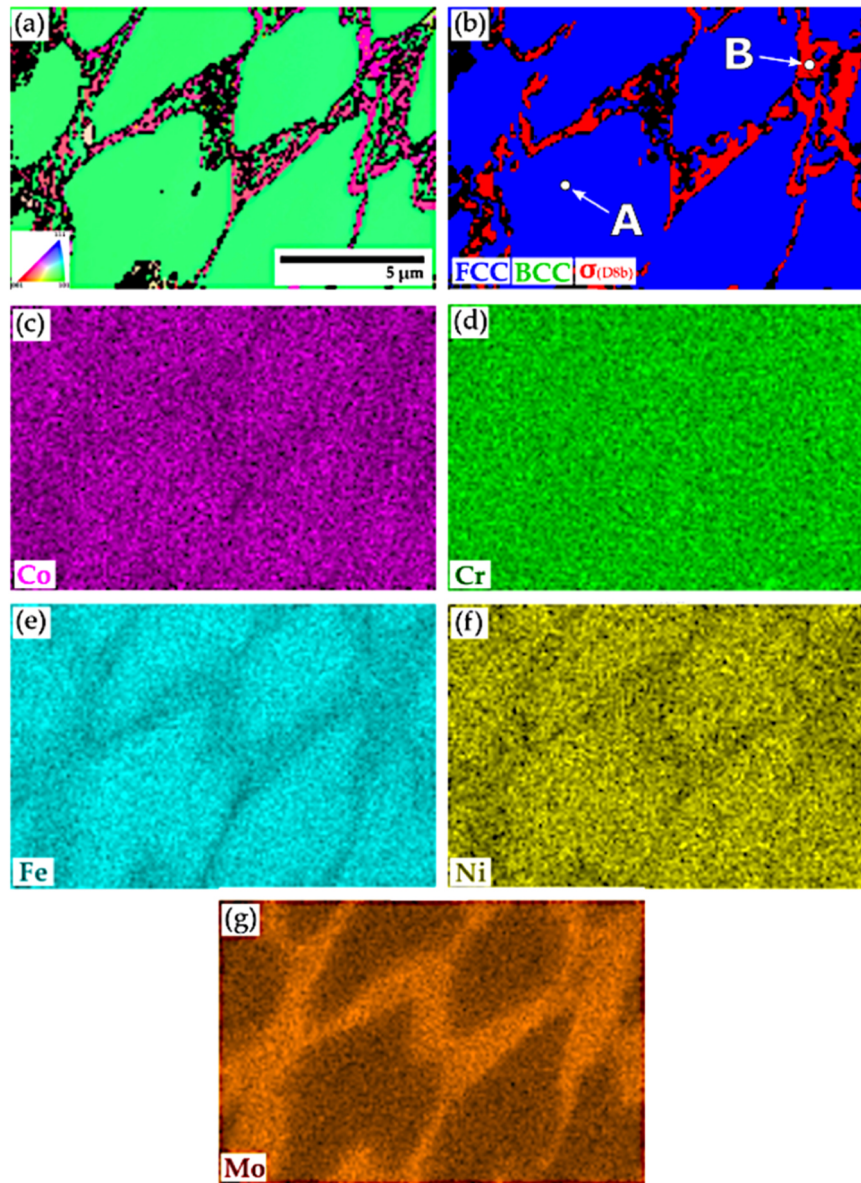


Fig. 5. EBSD orientation maps of gas atomized (GA) coating deposited by laser cladding. The white arrows indicate dendritic (A) and interdendritic (B) regions.

Table 4

Nominal and measured phase compositions of mechanically alloyed (MA) and gas-atomized (GA) CCA coatings deposited by laser cladding.

Elements [wt%]	Co	Cr	Fe	Ni	Mo
<i>Theoretical</i>					
CoCrFeMo_{0.85}Ni	19.2	16.9	18.2	19.1	26.6
<i>Mechanically Alloyed - (Fig. 4)</i>					
A (BCC)	6.5	5.3	45.6	8.6	34.0
B (FCC)	4.6	8.5	60.7	13.2	13.0
<i>Gas Atomized - (Fig. 5)</i>					
A (FCC)	14.3	11.5	45.3	14.5	14.4
B (σ)	12.0	12.1	36.1	10.7	29.1

compositionally uniform. Upon laser cladding, this promotes more homogeneous solute redistribution during solidification, suppressing excessive phase separation and enabling controlled σ -phase precipitation alongside refined grain structures. The inherent uniformity of GA powders stabilizes melt pool chemistry, allowing σ -phase to nucleate in thermodynamically favorable regions while restricting excessive growth under rapid solidification conditions, compared with MA-derived

coatings.

At elevated temperatures during deposition, Co transitions from HCP to FCC (above 450 °C) [21]. Incorporation of Mo (atomic radius (r) ~ 1.39 Å) into the FCC lattice induces lattice distortion, which can promote the formation of a dual FCC + BCC structure [40]. The lower packing density of the BCC lattice facilitates accommodation of larger atoms such as Mo, influencing crystallization behavior. Cr and Mo preferentially segregate to interdendritic or intercellular regions. Density functional theory (DFT) calculations indicate that Cr has a lower vacancy formation energy than Fe, Ni, and Co, implying a greater thermodynamic tendency to vacate lattice sites and segregate [41]. This tendency, combined with sluggish diffusion and strong chemical affinity between Cr and Mo, promotes redistribution during solidification in the CoCrFeMo_{0.85}Ni matrix. Both Cr and Mo are well-known promoters of σ -phase precipitation, particularly at grain boundaries in austenitic stainless steels and CCAs/HEAs with high equivalent Cr content. [8,22,36,42].

The evolution of these phases is governed by key thermodynamic and geometric parameters, including atomic size mismatch (δ), mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), and valence electron

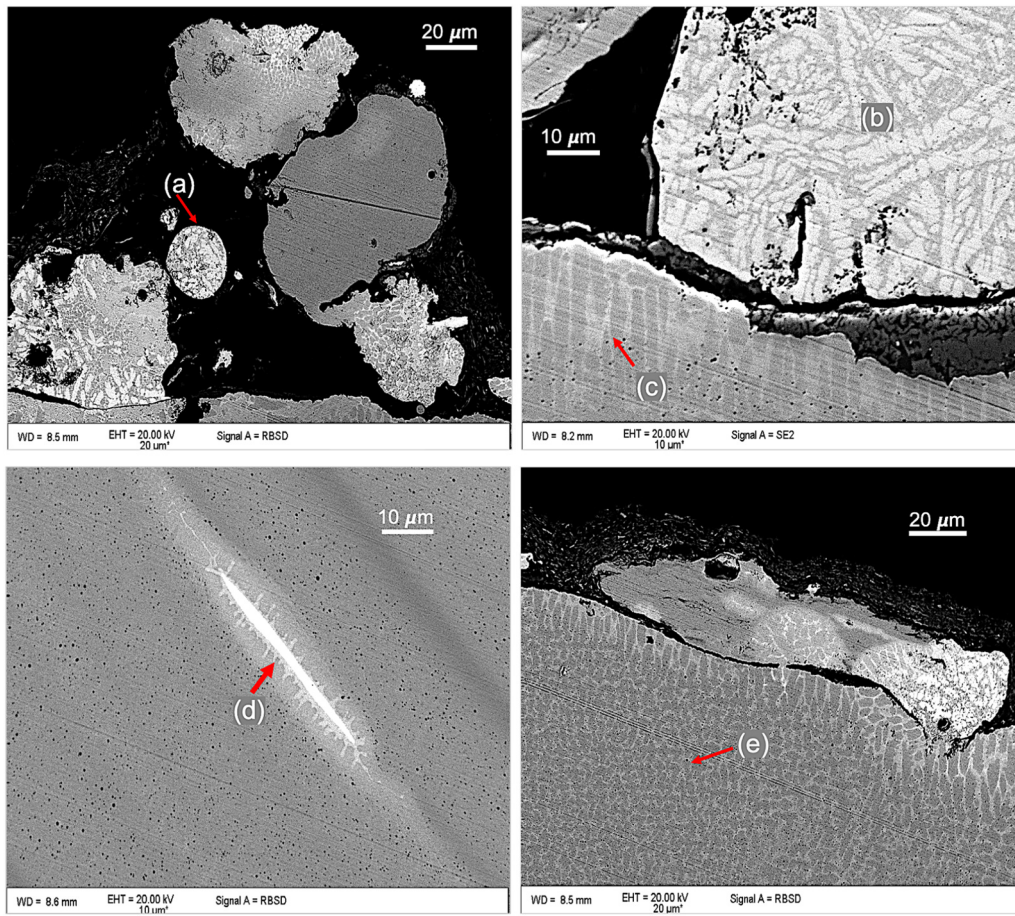


Fig. 6. Microstructure Evolution of CoCrFeMo_{0.85}Ni during solidification in laser cladding technique: (a) nucleation of eutectics in droplets, (b) formation of lamellar eutectics (c) columnar dendrites of same growth direction; (d) eutectic structure of interdendrite in the center of clad (e) equiaxed dendrites at the top.

concentration (VEC), in accordance with the design principles proposed by Yang et al. [43,44]:

$$\delta = \sqrt{\sum_{i=1}^n c_i (1 - r_i / \bar{r})} \quad (1)$$

$$\Omega = T_m \Delta S_{mix} / \Delta H_{mix} \quad (2)$$

$$\Delta S_{mix} = -R \sum_{i=1}^n c_i \ln c_i, \quad \Delta H_{mix} = \sum_{i=1}^n \sum_{j \neq i} 4 \Delta H_{ij}^{mix} c_i c_j \quad (3)$$

Where c_i is the atomic percentage of element i , r_i represents the atomic radius, $\bar{r}$ is the average atomic radius, and T_m is the average melting point of the CCA.

If $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ then the solid solution form [44] while a high VEC (≥ 8) favors the formation of FCC-type solid solutions, while a lower VEC (< 6.87) favors the formation of BCC-type solid solutions, according to Guo et al. [43]. The above Eq. (1 – 3) consider only the elemental composition and not the fabrication route, the calculated values for both GA and MA CoCrFeMo_{0.85}Ni powders are identical: $\Omega = 5.99$, $\delta = 4.27$, and VEC = 7.69. Additional cross-sectional SEM micrographs of clad droplets (refer to Fig. 6) clearly illustrate the transition from spherical, porous powder droplets to fully fused, dense coatings. In both cases, the final microstructure comprised a continuous FCC matrix (Ni, Fe, Cr) interspersed with discrete BCC/ σ -phase precipitates. Previous research by Niu et al. [12] reported a Mo mole fraction of approximately 5 % in CoCrFeNiMo_{0.2} alloy, while Askari et al. demonstrated the formation of a fully eutectic structure dominated by the σ -phase in CoCrFeNiMo_x alloys when $x = 0.8$ in clad alloy [39].

3.4. Hardness and wear resistance

Based on the average microhardness values, the GA-derived coating exhibits hardness approximately more than twice that of the MA-derived coating (209 HV_{0.1}), highlighting the significant influence of powder synthesis technique on mechanical performance.

Fig. 7 presents the microhardness profiles of both GA- and MA-CoCrFeMo_{0.85}Ni coatings, showing the GA derived coating maintains high hardness across the depth (typically between 450–550 HV_{0.1}). These fluctuations can be attributed to local compositional gradients

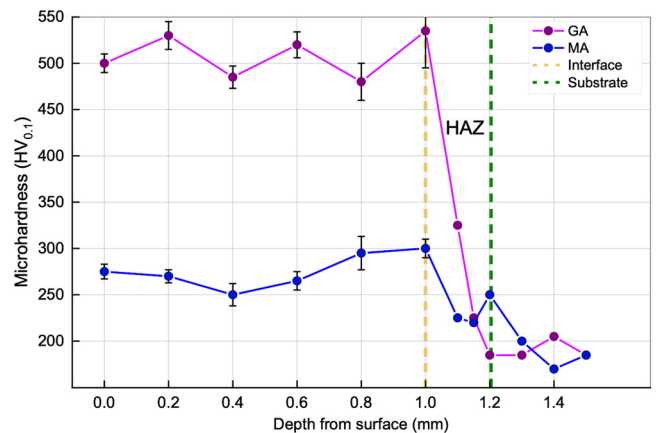


Fig. 7. Microhardness profiles of CCA coatings (mechanically alloyed – MA and gas-atomized – GA) deposited by laser cladding.

arising from the different co-existing phase structures [45] and inter-diffusion with the steel substrate (heat affected zone - HAZ), an observed characteristic of laser clad coatings [46] especially near the coating-substrate interface. In contrast, the MA-derived coating averaged around 209 HV_{0.1}, lower than the GA coating but still above the hardness of the P265GH steel substrate (~ 180 HV_{0.1}).

The high hardness of the GA-derived coating is linked to its refined dual-phase (FCC + σ) microstructure, where the dispersed Mo- and Cr-rich precipitates contribute to elevated resistance to plastic deformation and enhanced mechanical performance. The Mo concentration ($x = 0.85$) provides an optimal balance between strength and ductility in CoCrFeNiMo_x HEAs, largely due to atomic size mismatch quantified by δ_r (see Eq. (1)) between Mo and the 3d transition metals—Co (1.25 Å), Cr (1.26 Å), Fe (1.24 Å), and Ni (1.25 Å). This atomic radii mismatch introduces elastic lattice distortions that obstruct dislocation motion [47], thereby enhancing solid-solution strengthening of the FCC matrix. Moreover, Mo segregation at grain boundaries in GA-derived coating facilitated the formation of the intermetallic phases. Such structure contains many interfaces with coherent internal stresses (due to the mismatch) contributing a certain amount of hardening [45]. The smaller width would possess higher interface area and thus high hardness value similarly reported for tetragonal σ phases and/or rhombohedral/hexagonal μ hard intermetallic phases [48–50]. A further raise in yield strength through precipitation hardening and grain refinement has been reported [12,50]. The associated decrease in stacking fault energy (SFE) due to Mo enhances strain-hardening rate and activates twinning-induced plasticity (TWIP), reinforcing the alloy's strength-ductility synergy [51,52].

Fig. 8 illustrates the total volume loss after 1 h of dry sliding, with results summarized in Table 5. The coatings showed moderate material removal, with wear rates falling within the 'mild' wear range ($10^{-8} \leq K \leq 10^{-2}$) defined by Archard model [53]. The MA-derived CoCrFe-Mo_{0.85}Ni coatings exhibited the highest volume (mm³) of material removed from the surface, whereas the GA-derived coating shows a reduction in volume loss, corresponding to the lowest wear rate of 1.7×10^{-4} mm³/N·m. Although the GA is significantly harder than the MA-derived coating, the relatively modest reduction in wear volume suggests that wear resistance is controlled not only by hardness but also by microstructural and tribochemical effects during sliding. The enhanced wear resistance in GA-derived coatings is attributed to their higher hardness and smoother surface morphology, which help reduce friction and dissipate energy during sliding. The dual-phase (FCC + σ) microstructure also promoted precipitation hardening, as the uniform distribution of Mo- and Cr-rich precipitates impedes dislocation motion and enhances load-bearing capacity [47,50]. Additionally, the

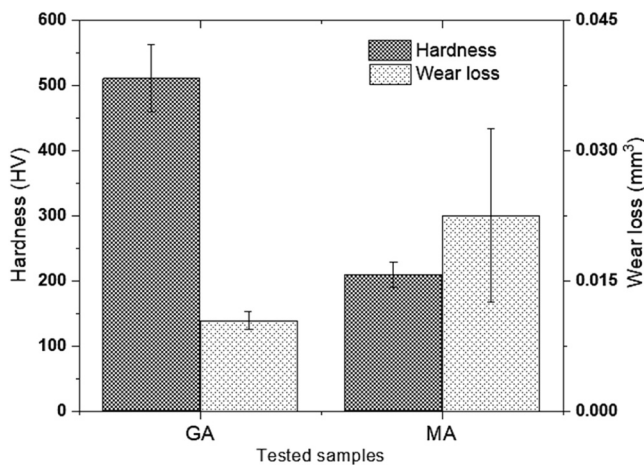


Fig. 8. Average surface hardness and total volume loss of CCA coatings (mechanically alloyed – MA, and gas atomized – GA) under dry sliding conditions.

Table 5

Summary of tribological results of the CCA coatings (both mechanically alloyed, and gas atomized) under dry sliding conditions.

Property	GA	MA
Coefficient of Friction (COF)	0.51	0.55
Hardness (HV _{0.1})	510	209
Wear Rate (mm ³ /Nm)	1.7×10^{-4}	4.4×10^{-4}
Wear Track Width (μm)	803	1103
Wear Track depth (μm)	35 – 53.6	24.1 – 73.2
Coating thickness (μm)	1051	1117
Surface Roughness (Ra, μm)	13.1	17.2

formation of a compact, continuous oxide film, arising from mild debris oxidation, further contributed to the reduced wear and improved tribological stability [32]. Collectively, these factors allowed the GA-derived coating to maintain a stable tribosystem under dry sliding conditions.

Fig. 9 shows the evolution of the coefficient of friction (COF) during sliding. The GA-derived coating achieved steady state sliding behavior more quickly, within the first few minutes, and maintained an average friction coefficient of 0.51 ± 0.16 throughout the test. In contrast, the MA-derived coating displayed more erratic behavior, with stability reached only after 18 min. This delay was due to the accumulation and compaction of oxidized debris in discontinuous wear zones. Zone 1 showed abrasive wear with parallel grooves along the sliding direction, while Zone 2 behavior differed significantly between the coatings. After initial fluctuations, the MA-derived coating stabilized at a higher average CoF of 0.55. This elevated friction and delayed stabilization are primarily attributed to its rougher, more irregular top surface, featuring angular unmelted or partially melted particles. In Zone 2, wear debris was continuously generated, locally fragmented and oxidized, forming clump-like or multilayered structures. The presence of hard intermetallic σ phases dispersed within a ductile FCC matrix contributed to abrasive wear dominated by micro-cutting and grooving. Critically, the brittle BCC/ σ phase, primarily located along grain boundaries enhanced overall hardness [54,55] but introduced mechanically vulnerable interfacial regions [32,49,55] that are prone to spallation (see zone 2 in Fig. 9), especially under repeated sliding stress. Likewise the in volume fraction of hard phases, resulting in enhanced hardness but a reduction in ductility due to the brittle nature of the phases [14].

The improved tribological performance of GA-derived coatings are largely due to microstructural refinement, reduced roughness, and a

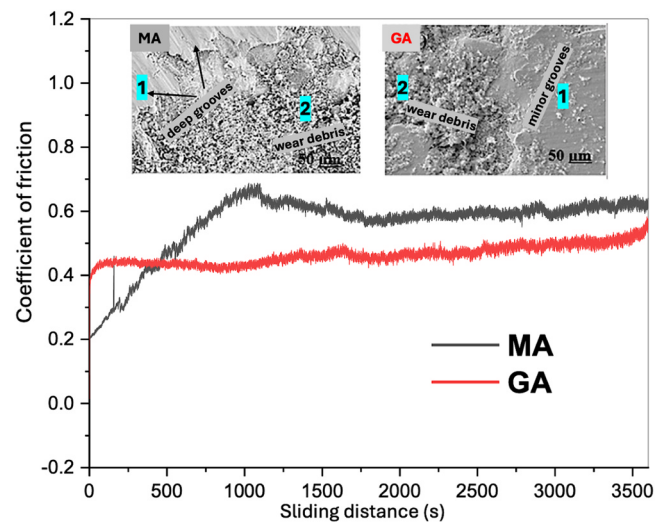


Fig. 9. Coefficient of friction curves (CoF) and corresponding surface morphologies of the CCA coatings produced via mechanical alloying (MA) and gas atomization (GA) under dry sliding conditions.

more stable tribological response. The refined, ductile FCC matrix remains continuous and load bearing, whereas hard σ -phase contributes to strengthening and hardness reducing plastic deformation during sliding, limiting abrasive grooving. In contrast, MA-derived coatings, with their rougher surfaces ($17.2 \mu\text{m}$) and blocky particles, led to greater debris generation and unstable friction behavior, particularly in the early stages of sliding (shown in Fig. 9). The atomization process promotes a homogeneous, spherical particle morphology with fewer angular defects, leading to reduced abrasion.

Solid solution strengthening from Mo and associated lattice distortion was a key factor in the mechanical performance of both coatings. The FCC matrix, composed mainly of Ni, Fe, and Cr, was further hardened by the dispersion of BCC and σ -phase precipitates, in line with the Hume-Rothery rules [53,54]. Prior studies [9,32] have also shown that Mo-rich intermetallic inhibit dislocation motion, aligning with the improved wear resistance observed here. Ultimately, the wear performance of the GA-derived coatings can be attributed to a combination of microstructural refinement, lower roughness, and reduced plastic deformation during sliding.

3.5. Electrochemical corrosion testing

To further evaluate the corrosion resistance and pitting susceptibility of the CoCrFeMo_{0.85}Ni CCA coatings, cyclic potentiodynamic polarization (CPDP) tests were conducted in 3.5 wt% NaCl solution at pH 4. The CPDP technique provides insight into the corrosion mechanisms, including passivation stability, breakdown characteristics, and the alloy's ability to repassivate after localized attack. The shape of the polarization curve, along with key electrochemical parameters, allows for a comparative interpretation of the protective behavior of the coatings.

The cyclic potentiodynamic polarization (CPDP) curves (Figs. 10 and 11) and the electrochemical parameters (Table 5) highlight clear differences in passivation and pitting resistance between the MA- and GA-derived coatings. The MA-derived coating (Fig. 10) exhibits a negative hysteresis loop, where the reverse scan intersects the forward scan at lower potentials and current densities. This behavior indicates partial repassivation after localized breakdown, suggesting limited resistance to sustained pitting. A stable passive region (E_{pp}) is not observed, and the continuously increasing current during the forward scan reflects ongoing active dissolution. Although the MA-derived coating exhibits

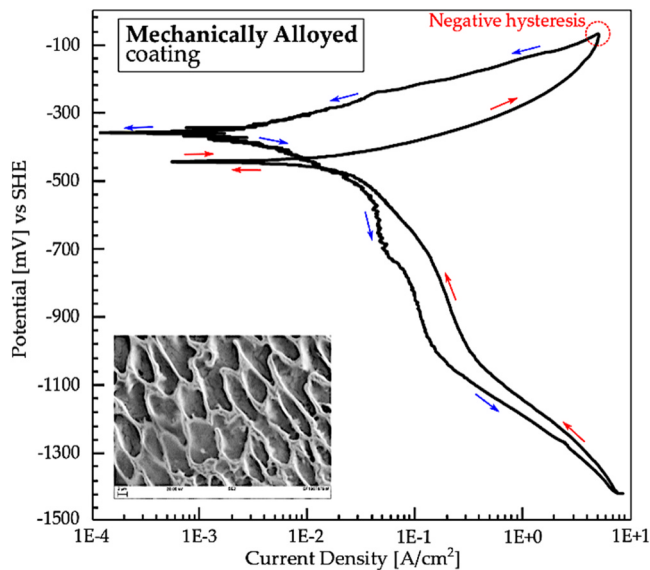


Fig. 10. Polarization curve of the MA-derived coating tested in 3.5 wt% NaCl at pH 4. The red and blue arrows indicate the scan direction, while the red circle highlights the negative hysteresis observed during the reverse scan.

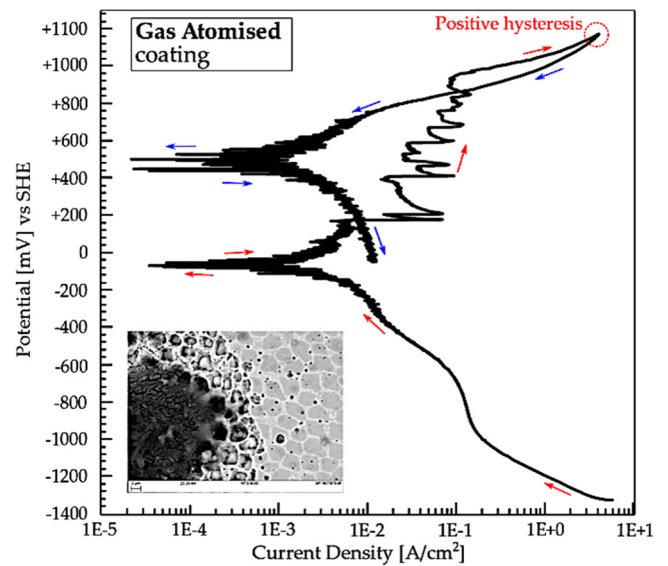


Fig. 11. Polarization curve of the gas atomized (GA) coating tested in 3.5 wt% NaCl at pH 4. The red and blue arrows indicate the scan direction, while the red circle highlights the positive hysteresis observed during the reverse scan.

higher corrosion current density and ongoing active dissolution, the negative hysteresis loop indicates comparatively easier repassivation following localized attack. The reverse scan shows a decrease in current density, consistent with some recovery of the passive film. The repassivation potential ($E_{rp} \sim -380 \text{ mV}$) lies above the corrosion potential ($E_{corr} \sim -470 \text{ mV}$), suggesting thermodynamically favorable repassivation, although the absence of a passive plateau implies that film stability is weak under these conditions.

The GA-derived coating (Fig. 11) shows a pseudo-passive region and a positive hysteresis loop, where the reverse-scan current remains above the forward-scan current beyond the breakdown potential. This indicates that localized corrosion initiated in the forward sweep persists in the reverse sweep, reflecting poor repassivation. This behavior suggests that, while the GA-derived coating delays pit initiation to higher potentials, once breakdown occurs, pit propagation is sustained. The coating displays a broad passive region between the primary passivation potential ($E_{pp} \sim +40 \text{ mV}$) and the breakdown potential ($E_b \sim +900 \text{ mV}$), with evidence of multiple pitting events associated with dissolution of secondary phases. Once breakdown occurs at $+900 \text{ mV}$, the reverse scan does not show a sharp current drop, and E_{rp} is not reached; current remains elevated even at $\sim 840 \text{ mV}$, confirming continued pit growth. Nevertheless, the high E_b suggests that a Cr- and Mo-rich passive film forms initially and delays pit initiation, though compositional heterogeneities or inclusions likely act as pit initiation sites [56–58].

The corrosion current density (I_{corr}) of the GA-derived coating is an order of magnitude lower ($1 \times 10^{-4} \text{ A/cm}^2$) than that of the MA ($1 \times 10^{-3} \text{ A/cm}^2$), implying better general corrosion resistance. Despite the higher I_{pass} observed in the GA-derived coating ($\sim 1 \times 10^{-1} \text{ A/cm}^2$ with fluctuation), its nobility and passive film breakdown resistance offset the impact of higher anodic currents. The corrosion rate (CR) is directly proportional to I_{corr} and equivalent weight (EW), which is derived from the atomic weight (W_i), mass fraction (f_i), valence (n_i), and density (ρ) of each alloying element. The equivalent weight and density of the CCAs are calculated as follows [58]:

$$EW = \left(\sum n_i f_i / W_i \right)^{-1}; \rho = \sum \rho_i f_i \quad (4)$$

$$CR \text{ (mm/yr)} = (3.27 \times 10^{-3} * i_{corr} * EW) / \rho \quad (5)$$

Corrosion rates for the MA and GA CoCrFeMo_{0.85}Ni laser-clad

coatings were estimated from forward-scan electrochemical measurements in 3.5 wt% NaCl at pH 4, using an equivalent weight of **21.78 g/equiv**, and a theoretical alloy density of **8.79 g/cm³**. The resulting rates are very low ($\sim 8 \times 10^{-6}$ mm/year for MA and $\sim 8 \times 10^{-7}$ mm/year for GA), reflecting the inherent corrosion resistance of these coatings. Therefore, the GA-derived coating exhibited lower corrosion activity in terms of corrosion current density and corrosion rate, indicating better resistance to uniform corrosion under chloride-rich conditions, despite reduced repassivation capability following localized breakdown.

4. Discussion

4.1. Microstructural influence on localized corrosion

In both coatings, localized dissolution was preferentially associated with oxide agglomerates and phase boundaries, particularly at BCC/ σ interfaces (Figs. 12a–c and 13a–b). Although not dominant, localized attack along interfacial regions suggests that microstructurally induced crevice-like conditions may develop under certain configurations, promoting localized breakdown of the passive film.

The MA-derived coating exhibited severe surface degradation characterized by pronounced pitting and localized dissolution, consistent with active-passive corrosion transitions observed electrochemically (Fig. 12a–d). In Fig. 12d, the development of an interconnected porous network suggests preferential dissolution of less corrosion-resistant regions, indicative of selective phase or compositional attack. The absence of a continuous and compact passive layer, combined with the presence of deep cavities, points to unstable passivation and limited repassivation capability. These features are attributed to the inherent chemical heterogeneity of the MA-derived microstructure, where residual oxides, incomplete alloying, and dual-phase (FCC + BCC) regions promote micro-galvanic interactions and passive film destabilization [58,59]. The poor film stability inferred from electrochemical measurements is therefore corroborated by direct SEM evidence of passive film breakdown, particularly at agglomerated and interphase regions.

The post-corrosion SEM micrograph of the GA-derived coating (Fig. 13) reveals a relatively compact surface morphology with localized corrosion features concentrated along grain boundaries and interdendritic regions. While shallower pits and fragmented surface oxides are observed, large-scale material removal or interconnected porosity is absent, indicating a more stable and protective passive film (Fig. 13c) compared to the MA-derived coating. The EDS analysis indicates compositional variations between the thin film regions (Figs. 13b, 13c). In Fig. 13b, spectrum (S1) corresponds to a Cr- and Mo-enriched area,

consistent with the formation of a protective Cr₂O₃/Mo-containing passive layer, whereas spectrum (S2) shows reduced Cr and Mo contents and relatively higher Fe levels, suggesting preferential dissolution in these regions. This compositional contrast supports the occurrence of localized corrosion driven by microchemical heterogeneity rather than uniform film breakdown. Metastable pitting, reflected by minor current transients in the polarization curves (pseudo-passive region) (Fig. 11), correlates with the isolated and shallow degradation observed in SEM (Fig. 13b), suggesting rapid repassivation following passive film disruption. The small potential difference between E_{pit} and E_{rep} and the narrow hysteresis loop further confirm the high resistance of the GA-derived coating to sustained localized corrosion.

Overall, localized corrosion initiation was strongly influenced by microstructural uniformity, precipitate morphology, and passive film chemistry. In CoCrFeMo_{0.85}Ni alloys, intermetallic precipitates may exert a dual influence: finely distributed Cr-rich phases (FCC phase) can support passive film stability [60], whereas excessive σ -phase segregation at grain boundaries introduces electrochemical heterogeneity that may promote pit initiation under aggressive conditions. Consistent with previous studies, residual lattice mismatch and interfacial stresses at phase boundaries can further exacerbate localized corrosion susceptibility. Wang et al. [45] researched the detailed microstructural characteristics of boundaries at co-existing phases. Discrete atomic steps at the FCC/C14 Laves interfaces in FeCrNiCoNb_{0.5} indicate semi-coherent boundaries [61], whose lattice mismatch and resulting residual stresses promote localized corrosion in aqueous environments. These results highlight that corrosion resistance in laser-clad CCA coatings is governed not by phase constitution alone, but by the combined effects of microstructural homogeneity, interfacial integrity, and passive film stability.

4.1.1. Pitting initiation and chloride effect

Pitting corrosion in both GA and MA-derived coatings initiates near the breakdown potential (E_b) due to localized chloride-induced disruption of the passive film, leading to anodic dissolution and pit stabilization under acidic, chloride-rich conditions [56,58]. The protective passive film composition, dominated by Cr₂O₃ and Mo-based oxides, plays a crucial role in corrosion resistance [42,62] by forming a dense barrier that hinders Cl⁻ penetration and facilitates partial film regeneration. The mechanistic role of chloride ions, as reported by Zhang et al. [63], further elucidates these observations. In Cl⁻-free electrolyte, the passive layer develops uniformly, yielding a relatively continuous and stable metal/film interface. In Cl⁻-containing environments, however, chloride ions preferentially adsorb at defective or non-uniform sites, inducing heterogeneous dissolution of Fe and, to a lesser extent, Cr, along with irregular interfacial migration. Such non-uniform adsorption produces an undulating, stressed interface that serves as a precursor to passive film breakdown.

In the present study, this mechanistic framework explains the contrasting behavior of GA and MA-derived coatings. The duplex microstructure of HEAs contributes to localized corrosion via phase-specific passive film formation and micro-galvanic coupling [59]. In the GA-derived coating, the chemically uniform FCC matrix and Cr–Mo enrichment promote the formation of a stable passive film, resulting in a wider passive region, lower corrosion current density, and delayed pit initiation. However, once breakdown occurs, often at σ -rich boundaries, localized corrosion persists due to limited repassivation, as evidenced by the positive hysteresis loop and absence of a distinct repassivation potential (E_{rp}).

In contrast, the MA-derived coating exhibits a heterogeneous FCC–BCC– σ microstructure that destabilizes the passive film and accelerates chloride-assisted breakdown, leading to higher anodic activity and earlier pit initiation. Despite this weaker passivity, selective dissolution of reactive phases enables partial repassivation at some sites, consistent with the negative hysteresis behavior observed in CPDP tests. In this system, the BCC phase preferentially acts as an anodic site due to

Table 6

Summary of electrochemical results for the CCA coatings (both mechanically alloyed, and gas atomized) after testing in 3.5 wt% NaCl, pH 4.

Parameter*	Mechanically Alloyed Coating (MA)	Gas Atomized Coating (GA)
E_{corr} (mV _{SHE})	-470	-160
I_{corr} (A/cm ²)	1×10^{-3}	1×10^{-4}
I_{pass} (A/cm ²)	not applicable	$\sim 1 \times 10^{-1}$ (fluctuating; mean)
E_{pp} (mV)	not observed	+ 40 (first metastable pitting)
E_b (mV)	not observed	+ 900 $\pm$ 30 (stable breakdown)
E_{rp} (mV)	-380	not reached (no clear repassivation)
E_{prot} (mV)	-70 $\pm$ 40 (apparent)	+ 540 $\pm$ 40 (apparent)
ΔE (mV)	not defined	+ 360 $\pm$ 60 ($E_b - E_{\text{prot}}$)

* E_{corr} = corrosion potential; I_{corr} = corrosion current density; I_{pass} = passive current density; E_{pp} = metastable pitting potential; E_b = breakdown potential; E_{rp} = repassivation potential; E_{prot} = apparent protection potential on reverse scan; $\Delta E = E_b - E_{\text{prot}}$. "Not observed/defined" indicates absence of the feature in the polarization curve. $\pm$ values indicate the estimated range of potential selection from the curve.

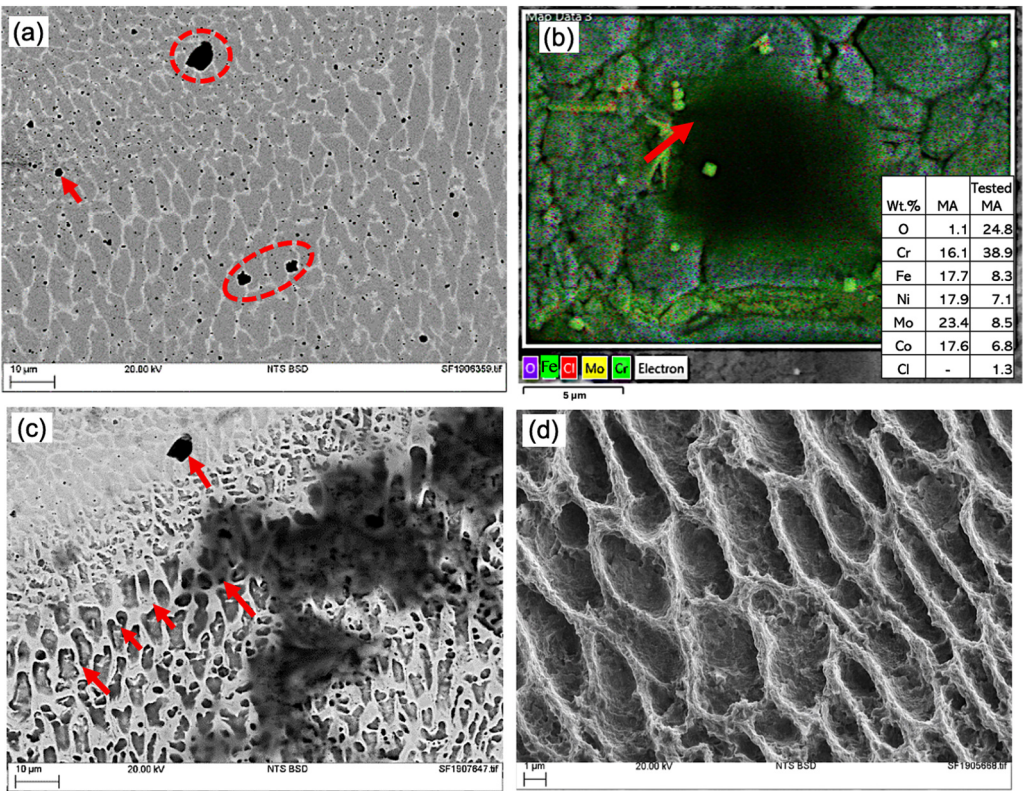


Fig. 12. SEM micrographs of the mechanically alloyed coating (MA) tested in 3.5 wt% NaCl at pH 4. The arrows and circles show pits and areas of partial or absent repassivation after passive film breakdown.

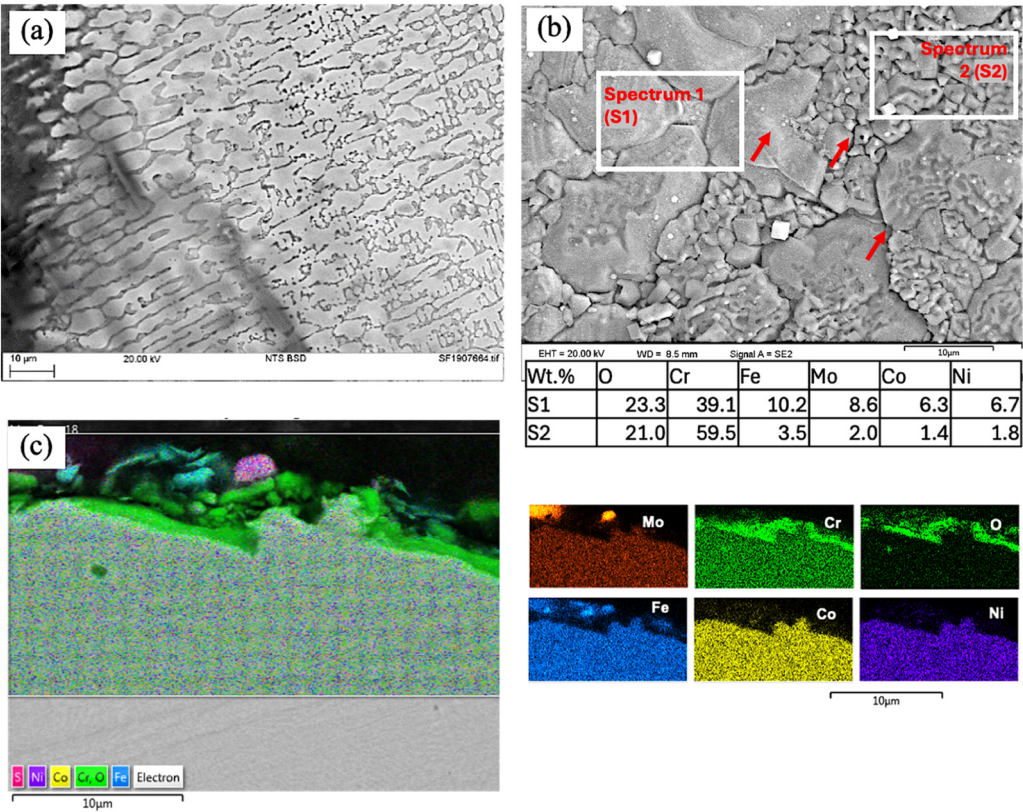


Fig. 13. SEM micrographs of the gas atomized coating (GA) tested in 3.5 wt% NaCl at pH 4. The arrows shows the protective $\text{Cr}_2\text{O}_3/\text{Mo}$ -containing passive layer.

elemental partitioning and phase-specific passivation, promoting localized dissolution and pit initiation. This effect is further amplified by

the cathodic area effect: the smaller volume fraction of the BCC phase concentrates anodic currents and drives localized material loss [64], creating zones depleted in protective elements and compromising film structure.

The compositional homogeneity and single-phase FCC structures in many GA systems are reported to play a beneficial role [65,66]. The low volume fraction and spatial segregation of σ -phase do not significantly disrupt passive film continuity and may locally enrich Cr and Mo, delaying pit initiation and suppressing micro-galvanic effects during early exposure [12,22,48] offering resistance to Cl^- -induced breakdown [37]. Despite this advantage, cyclic polarization reveals a positive hysteresis loop in the GA-derived coating, indicating that once passive film breakdown occurs, localized corrosion persists without full repassivation [67,68]. Unlike the GA-derived coating, the MA-derived coating exhibits negative hysteresis, indicating partial repassivation capability despite its higher corrosion current density and greater susceptibility to chloride-induced breakdown [64].

In summary, these results demonstrate that resistance to pit initiation and the ability to repassivate after breakdown are governed by different microstructural factors rather than corrosion current density alone.

4.1.2. Passive film stability and breakdown mechanisms

The pitting corrosion behavior of laser-clad $\text{CoCrFeMo}_{0.85}\text{Ni}$ coatings is strongly governed by microstructural heterogeneity, particularly phase distribution, elemental segregation, and grain boundary characteristics, which collectively control passive film integrity and susceptibility to localized breakdown in chloride-containing environments. In compositionally complex alloys, variations in Cr and Mo partitioning across FCC, BCC, and σ -phases play a central role in determining passive film stability and microscale pitting resistance.

Passive film formation proceeds through heterogeneous nucleation of oxide and hydroxide species at energetically favorable sites, influenced by local chemistry and phase morphology, as schematically illustrated in Fig. 14. Fig. 14a–b show that the GA-derived coating, fabricated from gas-atomized powders, develops a refined FCC matrix

with spatially segregated σ -phase and Cr–Mo-enriched grain boundaries. This microstructure promotes the formation of a compact, adherent passive film, delaying pit initiation. In contrast, the MA-derived coating, derived from mechanically alloyed powders, exhibits a heterogeneous FCC–BCC– σ microstructure with pronounced elemental partitioning and grain boundary segregation. These features generate local electrochemical inhomogeneities that favor passive film instability and pit nucleation under chloride exposure.

Despite initial passivation, the corrosion response differs markedly between the coatings. The MA-derived coating exhibits recurring depassivation–repassivation events, indicative of an unstable and discontinuous passive film. This behavior is consistent with its negative hysteresis loop, suggesting transient film repair at some sites but overall susceptibility to localized breakdown. Conversely, the GA-derived coating displays more uniform passivation and a wider passive region; however, once breakdown occurs, often at σ -rich boundaries, repassivation is limited, resulting in sustained pit propagation, as reflected by the positive hysteresis loop and absence of a distinct repassivation potential (Fig. 14c). These observations align with prior reports linking oxide density and continuity to corrosion resistance in acidic chloride media [16,49,69].

The apparent contrast between corrosion rate and pitting behavior arises because resistance to pit initiation and the ability to repassivate after breakdown are governed by different microstructural factors. In the GA-derived coating, the chemically uniform FCC matrix and moderate σ -phase precipitation promote Cr- and Mo-rich passive film formation, reducing micro-galvanic driving forces and delaying pit initiation. The diffusion of Mo into the FCC matrix and controlled σ -phase formation reduces compositional contrast between phases, stabilizing passivity [36,69]. However, excessive Mo enrichment or σ -phase concentration may locally deplete Cr or introduce brittle regions, limiting repassivation once breakdown occurs. This is consistent with the reported Mo-dependent competition between passive film stabilization and its selective dissolution [70].

In contrast, the MA-derived coating contains a heterogeneous multiphase microstructure (FCC + BCC + σ), leading to discontinuous

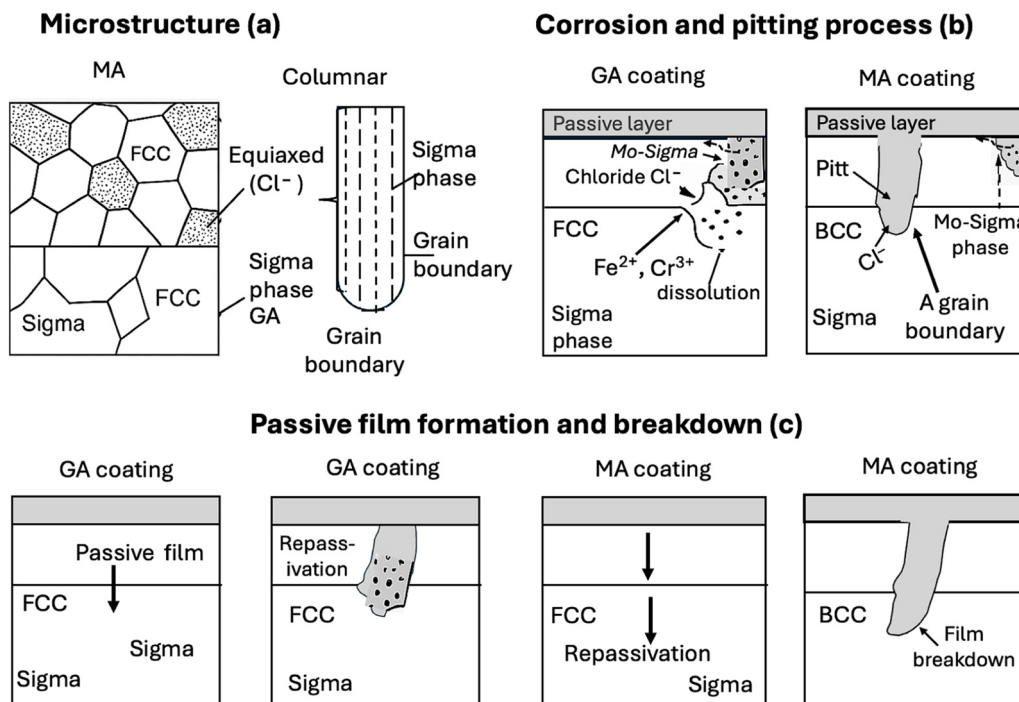


Fig. 14. Schematic illustrating (a) the characteristic microstructures, (b) passive film formation and preferential phase dissolution, and (c) repassivation or film breakdown mechanisms of the GA and MA CCA coatings in 3.5 wt% NaCl, pH 4. The GA-derived coating delays pit initiation through a more protective passive film, whereas the MA exhibits weaker passivity but may locally repassivate following breakdown.

and chemically unstable passive films. Under the mildly acidic chloride environment (pH 4), Cr_2O_3 can dissolve, while Mo-containing oxides (MoO_3) are thermodynamically unstable and prone to transformation into soluble molybdate species. Micro-galvanic coupling between Mo-rich BCC regions and adjacent FCC phases accelerates localized dissolution, resulting in deep, irregular pit formation. Nevertheless, selective dissolution of reactive phases allows partial repassivation at some locations, consistent with the observed negative hysteresis behavior.

EDS analysis supports these trends, showing higher and more uniform Cr content in the GA-derived coating compared to the MA, favoring continuous Cr_2O_3 formation. The corrosion resistance of both coatings is primarily associated with a compact Cr_2O_3 layer, supplemented by Mo-containing oxides that restrict chloride ingress and contribute to passivity [36,69]. Cr_2O_3 is a chemically stable, diffusion-controlled oxide that provides passivity through strong interfacial adhesion and slow growth kinetics. Although its Pilling–Bedworth ratio (PBR ~ 2.0 – 2.1) slightly exceeds the classical ideal range, PBR alone does not determine oxide protectiveness in multicomponent alloys [36,58]. Mo-containing oxides complement Cr_2O_3 by restricting chloride ingress and aiding repassivation, though their partial solubility under acidic conditions can limit long-term stability [58]. Consequently, passive film integrity in these coatings is governed by the combined effects of oxide chemistry, phase distribution, and microstructural continuity rather than PBR alone [9,25,36,69].

Overall, Fig. 14c summarizes the contrasting passive film formation and breakdown mechanisms. Corrosion resistance in these coatings is

governed by the interplay between microstructure, phase distribution, and passive film continuity rather than by composition or oxide chemistry alone. The GA-derived coating sustains a more continuous, though fluctuating, passive layer that delays pit initiation and limits propagation, whereas the MA-derived coating exhibits unstable passivation and accelerated localized degradation once breakdown occurs.

4.2. Tribo-oxidation and wear mechanisms

Protective oxides, particularly Cr_2O_3 and MoO_3 , not only mitigate electrochemical degradation but also influence wear resistance through tribo-oxidation during sliding contact. Molybdenum is mainly incorporated into the passive film as MoO_4^{2-} which is soluble, while MoO_3 is protective in solid form. The presence of Mo-containing oxides on the surface was clearly evident after dry sliding wear tests suggest surface oxidation may have occurred under contact stresses. Notably, high oxidation during the mechanical alloying powder metallurgy process is believed to contribute to surface oxidation in FeCoCrMoNi coatings, thereby enhancing wear resistance [32]. Thus, the presence of σ intermetallic, often considered detrimental due to brittleness, contributes positively, in this case. Their distribution enhances both corrosion and wear resistance through intermetallic strengthening and improved passive layer formation [36,71]. In addition to corrosion protection, the coatings were also investigated to evaluate surface evolution during sliding contact, where tribo-oxidation products and surface films play a crucial role in the observed tribological performance.

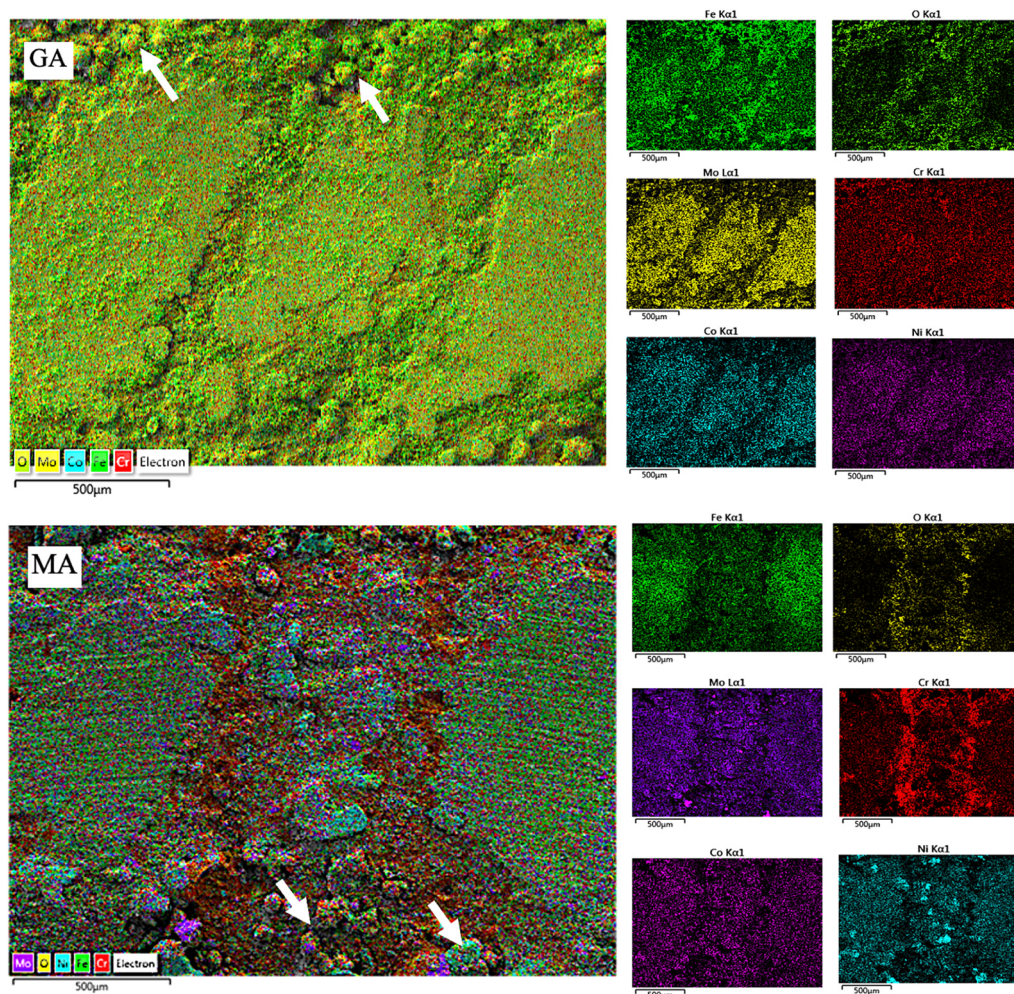


Fig. 15. SEM/EDS elemental surface maps of the CCA coatings (mechanically alloyed – MA, and gas atomized – GA) under dry sliding conditions. The arrows indicate the distinct surface morphologies: spherical grains in the GA and mixed-angular grains in the MA on the unworn areas in the coatings.

The wear track morphology (Fig. 15) revealed two main zones: Zone 1, dominated by abrasive grooves indicating two-body abrasion, while Zone 2, with fragmented debris and delamination, suggesting third-body wear mechanisms exacerbated by local softening and oxide layer breakdown, particularly in MA-derived coatings.

In Zone 2, GA-derived coatings ($R_a = 13.2 \pm 0.6 \mu\text{m}$) exhibited minor rolling-induced wear due to their smooth, spherical features and uniformly distributed debris. Conversely, the relatively rougher MA-derived coatings ($R_a = 17.1 \pm 0.7 \mu\text{m}$) experienced more intense third-body wear, marked by fractured asperities and the accumulation of flaky debris compacted into oxidized tribolayers. Delamination and flake-like debris were more prominent on MA surfaces (Fig. 15), correlating with greater friction instability. Generally, such surface topography differences stem from the deposition technique and powder morphology inherent to powder metallurgy. Furthermore, μ particles

coexisting with the σ -phase tend to nucleate at phase boundaries, enhancing intermetallic strengthening in CoCrFeMo_{0.85}Ni alloys [34]. These hard intermetallic and pseudo-binary diffusion couples improve the mechanical robustness of the ductile FCC matrix [9,17].

EDS analysis of the worn areas confirmed the formation of Cr, Co, Fe, Ni, and Mo oxides, particularly on MA-derived coatings, indicating that tribo-oxidation plays a significant role in surface evolution (Figs. 15 and 16). SEM maps of worn surfaces revealed prominent grooves aligned with the sliding direction, as well as diverse debris morphologies—adhered, flaky, and fragmented. EDS mapping of oxidized wear tracks and debris showed high levels of Mo and Cr, with lower concentrations of Ni, Co, and Fe—elements commonly associated with the BCC/ σ phase, known for its load-bearing capacity [54,72]. EDS point analysis (Fig. 16) showed oxygen content reaching 25.2 % in MA and 29.2 % in GA-derived coatings, indicating extensive atmospheric

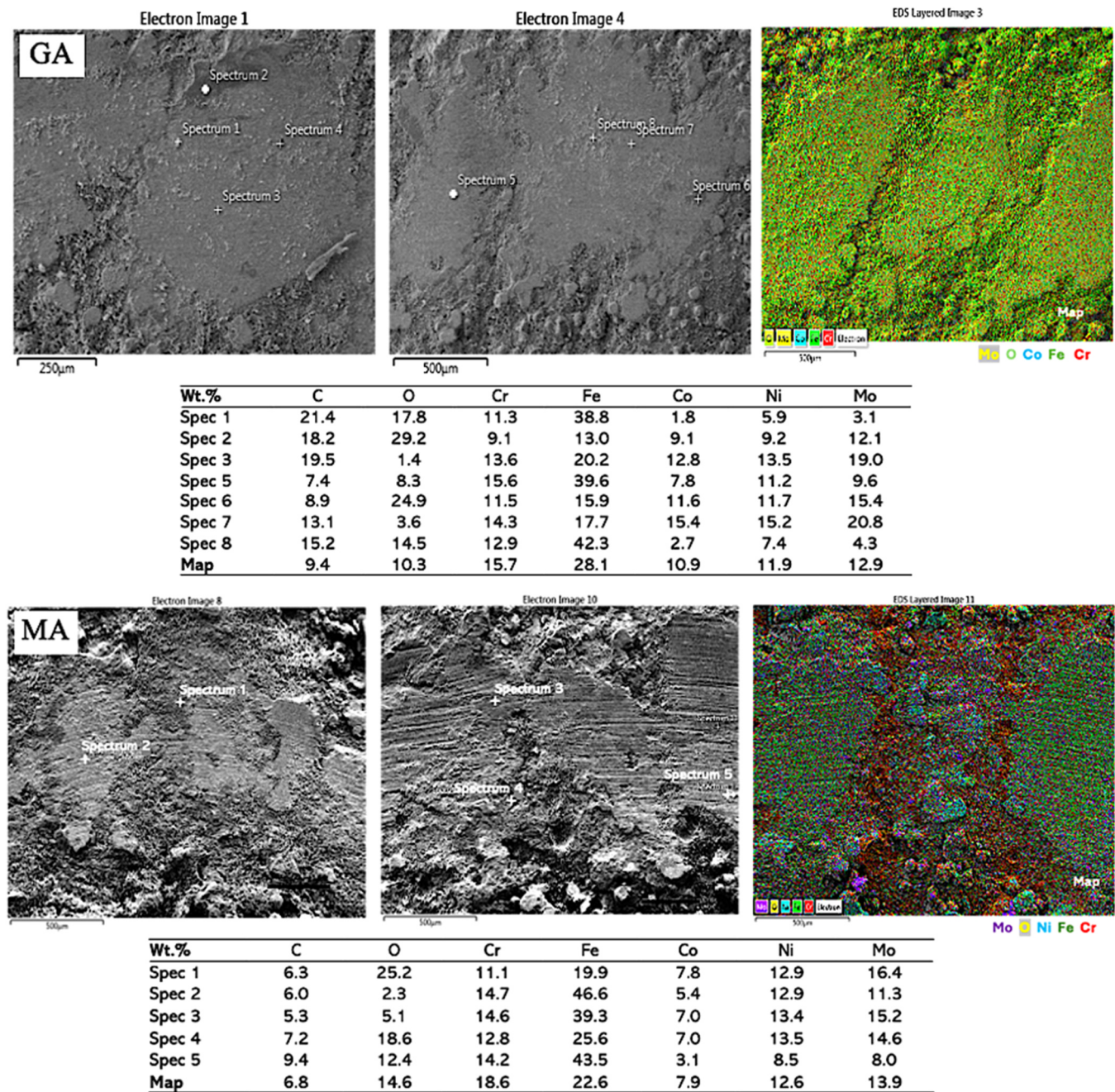


Fig. 16. Observations of CCA coatings after wear test under dry sliding conditions: SEM micrographs, EDS point analysis, and SEM/EDS compositional maps.

oxidation and mechanical mixing. The thermodynamically favored oxides under these conditions are Fe_2O_3 , Cr_2O_3 , and MoO_3 [32]. Abrasive wear was predominant, as indicated by groove and scratch marks. However, wear resistance was primarily governed by the formation and mechanical stability of the tribo-oxide layer during plastic deformation under sliding conditions. The GA-derived coating, with its denser and more adherent oxide film, showed high wear resistance.

SEM analysis (Fig. 16) revealed significantly narrower ($803 \pm 0.7 \mu\text{m}$) and shallower ($35.0 \pm 24.4 \mu\text{m}$) wear tracks on GA-derived coatings compared to MA ($1123 \pm 0.1 \mu\text{m}$ wide and $73.2 \pm 34.5 \mu\text{m}$ deep), in agreement with observed volume loss trends in Table 4. Large volume loss was compensated by WC counter ball abrasion reducing the wear rates. Notably, the lower hardness of MA-derived coatings translated to reduced resistance to plastic deformation and delamination. However, plastic deformation was limited to areas with adherent, oxidized debris, especially near the mid-junction region.

Discontinuous wear patterns, particularly in MA-derived coatings, underscore the detrimental role of their surface morphology. EDS analysis of selected groove points (2, 3, 5, and 7) showed minimal oxide content in Fe-rich regions, indicating that the steel substrate did not participate significantly in the wear process, further supporting the CCA coating's protective function [23,72]. Cross-sectional profiles (Fig. 17) confirmed that the wear depth remained below 10 % of the original $\sim 1 \text{ mm}$ coating thickness. No significant deviations from the nominal coating composition, particularly for Co, Cr, Ni, and Mo, were observed in the internal regions or below the worn surface (layers L2–L4), affirming the coatings' structural integrity post-test. However, composition analysis revealed a notable increase in oxygen and iron content at the top worn surface (L1), with O rising to 10.0 wt% (compared to 0.8 wt% in L2–L4) and Fe increasing to 42.1 wt% (vs. 24.7 wt% in L2–L4). These findings highlight that wear resistance in high-entropy-based coatings is governed not only by hardness, but also by the synergistic effects of oxide scale stability, intermetallic phase distribution, and microstructural homogeneity, particularly under dry sliding conditions where tribo-oxidation is dominant. It is acknowledged that lubricated or wet wear conditions may alter the prevailing wear mechanisms, by reducing adhesive interactions, modifying debris formation, or promoting tribochemical film development and may consequently influence the absolute wear rates and relative performance trends; therefore, evaluation under lubricated conditions is essential for applications involving fluid-mediated contact.

5. Conclusion

In this study, $\text{CoCrFeMo}_{0.85}\text{Ni}$ compositionally complex alloy (CCA) coatings were successfully fabricated by laser cladding using gas-atomized (GA) and mechanically alloyed (MA) powders. The main conclusions are summarized as follows:

1. The powder synthesis route strongly influenced the microstructural evolution of the coatings. GA-derived coatings exhibited a more chemically uniform FCC-based matrix with spatially segregated σ -phase, whereas MA-derived coatings showed pronounced microstructural heterogeneity and elemental segregation associated with the mechanically alloyed feedstock.
2. GA-derived coatings demonstrated better wear resistance compared to the MA. This behavior is attributed to their higher hardness arising from a refined FCC matrix and controlled σ -phase precipitation, which enhanced resistance to plastic deformation without compromising coating integrity. The formation of a Mo-oxide-rich tribo-layer during sliding further contributed to wear protection.
3. Localized corrosion was the dominant degradation mechanism in both coatings, with preferential attack associated with microstructural heterogeneities. Electrochemical measurements indicate that the GA-derived coating exhibits lower corrosion current density and delayed pit initiation, consistent with the formation of a Cr- and Mo-

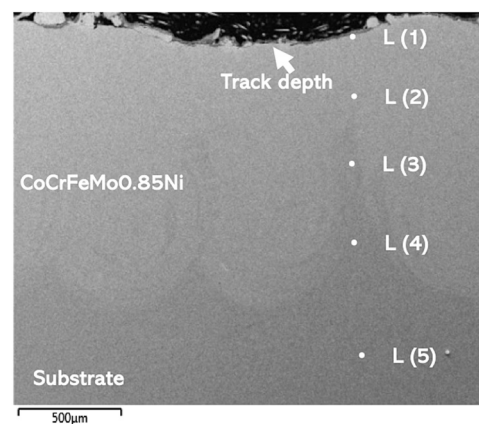


Fig. 17. Cross-sectional image of MA coating with track depth and EDS line profile (L1–L5)) analyses after dry sliding wear test. The arrow indicates the shallow wear track.

enriched passive film. However, once passive film breakdown occurs, repassivation is limited, resulting in sustained pit growth. In contrast, the MA-derived coating shows higher corrosion activity but retains partial repassivation capability following localized attack.

4. These results demonstrate that corrosion resistance in laser-clad $\text{CoCrFeMo}_{0.85}\text{Ni}$ coatings is governed by a balance between passive film stability and repassivation capability, rather than by any single electrochemical parameter.
5. Overall, GA-derived coatings exhibit improved resistance to both wear and pitting corrosion, highlighting the critical role of powder synthesis in tailoring microstructure and optimizing the surface performance of laser-clad CCA coatings for corrosive and wear-intensive environments.

CRediT authorship contribution statement

Ioana Csaki: Investigation, Data curation. **Sigrun N. Karlsdottir:** Writing – review & editing, Supervision. **Oppong Boakye Gifty:** Writing – review & editing, Writing – original draft, Investigation. **Francesco Fanicchia:** Writing – review & editing, Investigation, Conceptualization. **Josh Barras:** Data curation. **Emily Davison:** Data curation. **Laura E. Geambazu:** Writing – review & editing, Investigation, Data curation. **Shiladitya Paul:** Writing – review & editing, Supervision.

Funding

This work is part of the H2020 EU project Geo-Coat: “Development of novel and cost-effective corrosion resistant coatings for high temperature geothermal applications” funded by H2020 EU project no. 764086.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sigrun Nanna Karlsdottir reports financial support was provided by EU Framework Programme for Research and Innovation Future and Emerging Technologies. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would also like to acknowledge the resources and collaborative efforts provided by the consortium of the Geo-Coat project.

Data Availability

Data will be made available on request.

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2026-03

Elsevier

<https://doi.org/10.1016/j.mtcomm.2026.114878>

Oppong GB, Fanicchia F, Geambazu LE, et al., (2026) Effect of microstructure on corrosion and wear behavior of laser-clad CoCrFeMo0.85Ni compositionally complex alloy coatings. Materials Today Communications, Volume 52, March 2026, Article number 114878