



ISSN: 2617-6548

URL: www.ijirss.com



Nanochemical hardening and wear resistance of multi-component Cr-Ni-Co-N thin films synthesized via reactive rf plasma sputtering

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Abstract

Modifying AISI 4140 alloy steel via physical vapor deposition (PVD) is essential to mitigate surface degradation under demanding tribological conditions. This study investigates the phase evolution, surface topography, and nanomechanical performance of chromium-based nitride coatings co-sputtered with nickel and cobalt on AISI 4140 substrates using reactive radio-frequency (RF) sputtering at 13.56 MHz. By systematically varying the reactive nitrogen flow ratio (10%, 15%, and 20% N₂) and target surface metallic configurations (Cr, Cr–Ni, Cr–Co, and Cr–Ni–Co), the interplay between deposition dynamics and film properties was established. Cross-sectional thickness analysis revealed a reduction in film thickness from 2.9 μm to 1.3 μm with increasing N₂ content, governed by target poisoning and gas-phase scattering mechanics. X-ray diffraction (XRD) confirmed the formation of cubic (Cr,M)N structures with nano-crystallite sizes ranging from 19.44 nm to 53.50 nm. Surface topography via atomic force microscopy (AFM) demonstrated an increase in average surface roughness ($S_a = 8.42\text{--}12.30$ nm) as a function of N₂ incorporation. Nanoindentation characterization demonstrated a continuous increase in mechanical response with nitrogen flow: maximum hardness ($H = 25.5$ GPa) and reduced elastic modulus ($E = 285$ GPa) were obtained for Cr–Ni coatings at 20% N₂. The calculated elastic strain index ($H/E = 0.089$) and plastic deformation resistance ($H^3/E^2 = 0.204$ GPa) indicate high load-bearing capacity and crack-initiation resistance, demonstrating that metallic co-sputtering combined with optimized nitrogen stoichiometry significantly elevates the surface performance of AISI 4140 steel.

Keywords: (Cr,Ni,Co)N_x thin films, AISI 4140 steel, Nanoindentation, Reactive RF sputtering, Target poisoning, Wear resistance.

DOI: 10.53894/ijirss.v9i10.11958

Funding: This study received no specific financial support.

History: Received: 13 August 2026 / **Revised:** 2 October 2026 / **Accepted:** 7 October 2026 / **Published:** 26 October 2026

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Competing Interests: The authors declare that they have no competing interests.

Authors' Contributions: All authors contributed equally to the conception and design of the study. All authors have read and agreed to the published version of the manuscript.

Transparency: The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

Acknowledgment: The authors would like to express their sincere gratitude to the Center for Research in Nanotechnology Systems (PRSN), National Research and Innovation Agency (BRIN), for providing laboratory facilities to support this research. The authors also gratefully acknowledge Institut Teknologi Sepuluh Nopember (ITS) for assistance with atomic force microscopy (AFM) characterization. Furthermore, the authors thank Universitas Gadjah Mada (UGM) for its collaboration and research support.

Publisher: Innovative Research Publishing

1. Introduction

AISI 4140 medium-carbon chromium-molybdenum low-alloy steel is a crucial structural material widely deployed in automotive, aerospace, and power generation engineering due to its high tensile strength, favorable ductility, and excellent machinability [1]. However, when subjected to extreme mechanical contact stresses, elevated temperatures, and aggressive unlubricated sliding, untreated AISI 4140 exhibits severe tribological vulnerabilities, including micropitting, scuffing, and adhesive surface breakdown [1]. Because localized plastic deformation and tribo-oxidative failures originate predominantly at the material surface, surface modification techniques are essential to engineer a superior interfacial mechanical state while preserving bulk mechanical integrity [2-5]. Advanced surface engineering strategies, ranging from electro-spark deposition coatings [6] to combined quench-hardening with multi-element physical vapor deposition (PVD) nitrides [7] have demonstrated that optimizing substrate-film load-bearing capability and interfacial residual stress is paramount to suppressing premature component failure. Among surface modification technologies, reactive radio-frequency (RF) sputtering at a frequency of 13.56 MHz offers distinctive physical advantages, including high plasma density, atomistic flux uniformity, precise stoichiometric control, and dense thin-film synthesis at low deposition temperatures [8]. Reactive sputtering relies on energizing inert gas ions (Ar^+) alongside reactive gas species (N_2) to drive target atom ejection and subsequent chemical synthesis at the substrate surface [8]. Binary chromium nitride (CrN) coatings possessing a rock-salt cubic crystal structure have been extensively implemented in cutting tools and automotive components owing to their high chemical stability, corrosion resistance, and elevated mechanical hardness [9, 10]. Nevertheless, single-metal binary nitrides like CrN reach performance limits under extreme loading conditions, where moderate fracture resistance and limited plastic strain accommodation trigger shear localization and delamination [11]. To overcome the intrinsic physical boundaries of binary ceramics, recent thin-film research has focused on alloying multi-component transition metals ($\text{M} = \text{Ni}, \text{Co}, \text{Al}, \text{Ti}$) into the CrN matrix [12]. Incorporating secondary transition metal cations alters the valence electron concentration (VEC), induces solid-solution lattice distortion, and restricts dislocation movement via grain boundary constraint mechanisms [13]. Nanomechanical evaluation of advanced functional coatings on AISI 4140 steel reveals that tailoring intrinsic elastic modulus (E) and hardness (H) is critical to maximizing elastic strain capacity and energy dissipation under contact stress [11, 14]. Multi-component targets assembled via mosaic configurations present a versatile physical methodology to co-sputter complex metal-nitride matrices [15]. However, the atomistic phase separation behaviors, crystalline lattice stability, and phase transformation dynamics in co-sputtered ternary (Cr-Ni-N , Cr-Co-N) and quaternary (Cr-Ni-Co-N) systems remain insufficiently detailed within reactive RF plasma environments [16-18]. A fundamental physical driver during reactive PVD is the nitrogen partial pressure ratio ($\text{Ar}:\text{N}_2$), which dictates plasma-surface dynamics and target nitridation mechanics [12, 19]. Elevating nitrogen flow induces target poisoning, wherein a ceramic nitride layer forms on the metal target surface [20]. This target state transition substantially depresses the sputtering yield, reduces species arrival flux at the substrate, and modulates film growth kinetics and cross-sectional film thickness. Simultaneously, tuning nitrogen stoichiometry drives phase transformation from sub-stoichiometric ($\text{Cr}, \text{M})\text{N}_{1-x}$ to fully dense, stoichiometric cubic rock-salt ($\text{Cr}, \text{M})\text{N}$, which fundamentally dictates the crystallite nucleation rate, lattice strain, surface roughness, and intrinsic mechanical properties [21]. This study systematically investigates the physical correlation between target metallic composition (Cr , Cr-Ni , Cr-Co , and Cr-Ni-Co) and reactive nitrogen concentration (10%, 15%, and 20% N_2) during 13.56 MHz RF reactive co-sputtering on AISI 4140 steel. The interplay between target poisoning dynamics, film thickness evolution, crystallite size refinement (19.44–53.5 nm), and surface roughness evolution ($S_a = 8.42$ –12.3 nm) is established. Furthermore, nanoindentation characterization is utilized to elucidate the continuous nanomechanical hardening mechanism (H up to 25.5 GPa, E up to 285 GPa), and the tribological metrics of elastic strain index (H/E) and plastic deformation resistance (H_3/E_2) are quantified to clarify the physical strengthening mechanisms operating in multi-component transition metal nitrides [22, 23].

2. Materials and Methods

2.1. Substrate Preparation and Target Architecture

AISI 4140 low-alloy steel disks with a diameter of 10 mm and a thickness of 3 mm were used as deposition substrates. The nominal substrate chemical composition comprises 0.38–0.43 wt% C, 0.75–1.00 wt% Mn, 0.20–0.35 wt% Si, 0.80–1.10 wt% Cr, 0.15–0.25 wt% Mo, ≤ 0.035 wt% P, and ≤ 0.04 wt% S [24]. Prior to mounting on the anode holder, substrate surfaces were mechanically ground and polished using SiC abrasive papers from grade 80 down to grade 2000, followed by ultrasonic cleaning in acetone and ethanol baths to remove surface contaminants.

The sputtering cathode comprised a high-purity metallic chromium (Cr) target with a diameter of 75 mm. To co-sputter multi-element transition metal systems, high-purity nickel (Ni) and cobalt (Co) pieces were configured over the main Cr target using a mosaic target arrangement with a target area coverage ratio up to 10% [15]. Four distinct target configurations were evaluated: pure Cr, Cr–Ni (90:10 area ratio), Cr–Co (90:10 area ratio), and Cr–Ni–Co (80:10:10 area ratio).

2.2. Reactive RF Co-Sputtering Procedure

Thin-film depositions were conducted in a custom radio-frequency (RF) reactive sputtering system operating at a radio frequency of 13.56 MHz [25] as shown in Figure 1.

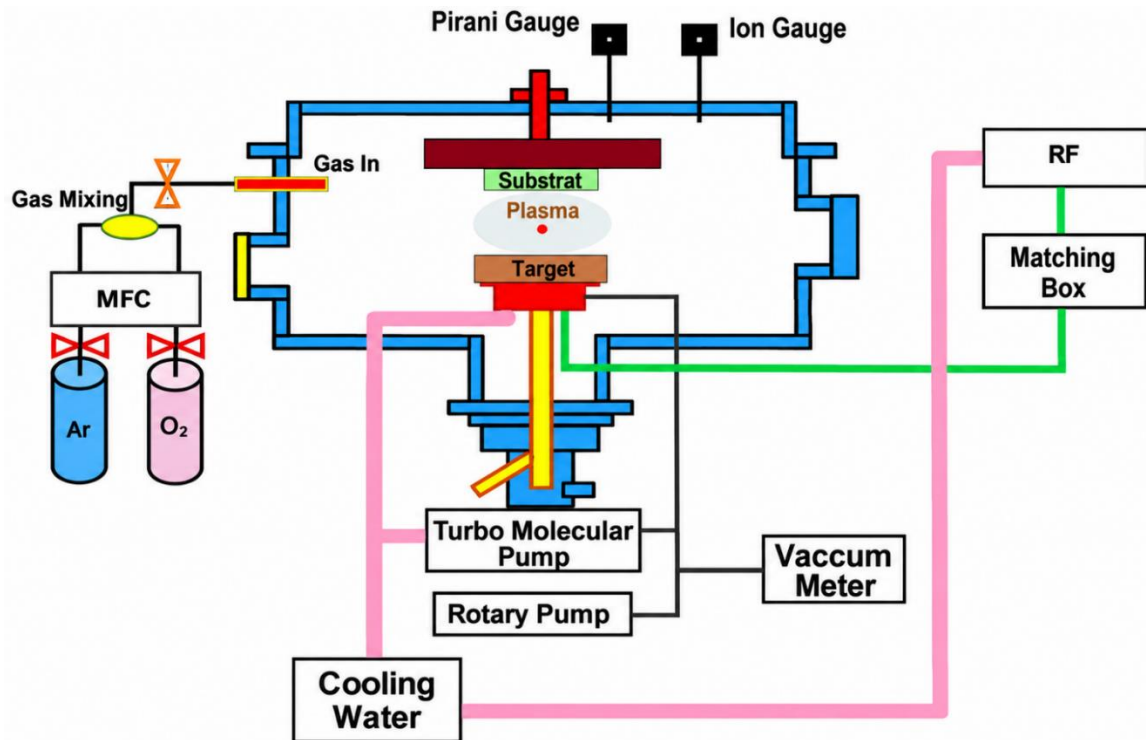


Figure 1.
The self-built RF Sputtering system for improving AISI 4140.

The sputtering chamber was evacuated to a base vacuum pressure of 5×10^{-6} mbar using a high-vacuum pumping assembly consisting of a mechanical rotary backing pump and a turbomolecular pump. Argon gas (Ar, 99.999 purity) was introduced through mass flow controllers to establish a working pressure of 3×10^{-2} mbar. High-purity reactive nitrogen gas (N₂, 99.999% purity) was subsequently introduced into the working plasma at flow ratios of 10%, 15%, and 20% relative to the total gas composition (Ar + N₂). All deposition processes were carried out for a fixed processing time of 30 minutes.

2.3. Structural, Morphological, and Chemical Characterization

Phase evolution and crystal structure were identified via X-ray diffraction (XRD) operating with Cu K α radiation ($\lambda = 1.5406$ Å) across a diffraction angle range of $2\theta = 20^\circ$ – 80° . Peak locations were matched against JCPDS reference files. Average crystallite sizes (D) were calculated using the Debye-Scherrer relation:

$$D = \frac{\kappa\lambda}{\beta \cos \theta}$$

where $\kappa = 0.9$, $\lambda = 1.5406$ Å, θ is the Bragg diffraction angle, and β is the full width at half maximum (FWHM) in radians, corrected for instrumental broadening (β_{inst}).

Coating cross-sections were examined using field-emission scanning electron microscopy (FE-SEM) to establish film thickness (t). Surface micro-topography and three-dimensional surface roughness parameters (S_a and S_z) were acquired using atomic force microscopy (AFM) operated in tapping mode across $10 \mu\text{m} \times 10 \mu\text{m}$ scanning areas. Elemental

composition was characterized via Energy-Dispersive X-ray Spectroscopy (EDX), with analytical interpretation accounting for the sub-film electron interaction volume within the underlying steel substrate.

2.4. Nanomechanical and Tribological Testing

Intrinsic mechanical properties, including nanoindentation hardness (H) and reduced elastic modulus (E), were measured using a nanoindenter equipped with a Berkovich diamond tip. To eliminate substrate compliance effects and avoid substrate punch-through, the maximum penetration depth (h_{max}) was strictly limited to $\leq 10\%$ of the measured coating thickness (t). The elastic strain to failure (H/E) and resistance to plastic deformation (H^3/E^2) were derived to quantify contact damage tolerance [11, 14]. Unlubricated sliding wear performance was evaluated using a pin-on-disc tribometer in accordance with ASTM G99 guidelines under ambient conditions.

3. Results and Discussion

3.1. Deposition Kinetics, Target Poisoning, and Film Thickness Evolution

The cross-sectional film thickness (t) of the reactive RF co-sputtered coatings as a function of target metal composition and reactive nitrogen ratio ($N_2\%$) is summarized in Table 1. Across all target configurations (Cr–Ni, Cr–Co, and Cr–Ni–Co), the film thickness decreased with increasing nitrogen concentration in the sputtering gas mixture. For a constant 30-minute deposition duration, the coating thickness drops from 2.9 μm at 10% N_2 down to 1.9 μm at 15% N_2 , and reaches a minimum of 1.3 μm at 20% N_2 . This corresponds to a significant reduction in net deposition rate from ≈ 96.7 nm/min down to ≈ 43.3 nm/min.

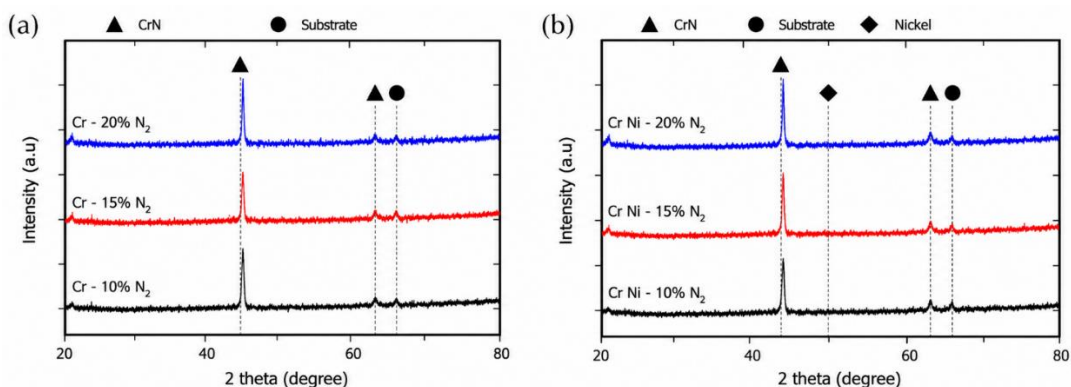
This pronounced attenuation in growth rate is primarily governed by target poisoning kinetics and plasma-gas phase collision physics characteristic of reactive physical vapor deposition [12, 20]. During reactive sputtering, as the partial pressure of nitrogen (N_2) is elevated from 10% to 20%, the sputtering regime transitions rapidly from the metallic mode to a fully poisoned ceramic mode [20]. At higher nitrogen flows, a compound nitride layer (CrN_x , NiN_x , CoN_x) forms dynamically on the erosion track of the cathode target surface [12]. Because transition metal nitrides possess substantially lower sputtering yields (atoms/ion) compared to their parent metallic elements, the ejection flux of metal species from the target surface is dramatically suppressed [12, 20].

Concurrently, altering the Ar:N_2 flow ratio modifies the ionic composition and momentum transfer efficiency within the plasma sheath [12, 19]. Reducing the relative concentration of heavier argon ions (Ar^+ , atomic mass ≈ 39.95 amu) in favor of lighter molecular and atomic nitrogen ions (N_2^+ , atomic mass ≈ 28.01 amu; N^+ , atomic mass ≈ 14.01 amu) lowers the average energy transfer efficiency during ion bombardment at the target surface [12]. Furthermore, increased nitrogen partial pressure reduces the mean free path (λ_{mfp}) of sputtered species, intensifying thermalizing elastic scattering collisions within the target-substrate distance [19]. This scattering disperses the adatom flux away from the normal substrate trajectory, further depressing the film accumulation rate [19].

The thickness evolution remains virtually invariant with respect to the mosaic target additions (Ni and Co). This consistency occurs because chromium, nickel, and cobalt possess comparable elemental sputtering yields under Ar^+ bombardment within the applied 13.56 MHz RF power density domain [15, 26]. Consequently, target surface nitridation kinetics rather than metallic species variations serve as the dominant physical driver of film thickness evolution in these multi-component transition metal nitrides.

3.2. Phase Evolution and Crystallographic Structure

The X-ray diffraction (XRD) spectra of thin films deposited using pure Cr, Cr–Ni, Cr–Co, and Cr–Ni–Co mosaic targets under varying reactive nitrogen flow ratios (10%, 15%, and 20% N_2) are depicted in Figures 2 (a)–(d). Across all experimental conditions, the dominant crystalline reflections correspond to the face-centered cubic (FCC) rock-salt structure of chromium nitride (CrN , JCPDS 96-100-8957). The primary diffraction peaks are identified at $2\theta \approx 43.45^\circ$ – 43.79° and $2\theta \approx 63.17^\circ$ – 63.56° , corresponding to the (200) and (220) crystallographic planes of cubic CrN , respectively. A low-intensity reflection originating from the underlying AISI 4140 steel substrate is consistently observed at $2\theta \approx 65.5^\circ$.



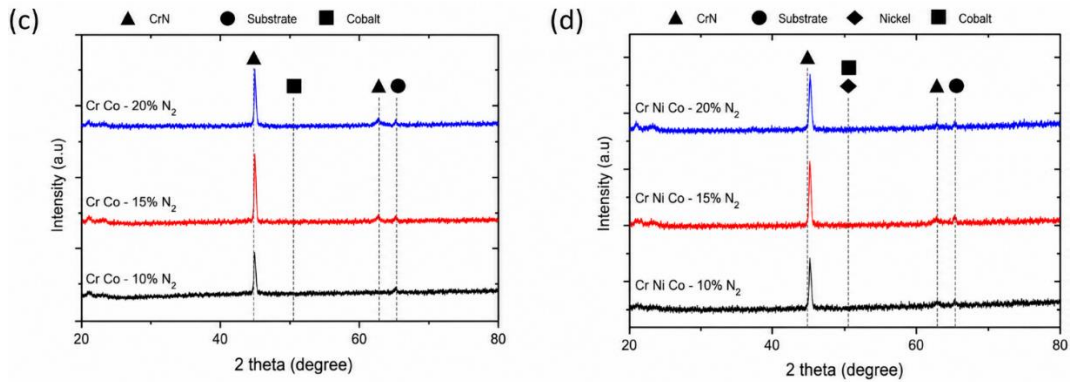


Figure 2.
The X-ray diffraction of thin films: (a) Cr, (b) Cr-Ni, (c) Cr-Co, (d) Cr-Ni-Co.

For coatings synthesized with Ni- and Co-containing targets [Figures. 2(b)–2(d)], secondary metallic reflections appear at $2\theta \approx 50.27^\circ$ – 51.91° and $2\theta \approx 50.91^\circ$ – 51.78° , assigned to the (200) planes of cubic Ni (JCPDS 96-210-2276) and cubic Co (JCPDS 96-901-2936), respectively. Significantly, no distinct binary nitride phases of nickel (Ni_xN) or cobalt (Co_xN) are detected within the 10%–20% N_2 range. This phase selectivity is thermodynamically driven by the standard Gibbs free energy of formation (ΔG_f°). The formation enthalpy of CrN ($\Delta G_f^\circ \approx -92.4$ kJ/mol) is substantially more negative than those of nickel nitrides (Ni_4N , Ni_3N) and cobalt nitrides (Co_4N , Co_3N), which remain thermally unstable or require nitrogen flow concentrations exceeding 22%–30% to nucleate [13, 16, 17]. Consequently, reactive nitrogen preferentially bonds with chromium to construct the rigid CrN lattice, while sputtered Ni and Co atoms are either incorporated into the rock-salt lattice as substitutional cations ($\text{Cr}_x\text{M}_y\text{N}$) or segregate as unreacted, nanoscale metallic domains along grain boundaries [18].

Systematic variations in the 2θ diffraction angle of the dominant (200) CrN peak reflect changes in interplanar lattice spacing (d), governed by Bragg's Law:

$$\lambda = 2d \sin\theta$$

As the nitrogen flow ratio is adjusted, subtle shifts toward higher 2θ angles (e.g., from 43.56° to 43.79° in Cr–Co coatings) correspond to a reduction in interplanar spacing (d), signaling lattice compression ($\Delta d < 0$) induced by residual compressive stresses or substitutional contraction. Conversely, shifts toward smaller 2θ angles (as observed in pure Cr at 15% N_2) indicate lattice expansion caused by interstitial incorporation of excess nitrogen or defect relaxation.

Table 1.

Cross-sectional film thickness (t), nanoindentation hardness (H), and reduced elastic modulus (E) of reactive RF co-sputtered coatings on AISI 4140 steel.

No.	Coating	N_2 Ratio (%)	Film Thickness t (μm)	Hardness H (GPa)	Reduced Modulus E (GPa)
1	Cr–Ni	10	2.9	14.5	195
2	Cr–Ni	15	1.9	22.0	265
3	Cr–Ni	20	1.3	25.5	285
4	Cr–Co	10	2.9	13.0	185
5	Cr–Co	15	1.9	20.5	250
6	Cr–Co	20	1.3	23.5	275
7	Cr–Ni–Co	10	2.9	14.0	190
8	Cr–Ni–Co	15	1.9	21.5	260
9	Cr–Ni–Co	20	1.3	24.5	280

Table 2.

Computed FWHM values and Debye-Scherrer crystallite sizes for co-sputtered coatings.

No.	Target Composition	Nitrogen Ratio (%)	2θ (deg)	FWHM (deg)	Crystallite Size D (nm)
1.	Cr	10	43.71	0.3198	26.76
2.	Cr	15	43.50	0.4398	19.44
3.	Cr	20	43.59	0.1599	53.50
4.	Cr–Ni	10	43.70	0.2799	30.57
5.	Cr–Ni	15	43.51	0.2399	35.65
6.	Cr–Ni	20	43.67	0.2399	35.67
7.	Cr–Co	10	43.56	0.1999	42.79
8.	Cr–Co	15	43.60	0.2000	42.78
9.	Cr–Co	20	43.79	0.2399	35.68
10.	Cr–Ni–Co	10	43.45	0.1999	42.77
11.	Cr–Ni–Co	15	43.72	0.1999	42.80
12.	Cr–Ni–Co	20	43.77	0.3198	26.77

The full width at half maximum (FWHM, β) of the dominant (200) diffraction peak was used to determine the average crystallite size (D) via the Debye-Scherrer equation. The calculated crystallite sizes, listed in Table 1, range between 19.44 nm and 53.50 nm, confirming that 13.56 MHz RF reactive co-sputtering yields nanostructured coatings. For the ternary Cr–Ni system, the average crystallite size increases slightly from 30.57 nm to 35.67 nm with increasing nitrogen content. In contrast, for the quaternary Cr–Ni–Co system, crystallite size decreases from 42.77 nm to 26.77 nm at 20% N₂. This crystallite refinement at elevated nitrogen flows stems from enhanced nucleation density driven by high reactive nitrogen ion fluxes, which interrupt continuous grain growth and promote a fine nanocrystalline microstructure.

3.3. Surface Topography and Roughness Dynamics

The three-dimensional surface topographies of the co-sputtered thin films acquired via atomic force microscopy (AFM) across 10 $\mu\text{m} \times 10 \mu\text{m}$ scanning domains are illustrated in Figures 3(1)–3(4).

Table 3.

Surface roughness parameters (S_a and S_z) of co-sputtered thin films as a function of target composition and nitrogen flow ratio.

No.	Target Composition	Nitrogen Ratio (%)	S_a (nm)	S_z (nm)
1.	Cr	10	9.60	105
2.	Cr	15	10.60	143
3.	Cr	20	11.40	167
4.	Cr–Ni	10	9.29	131
5.	Cr–Ni	15	9.82	136
6.	Cr–Ni	20	11.80	175
7.	Cr–Co	10	8.42	133
8.	Cr–Co	15	9.29	165
9.	Cr–Co	20	12.30	134
10.	Cr–Ni–Co	10	9.42	107
11.	Cr–Ni–Co	15	11.50	153
12.	Cr–Ni–Co	20	11.60	148

The corresponding surface roughness parameters—specifically the arithmetical mean height (S_a) and the maximum height (S_z)—are compiled in Table 3. Across all target compositions (Cr, Cr–Ni, Cr–Co, and Cr–Ni–Co), the average surface roughness exhibits a positive correlation with the reactive nitrogen flow ratio (10–20% N₂). The measured S_a values range from a minimum of 8.42 nm (for Cr–Co at 10% N₂) to a maximum of 12.3 nm (for Cr–Co at 20% N₂), with maximum peak-to-valley heights (S_z) scaling from 105 nm up to 175 nm.

This systematic roughening at elevated nitrogen partial pressures is governed by thin-film growth kinetics, adatom surface mobility, and plasma scattering phenomena [20, 21]. At low nitrogen concentrations (10% N₂), the deposition process operates primarily in the metallic or transition sputtering regime, characterized by higher kinetic energy of the sputtered metal atoms arriving at the substrate [20]. High kinetic energy enhances the surface diffusion length of incoming adatoms, enabling them to fill interstitial atomic valleys and promote layer-by-layer two-dimensional growth, which produces smoother film surfaces ($S_a < 10$ nm).

Conversely, elevating the nitrogen flow to 20% triggers severe target poisoning and increases gas-phase scattering within the plasma sheath [12, 20]. Sputtered metallic species undergo repeated thermalizing collisions with nitrogen molecules (N₂), which significantly attenuates their landing kinetic energy and reduces adatom surface mobility [19]. Simultaneously, the higher arrival rate of reactive nitrogen species induces rapid compound nucleation at random surface sites [21]. The combination of low adatom mobility and competitive island nucleation transitions the growth mode toward three-dimensional Volmer–Weber island coalescence and columnar grain termination, causing geometric shadowing effects and heightening surface roughness ($S_a > 11.5$ nm). Figure 3 shows the impact of varying nitrogen percentages on surface roughness.

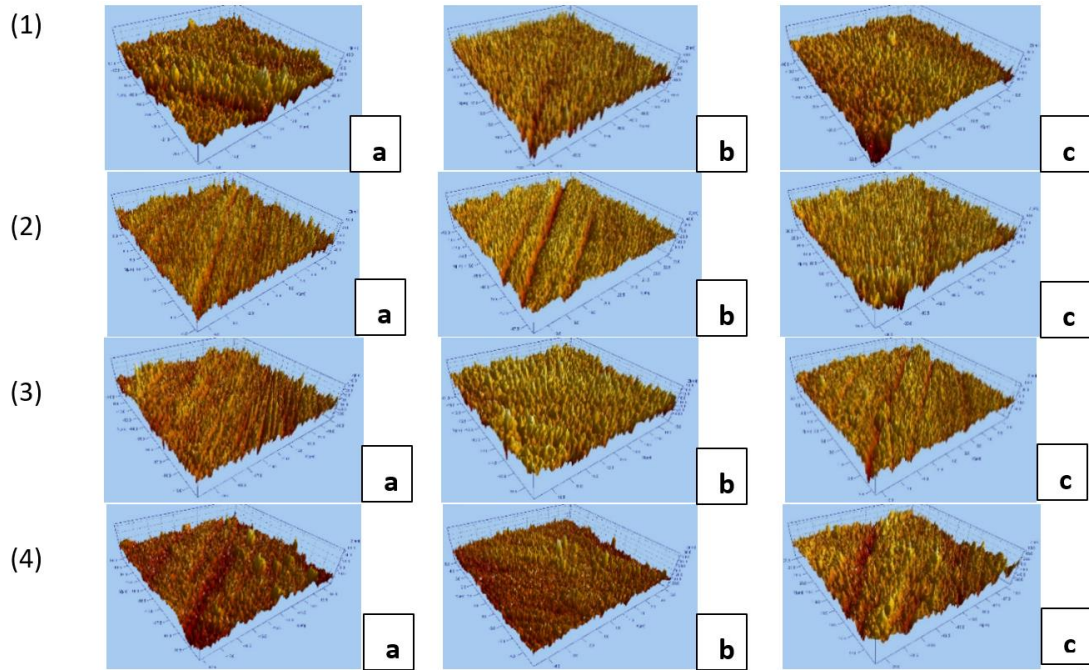


Figure 3.
AFM Results with Nitrogen incorporation of (a) 10%, (b) 15%, (c) 20%: (1) Cr , (2) Cr–Ni, (3) Cr–Co, (4) Cr–Ni–Co.

3.4. Chemical Composition and Electron Interaction Analysis

The elemental composition of the co-sputtered thin films determined via Energy-Dispersive X-ray Spectroscopy (EDX) is summarized in Table 4. The data reveal three distinct compositional phenomena: an apparent high iron (Fe) concentration (46.86–57.38 wt%), a systematic decrease in chromium (Cr) content, and a progressive increase in detected nitrogen (N) with rising N_2 gas fractions.

Table 4.
Energy-dispersive X-ray (EDX) elemental composition of thin films deposited on AISI 4140 steel.

No.	Target Composition	Nitrogen Ratio (%)	Cr (wt%)	N (wt%)	O (wt%)	Fe (%)	Ni (wt %)	Co (wt%)
1	Cr	10	42.18	2.41	5.95	49.45	—	—
2	Cr	15	33.17	3.00	6.44	57.38	—	—
3	Cr	20	30.42	3.36	10.53	55.68	—	—
4	Cr–Ni	10	42.67	2.99	5.62	46.86	—	1.85
5	Cr–Ni	15	37.46	3.32	7.32	50.21	1.68	—
6	Cr–Ni	20	30.79	4.37	9.13	54.18	1.52	—
7	Cr–Co	10	44.40	2.67	3.13	46.99	—	2.80
8	Cr–Co	15	37.39	3.39	3.75	52.72	—	2.74
9	Cr–Co	20	33.81	4.86	4.07	54.72	—	2.53
10	Cr–Ni–Co	10	39.78	3.33	4.37	47.10	1.74	3.67
11	Cr–Ni–Co	15	35.90	4.14	4.38	51.45	1.59	2.53
12	Cr–Ni–Co	20	31.71	4.70	5.70	53.93	1.63	2.33

The substantial concentration of iron (Fe) detected across all samples is a direct consequence of the primary electron beam interaction volume during EDX excitation. Under conventional SEM accelerating voltages (15–20 kV), the Monte Carlo electron penetration range (R_{KO}) within transition metal nitrides spans 1.5–2.5 μm . Because the coating thickness (t) ranges between 1.3 μm and 2.9 μm (as established in Table 1), the incident electron beam fully traverses the thin film and strongly excites the underlying AISI 4140 steel matrix. Consequently, the reported raw weight percentages reflect an integrated film-substrate composite signal rather than bulk stoichiometry, which also accounts for the apparent dilution of the light nitrogen element.

Evaluating the relative ratios among the deposited film constituents clarifies the reactive co-sputtering dynamics. For all systems, the detected Cr weight fraction decreases monotonically as the N_2 flow ratio increases from 10% to 20% (e.g., dropping from 42.18 wt% to 30.42 wt% in pure Cr coatings). This decline corresponds directly to target nitridation (target poisoning), which suppresses the Cr sputtering yield under reduced Ar^+ ion fractions [12, 19]. Concurrently, the detected nitrogen content rises from 2.41 wt% to 4.86 wt%, confirming enhanced nitrogen incorporation into the growing film lattice.

The inclusion of mosaic nickel and cobalt target elements yielded steady incorporation in the deposited layers: Ni contents of 1.52–1.85 wt% and Co contents of 2.33–3.67 wt% were successfully achieved. These measured values

correlate with the 10% geometric surface area coverage on the cathode, validating that the mosaic target configuration provides controlled multi-component vapor transport into the developing (Cr,Ni,Co)N_x matrix [15, 26].

3.5. Nanomechanical Response and Strengthening Mechanisms

The intrinsic mechanical characteristics of the co-sputtered coatings—specifically nanoindentation hardness (H), reduced elastic modulus (E), elastic strain to failure ratio (H/E), and resistance to plastic deformation (H^3/E^2)—are compiled in Table 5. Under low-load nanoindentation adhering to the Bückle 10% penetration rule ($h_{max} \leq 130$ nm), substrate compliance and punch-through artifacts from the AISI 4140 steel were eliminated. Across all target compositions (Cr–Ni, Cr–Co, and Cr–Ni–Co), the nanomechanical response exhibits a continuous, monotonic increase as the reactive nitrogen flow ratio rises from 10% to 20%.

Table 5.

Nanoindentation hardness (H) reduced elastic modulus (E), elastic strain index (H/E), and plastic deformation resistance (H^3/E^2) of co-sputtered coatings.

No.	Target Composition	Nitrogen Ratio (%)	H (GPa)	E* (GPa)	H/E*	H ³ /E* ² (GPa)
1	Cr–Ni	10	14.5	195	0.074	0.080
2	Cr–Ni	15	22.0	265	0.083	0.152
3	Cr–Ni	20	25.5	285	0.089	0.204
4	Cr–Co	10	13.0	185	0.070	0.064
5	Cr–Co	15	20.5	250	0.082	0.138
6	Cr–Co	20	23.5	275	0.085	0.172
7	Cr–Ni–Co	10	14.0	190	0.074	0.076
8	Cr–Ni–Co	15	21.5	260	0.083	0.147
9	Cr–Ni–Co	20	24.5	280	0.088	0.188

The progressive elevation in hardness from 13.0–14.5 GPa at 10% N₂ to peak values of 23.5–25.5 GPa at 20% N₂ is governed by phase stoichiometry and point-defect annihilation in the cubic rock-salt lattice [23]. At a low nitrogen flow ratio (10% N₂), the film deposits in a sub-stoichiometric (Cr,M)N_{1-x} state containing a high density of constitutional nitrogen vacancies, which facilitates dislocation mobility under shear stresses and reduces cohesive lattice energy [12, 23]. As the reactive nitrogen flow is elevated to 20%, the interstitial anion sub-lattice approaches full stoichiometric saturation ($x \rightarrow 1$), maximizing the population of strong, localized Cr–N and M–N covalent-ionic hybridized bonds (p – d orbital overlapping) [23]. Concurrently, the reduced crystallite sizes (19.44–35.68 nm, Table 2) contribute to Hall–Petch grain boundary strengthening, where a high density of grain boundaries blocks dislocation slip and shear band propagation across adjacent crystal domains.

Comparing the multi-component systems reveals that mechanical performance follows the ranking:

$$\text{Cr–Ni} > \text{Cr–Ni–Co} > \text{Cr–Co}$$

At 20% N₂, the Cr–Ni film achieves the highest hardness ($H = 25.5$ GPa) and reduced modulus ($E = 285$ GPa). This enhancement can be attributed to solid-solution lattice distortion and grain-boundary cohesive strengthening induced by Ni substitution into the CrN host structure [6, 13]. The atomic radius disparity between Ni (1.24 Å) and Cr (1.28 Å) creates localized strain fields that pin dislocation movements [13]. In contrast, Co addition provides slightly lower hardness (23.5 GPa at 20% N₂) while retaining elevated modulus (275 GPa). The quaternary Cr–Ni–Co system balances these effects, reaching $H = 24.5$ GPa and $E = 280$ GPa through multi-element solution hardening and crystallite refinement ($D = 26.77$ nm). These measured values compare favorably to recent surface-hardened and functionalized AISI 4140 coatings reported in the literature, such as ion-beam diamond-like carbon thin films ($H = 20.18$ GPa, $E = 188$ GPa; [14]) and high-load PVD multi-component nitrides [7, 11].

Beyond absolute hardness, the contact damage tolerance and fracture resistance of thin films under mechanical loading are evaluated by the elastic strain to failure (H/E) and resistance to plastic deformation (H^3/E^2) [11, 14]. As shown in Table 5, increasing the nitrogen flow ratio from 10% to 20% enhances H/E from 0.070–0.074 up to 0.085–0.089, while H^3/E^2 increases markedly from 0.064–0.080 GPa to 0.172–0.204 GPa. High H/E values indicate that the coating accommodates elastic strain over larger contact areas before initiating micro-fractures, whereas high H^3/E^2 values reflect strong resistance to plastic yield under concentrated normal and tangential contact stresses [11, 22]. The Cr–Ni system at 20% N₂ yields the highest plastic deformation resistance ($H^3/E^2 = 0.204$ GPa), confirming its superior capability to protect soft AISI 4140 substrates against localized plastic deformation.

3.6. Tribological Performance and Wear Kinetics

The unlubricated sliding wear behavior of the co-sputtered thin films on AISI 4140 steel was evaluated using pin-on-disc tribometry under ambient conditions in accordance with ASTM G99 standards. The specific wear rates (k) of the coated systems across varying reactive nitrogen flow ratios are summarized in Table 6.

Table 6.

Specific wear rates (k) of reactive RF co-sputtered coatings on AISI 4140 steel.

No.	Target Composition	Nitrogen Ratio (%)	Specific Wear Rate, k ($\times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$)
1	Cr	10	8.9
2	Cr	15	8.3
3	Cr	20	8.6
4	Cr–Ni	10	4.8
5	Cr–Ni	15	4.0
6	Cr–Ni	20	4.6
7	Cr–Co	10	6.4
8	Cr–Co	15	7.0
9	Cr–Co	20	8.1
10	Cr–Ni–Co	10	5.6
11	Cr–Ni–Co	15	4.2
12	Cr–Ni–Co	20	5.1

All deposited coating systems substantially improve the wear resistance of the AISI 4140 substrate, exhibiting specific wear rates in the order of $10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$. Across all nitrogen concentrations, multi-component alloying with Ni and Co produces superior tribological protection compared to binary CrN coatings. Specifically, the Cr–Ni coating deposited at 15% N_2 achieves the lowest specific wear rate of $4.0 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$, representing an improvement in wear resistance of over 50% relative to the binary Cr coating ($8.3 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$). Similarly, the quaternary Cr–Ni–Co coating displays high wear resistance at 15% N_2 , yielding a specific wear rate of $4.2 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$.

The physical wear mechanisms governing these coatings correlate directly with the nanomechanical contact parameters (H/E and H^3/E^2) established in Section 3.5 [22, 27]. According to classical Archard wear mechanics, volumetric wear loss (V) is inversely proportional to intrinsic hardness (H):

$$V = K \frac{F_N \cdot s}{H}$$

where K is the dimensionless wear coefficient, F_N is the applied normal load, and s is the total sliding distance [7]. However, in thin ceramic coatings subjected to cyclic contact stresses, tribological failure is governed by elastic strain recovery (H/E) and resistance to plastic indentation damage (H^3/E^2) rather than absolute hardness alone [11, 14].

Coatings synthesized at 15% N_2 exhibit a combination of high plastic deformation resistance ($H^3/E^2 = 0.138\text{--}0.152 \text{ GPa}$) and moderate surface roughness ($S_a = 9.29\text{--}11.50 \text{ nm}$), which minimizes micro-crack initiation during cyclic asperity contact [21, 28]. The incorporation of Ni modifies the interfacial shear response by providing grain-boundary sliding constraints, preventing severe subsurface shear localization and suppressing micro-delamination along the sliding track [6, 13].

At an elevated nitrogen flow ratio of 20%, a slight increase in specific wear rate is observed across the Cr–Ni ($4.6 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$) and Cr–Ni–Co ($5.1 \times 10^{-6} \text{ mm}^3/\text{N}\cdot\text{m}$) coatings, despite these samples exhibiting peak nanoindentation hardness ($H = 24.5\text{--}25.5 \text{ GPa}$). This behavior is attributed to the increased surface roughness ($S_a = 11.60\text{--}12.30 \text{ nm}$, Table 3) induced by target poisoning and Volmer–Weber island growth at high nitrogen partial pressures. The sharp asperity peaks undergo micro-fracture during the initial running-in stage of sliding wear, generating loose ceramic debris that acts as third-body abrasive particles [22, 23]. Consequently, optimizing the reactive N_2 flow ratio to 15% achieves a balanced compromise between high plastic deformation resistance (H^3/E^2) and low surface roughness (S_a), providing the best wear durability for surface-engineered AISI 4140 steel [2, 7].

4. Conclusion

Multi-component (Cr,Ni,Co) N_x thin films were successfully deposited onto AISI 4140 low-alloy steel via 13.56 MHz reactive radio-frequency (RF) co-sputtering by combining mosaic target configurations (Cr, Cr–Ni, Cr–Co, and Cr–Ni–Co) with varying reactive nitrogen flow ratios (10%, 15%, and 20% N_2). The primary findings regarding growth kinetics, microstructural evolution, nanomechanical response, and tribological behavior are concluded as follows:

1. Target Poisoning and Deposition Kinetics: Cross-sectional analysis demonstrated a monotonic decrease in film thickness from $2.9 \mu\text{m}$ (10% N_2) to $1.3 \mu\text{m}$ (20% N_2). This reduction in deposition rate is governed by cathode target poisoning—wherein compound nitride formation suppresses elemental sputtering yields—and intensified gas-phase scattering under elevated nitrogen partial pressures.
2. Phase Evolution and Nanostructure: X-ray diffraction confirmed the dominant crystallization of a face-centered cubic (FCC) rock-salt (Cr,M) N solid-solution structure alongside unreacted metallic Ni and Co phases. Binary Ni_xN and Co_xN phases were absent due to the significantly more negative formation enthalpy of CrN ($\Delta G_f^\circ \approx -92.4 \text{ kJ/mol}$). Debye–Scherrer calculations yielded nanocrystallite sizes between 19.44 nm and 53.50 nm .
3. Surface Topography Evolution: Atomic force microscopy revealed an increase in average surface roughness ($S_a = 8.42\text{--}12.30 \text{ nm}$) with increasing N_2 flow ratio. This topographical roughening is driven by reduced adatom surface kinetic energy and a shift toward three-dimensional Volmer–Weber island growth at higher reactive gas fractions.
4. Nanomechanical Hardening Mechanics: Nanoindentation revealed a continuous increase in mechanical properties with nitrogen content up to 20% N_2 , driven by stoichiometric lattice saturation and Hall–Petch grain boundary

strengthening. The Cr–Ni system at 20% N₂ exhibited the highest hardness $H = 25.5$ GPa) and reduced elastic modulus ($E = 285$ GPa), yielding a high elastic strain index ($H/E^* = 0.089$) and plastic deformation resistance ($H^3/E^2 = 0.204$ GPa).

5. Tribological Optimization: All deposited coatings significantly reduced the specific wear rate of the AISI 4140 substrate down to the order of 10^{-6} mm³/N·m. The optimal wear resistance was achieved by the Cr–Ni coating deposited at 15% at N₂ ($k = 4.0 \times 10^{-6}$ mm³/N·m), which established an effective synergy between elevated plastic deformation resistance ($H^3/E^2 = 0.152$ GPa) and low asperity roughness ($S_a = 9.82$ nm), suppressing third-body abrasive wear during unlubricated contact.

Co-sputtering transition metal elements (Ni, Co) into a reactive CrN matrix under optimized N₂ partial pressure (15%–20%) provides a viable surface modification route to enhance the mechanical integrity and wear resistance of AISI 4140 steel components.

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