



Article The Characteristics of Light (TiCrAl_{0.5}NbCu)C_xN_y High-Entropy Coatings Deposited Using a HiPIMS/DCMS Technique

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Abstract: Multi-component high-entropy (TiCrAl_{0.5}NbCu)C_xN_y coatings targeting applications requiring medium-to-high friction and wear-resistant surfaces were fabricated through the co-sputtering of elemental targets in an Ar + CH₄ + N₂ reactive atmosphere using a hybrid HiPIMS/DCMS technique. Two sets of samples were fabricated: (a) (TiCrAl_{0.5}NbCu)C_x high-entropy carbides (HEC) and (b) (TiCrAl_{0.5}NbCu)C_xN_{0.13} high-entropy carbonitrides (HECN), $0 \le x \le 0.48$. The structural, mechanical, tribological, and corrosion resistance properties were thoroughly investigated. The metallic sample exhibits a single BCC structure that changes to FCC via an intermediary amorphous phase through the addition of C or N to the content of the films. The crystallinity of the FCC phases is enhanced and the density of the films decreases down to 5.5 g/cm^3 through increasing the carbon fraction up to 48%. The highest hardness of about 16.9 GPa and the lowest wear rate of about 5.5×10^{-6} mm³/Nm are presented by the samples with the largest carbon content, x = 0.48. We found a very good agreement between the evolution of H/E and H^3/E^2 parameters with carbon content and the tribological behavior of the coatings. The best corrosion resistance was presented by the low-carbon carbonitride samples, showing a charge transfer resistivity of about $3 \times 10^8 \Omega$ cm, which is more than three times larger than that of the metallic HEA. The best tribological characteristics for envisioned application were presented by (TiCrAl_{0.5}NbCu)C_{0.3}N_{0.13}, showing a coefficient of friction of 0.43 and a wear rate of about 7.7 \times 10⁻⁶ mm³/Nm.

Keywords: high-entropy alloys; structure; surface morphology; mechanical properties; electrochemical properties

1. Introduction

The automotive industry, machinery tools, and structural components demand materials with exceptional mechanical and thermal properties, high wear resistance, high thermal stability, and high corrosion resistance. All these features are essential to prevent parts from experiencing tribological damage during work at high speeds, when high temperatures develop. In the automobile industry, a primary objective is to utilize lighter components while maintaining the aforementioned properties [1–3]. While bulk materials can be employed, achieving the required properties can also be accomplished through coating the components with special alloys. Two or more components intimately joined in a phase build an alloy. Common alloys can be pictured as a solvent–solute combination, i.e., a large amount of an element hosts smaller amounts of one or more other elements [4]. The order can vary from crystalline to highly disordered structures, degrading sometimes to very



Citation: Zoita, N.C.; Dinu, M.; Parau, A.C.; López-Ortega, A.; Pana, I.; Grigorescu, C.E.A.; Mondragon, M.; Sobetkii, A.; Almandoz, X.; Rodriguez, J.C.; et al. The Characteristics of Light (Ti $CrAl_{0.5}NbCu$) C_xN_y High-Entropy Coatings Deposited Using a HiPIMS/DCMS Technique. *Crystals* **2023**, *13*, 1565. https://doi.org/ 10.3390/cryst13111565

Academic Editor: Dah-Shyang Tsai

Received: 10 October 2023 Revised: 19 October 2023 Accepted: 27 October 2023 Published: 2 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). short distance order. As a bulk material, random solid solutions with a high configurational entropy usually result from mixing a definite number of elements and subsequently melting them together or allowing them to undergo a solid-state reaction. More efficiency is, however, gained when such alloys are grown as thin, or thick, layers, and the bulk is used as a target for various vapor deposition techniques. The actual trend focuses on carefully engineered materials built of multi-principal elements, the so-called high-entropy alloys (HEAs) [5,6]. Typically composed of at least five principal metal elements in close atomic ratios, they exhibit a high entropy of mixing, lattice distortion, and cocktail effects [7], which favor the development of thermodynamically stable simple solid-solution structures, i.e., face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP) structures, characterized by excellent thermal stability, as well as outstanding mechanical, tribological, and corrosion resistance properties [8,9]. These remarkable capabilities have opened up new avenues for research, such as high-entropy ceramics (HECs) [10]. Primarily as a proof of concept, a few types of HECs have been developed to date through incorporating p-type elements (boron, carbon, nitrogen, oxygen) into the metallic matrix to form high entropy borides [11,12], carbides [13–15], nitrides [16,17], oxides [18,19], and silicides [20,21]. These materials have demonstrated great potential for structural and functional applications. Specifically, coatings of high-entropy nitrides (HEANs) [22–24] and carbides (HEACs) [8,14,23] have been investigated for their promising use as protective coatings. HEANs have exhibited high hardness and a high coefficient of friction but poor self-lubricating performance, while HEACs, in addition to their relatively high hardness, have shown excellent tribological properties, particularly when a graphite phase is present in the films [14]. Enhanced mechanical and tribological performances can be achieved through combining metal nitrides and carbides to form high-entropy carbonitride systems (HECNs) [24,25]. To date, only a few HECN systems have been synthesized as thin films [24,26] or in bulk [27,28].

For machining and automotive applications that require medium-to-high coefficients of friction and highly wear-resistant surfaces, this work focuses on the development of highentropy carbide and carbonitride coatings. The structural, tribological, and mechanical properties of these coatings have been investigated. The proposed high-entropy system is composed of titanium (Ti), chromium (Cr), aluminum (Al), niobium (Nb), and copper (Cu). These are low-density elements known for their high strength and wear resistance, making them suitable for tribological applications. Specifically, Cr, Nb, and Ti are known for their effectiveness in creating wear-resistant alloys [29–31], while Al, Nb, Cr, and Cu are commonly utilized to enhance strength, corrosion resistance, and thermal stability [32,33]. Copper could also contribute to improving wear resistance due to its ductility and lubricity properties [34,35]. Furthermore, nitrides and carbides based on Ti, Cr, Ni, and Al are characterized by their hardness, wear resistance, and exceptional corrosion resistance [36,37].

To the best of our knowledge, high-entropy ceramics (HECs, HECNs) based on the Ti-Cr-Al-Nb-Cu system had not been previously produced and investigated. The primary objective of this research was to synthesize these materials in the form of coatings and assess their structural, tribological, and corrosion resistance characteristics. The aim was to determine their suitability for applications demanding surfaces with high levels of friction and exceptional wear resistance. There exists a clear industry demand for such materials due to the limitations of conventional organic-based frictional materials, typically composed of polymer resins with additions of different components like carbon fibers, asbestos, metal wires, and powders [38]. While these conventional materials offer medium-to-high friction coefficients (less than 0.5 [38,39]), along with cost-effectiveness and ease of production, they present relatively high wear rates ranging from 10^{-5} to 10^{-4} mm³/Nm [39], thermal instability, and potential carcinogenic risks (associated with resin and asbestos).

In this study, a promising candidate for applications requiring surfaces with both high friction and wear resistance was identified. The $(TiCrAl_{0.5}NbCu)C_{0.3}N_{0.13}$ HECN exhibited a coefficient of friction of about 0.43 and a wear rate of approximately 7.7×10^{-6} mm³/Nm.

2. Materials and Methods

The coatings were developed using a hybrid magnetron sputtering deposition technique, combining the direct current (DCMS) and high-power impulse magnetron sputtering (HiPIMS) methods. The hybrid HiPIMS/DCMS technique was adopted in order to improve the adhesion, to increase the density of the films, and to tailor the microstructure of the films, which are usual consequences of the high current density of ionized particles bombarding the films' growing surface during the deposition process, generated by the high-power pulsed discharge [40-45]. The samples were prepared via reactive co-sputtering in an Ar + CH₄ + N₂ atmosphere of high-purity elemental targets (5 mm thick, 50.8 mm diameter, 99.99% purity from Testbourne Ltd., Basingstoke, UK) using a con-focal AJA ATC-ORION magnetron sputtering system (AJA International Inc., Scituate, MA, USA). The deposition unit was equipped with five unbalanced magnetrons fed by HiPIMS (for Al and Cr targets) and DCMS (for Ti, Nb, and Cu targets) power supplies. An additional RF source was used for substrate bias. All power supplies are manufactured by AJA International Inc., except for the HiPIMS power supply, which is custom-made in the laboratory. It is designed with a 1.5 Ω output impedance and capable of delivering a maximum output power of 1000 V/150 A.

Prior to each deposition run, the substrates were ultrasonically cleaned in acetone and isopropyl alcohol and dried in nitrogen gas flux before mounted on a substrate holder (100 mm in diameter) and placed in the vacuum chamber on a rotating mount, 150 mm away from the sputtering targets. Prior to each deposition process, the deposition chamber was evacuated down to 8×10^{-6} Pa, while the substrates were heated to 300 °C for degassing. Then, the substrates were plasma-etched for 10 min at -300 V bias in radio-frequency (RF) Ar plasma at 0.67 Pa. In order to deposit films with homogeneous composition, the sputtering targets were etched in Ar plasma for 10 min.

Two set of samples were fabricated on p-type Si(100) wafer ($25.0 \times 25.0 \times 0.5$ mm, Testbourne Ltd., UK) and C45 substrates (25.0 mm diameter, 2.0 mm thickness, COS Targoviste S.A., Romania—see Table 1 for C45 composition), at a substrate temperature of 300 °C [8,14,23]: (a) The first set consisted of carbides. It began with a metallic sample, and varying amounts of carbon were introduced into the film composition through supplying corresponding proportions of CH₄ to the process gas. (b) The second set comprised carbonitrides. It originated from a nitride sample, and a similar quantity of carbon was added compared to the carbide samples (refer to Table 2 for details).

Table 1. C45 substrate elemental composition.

Elements	С	Cr	Ni	Mn	Si	Mo	S	Р	Fe
C45 (wt.%)	0.436	0.351	0.294	0.639	0.291	0.089	0.031	0.027	balance

Tab	le	2.	De	position	parameters	(mass f	lows of	process	gases),	filn	n thio	kness,	and	comp	osition.
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Sample	Ar (sccm)	CH ₄ (sccm)	N ₂ (sccm)	Thickness (µm)	Composition (at. Ratio)
М	20	0	0	1.94	TiCrAl _{0.5} NbCu
C1	19.0	1.0	0.0	1.87	(TiCrAl _{0.5} NbCu)C _{0.09}
C2	18.0	2.0	0.0	1.73	(TiCrAl _{0.5} NbCu)C _{0.2}
C3	17.0	3.0	0.0	1.62	(TiCrAl _{0.5} NbCu)C _{0.3}
C4	16.0	4.0	0.0	1.41	(TiCrAl _{0.5} NbCu)C _{0.48}
Ν	18.9	0.0	1.1	1.85	(TiCrAl _{0.5} NbCu)N _{0.13}
CN1	18.0	0.95	1.0	1.69	(TiCrAl _{0.5} NbCu)C _{0.09} N _{0.12}
CN2	17.1	1.9	1.0	1.60	(TiCrAl _{0.5} NbCu)C _{0.2} N _{0.13}
CN3	16.2	2.8	1.0	1.53	(TiCrAl _{0.5} NbCu)C _{0.3} N _{0.13}
CN4	15.3	3.8	0.9	1.28	(TiCrAl _{0.5} NbCu)C _{0.45} N _{0.13}

The sputtering yield of targets is altered through changing the composition of the process gas mixture due to chemical reactions between the reactive gas components (CH₄, N₂) and the target material. In order to maintain a similar metallic composition of the films, the electrical power applied to the sputtering targets was adjusted before depositing each sample type. Short deposition runs, lasting approximately 15 min, were carried out on test substrates to determine the atomic composition of the resulting films. The atomic content of copper (Cu) was used as a reference point. Therefore, the electrical power applied to the Cu target remained constant, while the electrical power applied to the other targets was readjusted based on the atomic composition observed in the test runs. For further details, please refer to Table 2, which provides information about the process gas mixture used for the fabrication the two sets of samples, along with the labels assigned to each sample. The labels include M for metallic samples, N for nitride samples, C1–C4 for carbide samples, and CN1–CN4 for carbo-nitride samples. For M samples, the electrical power applied to the Ti, Cu, Nb, Cr, and Al targets was 246 W, 84 W, 153 W, 139 W, and 203 W, respectively, where the electrical power values corresponding to Cr and Al targets, with HiPIMS polarized, represent the equivalent DC power. The HiPIMS pulse voltage, current, width, and frequency applied to the Cr and Al targets were 800 V, 12 A, 100 μ s, and 145 Hz and 580 V, 30 A, 100 μ s, and 116 Hz, respectively.

Unless otherwise stated, all investigations were performed on films deposited on C45 substrates. The elemental composition of the multi-principal element coatings deposited on Si substrates was assessed via energy-dispersive X-ray spectroscopy (EDS) using a Hitachi TM3030 Plus scanning electron microscope (SEM) equipped with a Bruker's Quantax70 EDS. EDS spectra linear calibration was carried out using the Cu-K_{α} (8.037 keV) and Cu-L_{α} (0.926 keV) lines obtained from a standard Cu sample. The EDS spectra of the samples were recorded over the 0–15 keV energy range for 1200 s. An accurate elemental composition analysis was not feasible using EDS on samples deposited on C45 substrates due to the presence of chromium and carbon, which are constituent elements found in both the films and the C45 substrate. Therefore, the EDS analysis was conducted on samples deposited on Si substrates to avoid this interference.

The crystallographic structure was investigated via out-of-plane X-ray diffraction (XRD) using a SmartLab diffractometer (Rigaku, Tokyo, Japan) equipped with a 9 kW Cu rotating anode and a 5-axis vertical goniometer of 0.3 m radius. The diffractometer was operated in parallel beam mode with high-resolution optics on the incident beam (2-bounces Ge(220) monochromator) to select Cu-K_{α 1} radiation (λ = 1.5406 Å). The horizontal and vertical incident slits were set to 1.0 mm and 5.0 mm, respectively. The XRD patterns were recorded over a 2 θ range of 20° to 100° with a resolution of 0.005° and an acquisition speed of 1.0°/min. The crystallographic structure analysis was performed using the powder X-ray diffraction profile analysis software, PDXL (version 2.7), making use of ICDD PDF-4+ XRD reference database.

The SmartLab diffractometer was additionally employed for assessing the average mass density of the films through the X-ray reflectivity (XRR) technique. The XRR patterns were recorded with horizontal and vertical incident slits set to 0.15 mm and 5.0 mm, respectively. The measurements were conducted over a 2 θ range of 0.1°–3.0° with a resolution of 0.001° and an acquisition speed of 0.16°/min. The experimental XRR patterns were simulated using the Rigaku GlobalFit Ver. 2.1.1 software package. A two-layer model was adopted, including a topmost layer of a few nm describing the air-contaminated layer of the films and a second layer describing the film's actual properties. Since the thickness of the films is much larger than the X-ray penetration depth (<500 nm), the second layer was considered bulk in relation to the XRR technique. The XRR simulation provided the iteratively adjusted fitting parameters such as the average density, thickness of the layers, and the roughness of the interfaces once the goodness-of-fit value (χ^2) dropped below 0.01. However, it is recognized that the XRR technique tends to overestimate the surface roughness. In consequence, this paper presents only the AFM surface roughness values, which are considered to be more accurate [42,46–48].

The film's surface morphology was assessed using a vibration-damped atomic force microscope—AFM (Innova—Veeco)—working in intermittent contact mode. The AFM images were recorded from 5 μ m × 5 μ m areas, with a matrix resolution of 1024 × 1024 pixels, at a scan rate of 0.7 Hz, using commercial pyramidal p-doped silicon tips (model RTESPA) mounted to a 125 μ m cantilever, presenting a resonance frequency of about 332.2 kHz and a nominal force constant of about 40 N/m. Surface roughness and surface porosity analyses were conducted on the entire surface area recorded via AFM using Gwyddion v.2.30 software, Czech Metrology Institute [49], using the implemented surface statistical quantities and grains function, respectively. The edge detection grain marking algorithm was utilized to identify grains and calculate the overall grain surface area, A_{grains}, and the overall surface area, A_{total}. The surface porosity, P, was calculated as the ratio of the surface area of pores (voids), A_{pores} = A_{total} – A_{grains}, to the total surface area, i.e., P = (1 - A_{grains}/A_{total}) [50].

The nanoindentation tests were carried out using a Hysitron TI Premier unit equipped with a Berkovich tip characterized by a 100 nm radius of curvature and a corresponding total including angle of 142.3°. Prior to nanoindentation measurements, several sources of uncertainties and errors were taken into account such as the thermal drift, initial penetration depth, machine compliance, and indenter area function [51]. The force calibration was conducted on the standard fused quartz sample with H = 9.25 GPa \pm 10% and $E = 69.6 \text{ GPa} \pm 10\%$. According to ISO 14577-1:2015 [52], the following two aspects were considered in order to avoid both the influence of C45 substrate on the resulting mechanical properties and the limitation given by the geometrical characteristics of the used Berkovich tip. Therefore, all the maximum indentation and contact depths were smaller than 1/10 of the total films thickness and higher than 40 nm, respectively [53]. The load-displacement curves availed to derive the hardness (H) and reduced modulus (Er) were obtained through using a maximum indentation load of 3 mN. The corresponding time intervals for a complete indentation in terms of loading, hold, and unloading were 7 s, 2 s, and 7 s, respectively. A total of 15 points on different areas for each sample were selected for indentation, while the distance between points was chosen to be at least 5 μ m apart in order to prevent any potential interference.

Tribology tests were conducted using a laboratory-made pin-on-disc tribometer to assess the wear rate and the coefficient of friction of the samples. All the tests were performed at a room temperature of 23 °C and a relative humidity of 40%. The pin used was a synthetic sapphire ball with a diameter of 6 mm. Before each test, both the ball and the samples were cleaned with isopropyl alcohol. The tribological tests were performed using the following parameters: a normal applied load, F, of 1 N; a sliding speed, v, of 0.1 m/s; and a sliding track radius, r, of 8 × 10⁻³ m. The sliding distance, D, was 115 m for all samples, except for the *M*, *N*, and C1 samples. For sample *N*, the sliding distance was reduced to 70 m, while for samples *M* and C1, the sliding distance was set to 35 m, in order to avoid substrate influence. The wear track profiles were recorded using a surface profilometer (Dektak 150, Bruker, Billerica, MA, USA), from which the volume of the wear track, V, was determined. The wear rate, K, was calculated using the equation K = V/(F·D).

The electrochemical behavior of the investigated samples was evaluated using the electrochemical impedance spectroscopy (EIS) technique, through applying a sinusoidal signal of 10 mV RMS vs. open circuit potential (EOC), in a frequency range of $0.5-10^4$ Hz. The tests were performed in 0.9% NaCl (Hemofarm, Timisoara, Romania) at room temperature (22 ± 1 °C), using a VersaSTAT 3 potentiostat (Princeton Applied Research, Oak Ridge, TN, USA). The corrosion cell consisted of an Ag/AgCl saturated electrode (reference electrode, RE) (0.197 V vs SHE), a platinum electrode (counter electrode, CE), and the investigated samples (the working electrode, WE). The EOC was monitored for 12 h, and the EIS data were recorded after 1 h and 12 h immersion time in NaCl, respectively. The data acquisition was made using VersaStudio software (version 2.60.6, Princeton Applied Research, Oak Ridge, TN, USA) and for the data fitting procedure, we used the ZView software package (version 12136-4, Scribner Associates Inc., Southern Pines, NC, USA).

3. Results

3.1. Thickness and Elemental Composition

The thickness of the films, as determined via surface profilometry, falls within the range of $1.28-1.94 \mu m$ (as shown in Table 2). The EDS investigations showed that the stoichiometry of metallic components remains consistent across different samples (as depicted in Figure 1). For both sets of samples, the carbon content varies from 9% to 48% relative to the metallic constituents, while all nitrogen-containing samples exhibit a nitrogen concentration of approximately 13% (as shown in Figure 1 and Table 2).



Figure 1. Elemental composition of (a) (TiCrAl0.5NbCu)C_x and (b) (TiCrAl0.5NbCu)C_xN_{0.13}.

3.2. Structure and Phase Composition

Figure 2 presents the diffraction patterns of carbide (Figure 2a) and carbo-nitride (Figure 2b) sets of samples. Notably, the metallic sample, *M*, presents a well-crystallized structure that is fully textured along a single out-of-plane direction. The solitary visible diffraction line, identified at about $2\theta = 36.6^{\circ}$ should be attributed to a BCC structure, in agreement with the valence electron concentration (VEC) rule, which represents a good indicator of phase stability. The VEC rule is a empirically established criteria proposed to predict the structure of HEAs [54,55]. It posits that a high-entropy alloy will primarily form a FCC solid solution phase if VEC \geq 8.0, a BCC phase if VEC < 6.87, and a mixture of FCC and BCC phases if VEC falls between these thresholds (6.87 \leq VEC < 8.0). The VEC value of an alloy is calculated from the weighted average valence electron concentration of the constituent components, i.e., VEC = $\Sigma C_i (VEC)_i$, where C_i and $(VEC)_i$ are the atomic percent and the VEC of the i-th element, respectively [54–56]. Using the (VEC)_i values from reference [56], it can be determined that the VEC value corresponding to the metallic sample, M, is about VEC = 5.98, which is less than 6.87. This suggests that the M sample is likely to possess a BCC structure. Consequently, the diffraction line identified at $2\theta = 36.6^{\circ}$ in the XRD pattern corresponding to the sample M could be attributed to (110) reflection of a BCC structure with a lattice parameter of about 3.469 Å. This is in line with other high-entropy systems [57–62].

The C1 and *N* samples exhibit an amorphous structure. The only XRD features arising from these films are broad and are identified at about $2\theta = 39.8^{\circ}$ and $2\theta = 39.9^{\circ}$, respectively. These peaks have a full width at half maximum (FWHM) of about 4.9° and 5.2° , respectively, indicating an average crystallite size of 1.8 nm and 1.7 nm, respectively, which is typical for amorphous materials.



Figure 2. X-ray diffraction patterns of (a) (TiCrAl_{0.5}NbCu)C_x and (b) (TiCrAl_{0.5}NbCu)C_xN_{0.13} samples.

In contrast, the diffractograms of C2–C4 and CN1–CN4 samples display more distinct features observed at about 36.0°, 41.9°, 61.1°, and 73.0°. These features can be attributed to the (111), (200), (220), and (311) reflections, respectively, corresponding to a FCC-type crystallographic structures, similar to PDF 00-031-1400 reference [63] and other FCC high-entropy carbide and nitride systems [22,64–69].

A noticeable trend in Figure 2 is the evident narrowing of the diffraction lines as the carbon concentration increases. This suggests an enhancement in the crystallinity of the films. Following the Scherrer equation [70], Figure 3 illustrates the dependence on C concentration of the average crystallite sizes in the direction perpendicular to the (200) lattice planes of the FCC structures, and in the direction perpendicular to the (110) planes of the metallic BCC structure. In general, the carbonitride films exhibit superior crystallinity when compared to the carbide films of same carbon content. The lattice parameter values of the carbide and carbonitride FCC structures fall within the region of 4.4 Å, which aligns with typical values for transition metal carbides and carbonitrides [71–73].



Figure 3. Mean crystallite size derived from (111) planes (sample *M*) and (200) planes (samples C2–C4, CN1–CN4).

3.3. Density of the Films

The density of the films was investigated via the XRR technique. Figure 4a presents the reflectivity spectra corresponding to the carbide set of samples. One can observe that as the carbon content in the films increases, the critical angle for total X-ray reflection shifts towards lower angles. This shift is a consequence of the decreasing film density due to the elevated concentration of low-mass atoms such as carbon and nitrogen and/or the inclusion of pores/voids in the films. The dependence between film density and carbon concentration is presented in Figure 4b, clearly displaying the decreasing trend. The density decreases from about 7 g/cm³ to about 5.5 g/cm³.



Figure 4. (a) Examples of XRR profiles. (b) The mass density of the films versus carbon concentration, x.

It's worth noting that the mass density value of the metallic sample, about 7.0 g/cm³, is consistent with that of other BCC HEA systems with similar elemental constituents, which typically falls in the range of 6-8 g/cm³ [74–76]. When nitrogen is added to the composition of the processing gas, the mass density of the resulting nitride film, N, slightly increases to about 7.1 g/cm³. However, when methane is added to the composition of the processing gas, the concentration of the low-mass carbon atoms is increased in the film's composition, and the mass density of the carbide and carbonitride films progressively decreases down to about 5.5 g/cm³. This is a common trend [77], which can be accentuated by the development of pores/voids.

3.4. Surface Morphology

Surface morphology investigations confirm the X-ray diffraction findings. Figure 5a presents AFM images of the sample surfaces covering a 5 μ m² area. Figure 5b,c further highlight the correlation between the carbon concentration of the films and the corresponding average surface roughness, Ra, and surface porosity, P, respectively, calculated from the AFM data. The surface morphology of the metallic sample exhibits a surface roughness and porosity of approximately Ra = 2.4 nm and P = 2.3%, respectively. The addition of carbon and/or nitrogen to the composition of the films initially leads to an abrupt decrease in the surface roughness to about Ra = 0.4 nm (sample C1) and Ra = 0.5 nm (sample *N*), accompanied by a sharp decrease in the surface porosity to about P = 0.95% and P = 0.68%, respectively. This is followed by a progressive increase in the surface roughness when the carbon concentration is enhanced, reaching approximately Ra = 12.1 nm (sample C4) and Ra = 15.5 nm (sample CN4), respectively, and an increase in the surface porosity up to about P = 11.4% (sample C4) and P = 16.1% (sample CN4), respectively.



Figure 5. (a) AFM surface images $(5 \times 5 \ \mu m^2)$ of the investigated specimens. The dependence on film's C concentration of: (b) mean surface roughness, Ra, and (c) surface porosity, P.

3.5. Nanoindentation

Figure 6a presents representative load–displacement curves recorded during nanoindentation tests of the carbonitride coatings. The dependence on the film's carbon concentration of the hardness (H) and elastic modulus (E), corresponding to the carbide and carbonitride sets of samples, is presented in Figure 6b,c.

The hardness and the elastic modulus corresponding to the metallic sample is $H = 6.65 \pm 0.20$ GPa and $E = 138.9 \pm 5.0$ GPa, respectively. The addition of a small fraction of carbon (9%) or nitrogen (13%) to the metallic film composition led to an increase in H and E to about $H = 11.3 \pm 0.67$ GPa and $E = 150.7 \pm 6.1$ GPa (sample C1), and $H = 11.7 \pm 0.70$ GPa and $E = 190.7 \pm 6.2$ GPa (sample N), respectively. With further increases in the C concentration, the hardness progressively increased up to $H = 16.83 \pm 0.28$ GPa (sample C4) and $H = 16.97 \pm 0.28$ GPa (sample CN4) The elastic modulus slightly increased up to a maximum value of $E = 202.15 \pm 1.2$ GPa (sample C4) and $E = 227.94 \pm 6.8$ GPa (sample CN4) after reaching a local minimum value of 126.3 ± 5.6 (sample C3) and 152.08 ± 1.3 (sample CN2) for the carbide and carbonitride set of samples, respectively.

Additional information on the coatings mechanical properties can be obtained through analyzing the elastic strain to failure factor (H/E ratio) and the plastic deformation resistance factor (H^3/E^2 ratio). Based on a theory proposed by Leyland [78], the tribological property of films can be characterized using H/E and H^3/E^2 ratios. A high H/E ratio is related to the highest elastic strain a film can accumulate prior to a plastic deformation. A high H/E value means better film toughness and, thus, superior wear resistance. The plastic deformation resistance factor, H^3/E^2 , is considered more sensible to the wear resistance property of a material, and it represents the contact yield stress, i.e., the capability of the material to resist elastic deformation. The higher the H^3/E^2 is, the larger the load born on



the material is, and hence the higher the wear-resistance behavior could be. Also, H^3/E^2 can better predict the change in friction coefficient than H/E for film materials [79].

Figure 6. (a) Load–displacement curves corresponding to carbo-nitride samples. The dependence on the carbon concentration of (b) hardness, H; (c) elastic modulus, E; (d) H/E ratio; and (e) H^3/E^2 ratio corresponding to the carbide and carbonitride sets of samples.

The dependences on the film's carbon concentration of the H/E and H^3/E^2 ratios, corresponding to the carbide and carbonitride sets of samples, are presented in Figure 6d,e, respectively. A maximum value of 0.11 and 0.16 is reached by H/E and H^3/E^2 , respectively, corresponding to a carbon-to-metal ratio, x, of about 0.3 in the carbide film (sample C3) and a maximum value of 0.08 and 0.10 for a carbon-to-metal ratio of about 0.2–0.3 in the carbonitride films (samples *CN2* and *CN3*). Note that the maximum values of the H/E and H^3/E^2 ratios are comparable to those observed for other HEA ceramics [80].

Comparing the H/E and H^3/E^2 values between the two sets of samples, one can observe a significant difference occurring at approximately x = 0.3. The C3 sample exhibits much higher H/E and H^3/E^2 values compared to those of the CN3 sample. It is expected to observe significant differences in the tribological behavior between these two samples.

3.6. Tribology

The evolution of the friction coefficient, μ , over the sliding distance for both the carbide and the carbonitride sets of samples is presented in Figures 7a and 7b, respectively. Generally, after a running-in period of 5–10 m of sliding distance, the friction coefficient reaches a steady state and remains constant. The mean value of μ calculated over the last 20 m of sliding distance, along with the corresponding calculated value of the wear rate, K, is presented in Table 3. Figure 8a,b depict the evolution of the mean value of μ and K, respectively, as functions of the carbon-to-metals atomic concentration ratio of the films.



Figure 7. The evolution of the friction coefficient μ over the sliding distance corresponding to (a) (TiCrAl_{0.5}NbCu)C_x and (b) (TiCrAl_{0.5}NbCu)C_xN_{0.13} samples.

Table 3. Wear rate (K) and the friction coefficient (μ) of the investigated specimens.

Sample	K (10 ⁻⁶ mm ³ /Nm)	μ	Sample	K (10 ⁻⁶ mm ³ /Nm)	μ
М	382.4	0.80	Ν	184.7	0.65
C1	266.2	0.58	CN1	32.8	0.60
C2	27.5	0.5	CN2	27.0	0.55
C3	7.2	0.23	CN3	7.7	0.43
C4	5.5	0.23	CN4	6.3	0.21



Figure 8. The dependence on the C concentration of the (a) wear rate, K, and (b) the friction coefficient, μ .

As expected, both the coefficient of friction and the wear rate decrease with increasing carbon content, reaching low values, specific of carbides [73,81]. The metallic sample exhibits a wear rate coefficient of K = $382.4 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and an average friction coefficient of $\mu = 0.80$. The addition of carbon or nitrogen to the content of the metallic sample leads to a decrease in K to $266.2 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $184.7 \times 10^{-6} \text{ mm}^3/\text{Nm}$, and of μ to 0.58 and 0.65 (samples C1 and *N*), respectively. The further addition of carbon to the content of the films lowers K down to $5.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and $6.3 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and lowers μ to 0.23 and 0.21 (samples C4 and CN4), respectively.

In general, the carbonitride samples exhibit higher coefficients of friction compared to carbide samples with the same carbon content. The largest difference is observed between the samples C3 and CN3, containing a fraction of 0.3 of atomic carbon relative to the sum of metal atoms. The coefficient of friction is twice as large for the carbonitride sample, while the wear rate values are comparable. In consequence, the CN3 sample exhibits the appropriate characteristics for applications requiring a low wear rate and a medium-to-high coefficient of friction.

3.7. Corrosion

The electrochemical performance of the investigated systems and their behavior after 1 h and 12 h immersion in NaCl is presented in Figures 9 and 10, respectively. Nyquist impedance plots recorded after 1 h of immersion (Figure 9a) reveal a distinct AC polarization response in the case of metallic coating compared to that corresponding to carbide samples, ascribed to higher charge transfer resistance. This assumption is sustained by the Bode magnitude plot (Figure 9b). One can remark that the carbide samples, C1-C4, exhibit similar impedance modulus, |Z|, over the applied frequencies range. However, after 12 h of immersion, a significant drop of |Z| is observed for all investigated systems (Figure 9d), which can be attributed to electrolyte intake. This effect is more pronounced in the case of metallic coating (M) and can be correlated with its higher crystallinity, as demonstrated by the XRD investigations.



Figure 9. Nyquist and Bode magnitude plots of $(TiCrAl_{0.5}NbCu)C_x$ samples after immersion in 0.9% NaCl at RT of 1 h (**a**,**b**), and 12 h (**c**,**d**), respectively.

The recorded impedance patterns corresponding to carbonitride samples are presented in Figure 10. We note that contrary to carbide samples, the measured impedance spectra obtained for carbonitride samples exhibit significant variations in the low-frequency region. After 1 h of immersion in 0.9% NaCl, the investigations revealed different behaviors for the analyzed coatings as a function of their carbon composition. We can see that after 12 h of immersion, the nitride coating showed the highest charge transfer resistance among all measured samples, apart from the metallic system previously discussed.

The results showed an evident influence of carbon concentration on impedance magnitude (Figure 10c,d): a higher amount of carbon leads to lower protective coatings and, consequently, a lower charge transfer resistance. The as-demonstrated electrochemical behavior induced by structural changes can be attributed to the different chemical composition and microstructure, as reported in literature [82,83]. The EIS results presented by Yang et al. [84] showed a deterioration in corrosion resistance due to new diffusion channel formation for electrolyte ingress, caused by carbide precipitates as well as inter-columnar voids that developed during film growth, more pronounced with increasing carbon con-



tent [83], as demonstrated by surface porosity data deduced from AFM data and confirmed through cross-sectional SEM investigations, not shown here.

Figure 10. Nyquist and Bode magnitude plots of $(TiCrAl_{0.5}NbCu)C_xN_{0.13}$ samples, after immersion in 0.9% NaCl, RT, for 1 h (**a**,**b**), and 12 h (**c**,**d**).

In order to gain a clearer understanding of the interfacial changes at both the electrolytecoating interface and electrolyte-substrate interface, the EIS data were fitted using an equivalent electrical circuit (EEC). This circuit considered several elements, including the electrolyte resistance (Rel), the coating capacitance (CPEcoat), resistance associated with the current flow through the pores (Rpor), a capacitance associated with the double layer formed during immersion (CPEdI), and a charge transfer resistance (Rct). A constant phase element (CPE) was used in this case to model the deviations from the ideal behavior due to surface disorder, inhomogeneity, geometric irregularities, defects, or electrode porosity [85,86]. The EEC used is presented as an inset in Figure 11. The low values of goodness of fit, χ^2 , obtained during the fitting procedure, which is in the range of 10^{-4} – 10^{-3} , demonstrate that the proposed model can effectively describe the physical behavior of the systems under investigation. Figure 11 presents the evolution of resistivity (ρ) as a function of the coating's composition, with values obtained after 1 h and 12 h of immersion. The ρ value was calculated based on the charge transfer resistance obtained from the impedance fitting procedure normalized to the thickness of each coating. As shown, ρ gradually decreases for both the carbide (C1-C4) and carbonitride (CN1-CN4) samples, suggesting a reduction in corrosion resistance of increasingly crystalline coatings caused by carbon addition.

The amplitude plots of the impedance data recorded after 1 and 12 h of immersion are further compared in Figure 12. Thus, the electrochemical evolution of the coatings during the testing period was mainly investigated in the low frequency range, which is indicative of the interfacial changes that can occur between the electrolyte and the substrate. The results demonstrated a maximum decrease of 90% in impedance magnitude for the metallic coating (*M*), calculated at the lowest excitation frequency (0.5 Hz). In the case of carbides, the decrease in the impedance magnitude as a function of immersion time was 6% for the C1 sample, which exhibited an amorphous structure, while the maximum

decrease (~47%) was observed for the C4 sample, which showed a crystalline columnar microstructure. The penetration of the electrolyte through pores (inter-columnar voids) can initiate the corrosion process of the substrate [83,87]. The *N* coating proved to maintain its electrochemical protection for the substrate even after 12 h of immersion, since only a 19% decrease in impedance magnitude was calculated in this case at the lowest excitation frequency (Figure 12b). A relatively similar decreasing tendency was observed for *CN* coatings; a maximum of 80% decrease was seen for the *CN*4 sample. This dependence of the corrosion assessment on the structural transition from an amorphous to a crystalline structure was also noted in the case of carbide coatings.



Figure 11. The charge transfer resistivity (ρ_{ct}) measured after 1 h and 12 h of immersion for (a) carbide coatings and (b) carbonitride coatings.



Figure 12. The impedance vs. excitation frequency curves corresponding to (**a**–**e**) *M*, C1–C4 samples and (**f**–**j**) *N*, *CN*1–*CN*4 samples, measured after 1 h (black dots) and 12 h (red dots) of immersion.

4. Discussion

The deposition rate slightly decreases when reactive gases (CH_4 and N_2) are added to the composition of the processing gas (Ar) due to the poisoning effect of the surface of the sputtering targets. This effect results from the partial covering of the target's surface by ceramic material [47,88]. Additionally, the sputtering efficiency of targets by the gas mixture ions is lower compared with that of pure argon ions, primarily because of the lower mass of N₂ and CH₄ ions [89].

Through adding only a small fraction of carbon (9%) or nitrogen (13%) to the metallic film composition, the crystallographic structure changes from a BCC solid solution to an amorphous one, as observed for samples C1 and N. With further increases in the carbon concentration of the C1 sample, i.e., the C2–C4 samples, or through adding carbon to the composition of the nitride sample N, i.e., the CN1–CN4 samples, FCC-structured solid solution phases are formed in both cases, well-identified by a few diffraction lines, such as (111), (200), (220), (311) [67–69]. Consequently, the addition of carbon and nitrogen to the metallic sample leads to a BCC-to-FCC phase transition via an intermediary amorphous phase. The formation of the amorphous phase is attributed to the disorder generated by the conflict between the BCC and FCC structures [90–94]. The metal atoms preferentially combine with the nitrogen and carbon atoms to form metal nitrides, carbides, or carbonitrides because the bond energy between metal atoms and nitrogen or carbon (Me-N, Me-C) is greater than the bond energy between the metals (Me-Me) [75,76]. Ti, Cr, Al, and Nb in the film can form FCC-structured nitrides, while Ti, Cr and Nb can form a FCC-structured carbides with nitrogen and carbon, respectively. The increase in carbon content promotes the formation of FCC carbides and carbonitrides with comparable lattice parameters, as demonstrated through XRD investigations, promoting long distance ordering, effectively improving the crystallinity of the film when carbon content is increased. This effect is sustained by the high entropy effect, which increases the solid solubility between the elements, promoting the formation of a single-phase crystallographic structure and inhibiting the formation of complex intermetallic compounds. An obvious increase in crystallite size with increasing carbon concentration is observed for both sets of samples, proving that carbon promotes the ordering of high-entropy crystal lattices. Similar observations have been reported for other multi-element high-entropy ceramics [26,72,76,77,81].

For low concentration of carbon (*C*1, *C*2, *CN*1, and *CN*2 samples), the FCC structures are predominantly (200) textured. However, for higher carbon concentrations (*C*3, *C*4, *CN*3, and *CN*4 samples), the out-of-plane preferential orientation is reduced, and the intensity of other diffraction lines corresponding to other orientations, such as (111), becomes comparable.

The surface morphology of the metallic sample is dominated by large spherical grains, yielding an average surface roughness value of about Ra = 2.4 nm and a surface porosity of about P = 2.3%. The mass density of the deposited material is about 7.0 g/cm³. Upon the addition of a small amount of carbon (sample C1) or nitrogen (sample N), the surface morphology changes from granular to glassy, which is characteristic of amorphous materials. This transition is in agreement with XRD investigations that concluded that samples C1 and N are amorphous. Consequently, the surface roughness decreases down to 0.45 nm (sample C1) and 0.57 nm (sample N), respectively, accompanied by a decrease in surface porosity to approximately 0.96% and 0.68% and a slight increase in mass density $(7.1 \text{ g/cm}^3 \text{ in the case of sample N})$. Upon further increasing the carbon concentration (samples C2-C4) or adding carbon to the nitride sample (CN2-CN4), the crystallites and grains grow larger, leading to an increase in surface roughness up to 12.1 nm and 15.5 nm for the carbide and carbonitride samples, respectively. Cross-sectional scanning electron microscopy (SEM) investigations, (Figure S1 in Supplementary Materials), confirmed a higher density of low carbon samples (M, N, C1 CN1), in agreement with Figure 4b, and demonstrated a columnar growth of carbide and carbonitride samples, especially the C2–C4 and CN2–CN4 samples. Consequently, with the increase in carbon concentration, the crystallinity of the samples is improved, the columnar growth is stimulated, and larger inter-columnar voids develop inside the coatings, leading to increased surface porosity up to about 11.4% (sample C4) and 16.1% (sample CN4), accompanied by a strong decrease in mass density down to 5.5 g/cm^3 . In general, the carbo-nitride samples exhibit higher surface roughness, surface porosity, and volume porosity and lower mass density when

compared to carbide samples with the same carbon content (Figure 5a,b). High-porosity samples are generally expected to provide lower corrosion protection for the substrate due to the increased pathways for corrosive agents to penetrate and reach the substrate.

The addition of carbon and nitrogen leads to an increase in hardness. The difference between metallic and carbide or carbonitride coatings arise from the introduction of strong covalent-like carbon and nitrogen bonds, resulting in the formation of carbide or carbonitride phases in the films. These phases contribute to improved mechanical performance, specifically an increase in hardness. According to Archard's law [95], the wear rate varies inversely proportional to the hardness of the alloy.

Since the hardness of the high-entropy carbide and carbonitride films is increased due to the formation of the ceramic phases, the wear rate of the carbide and carbonitride samples is reduced [75,81]. However, in sliding contacts, the tribological behavior of a coating is influenced not only by film hardness but also by factors such as surface chemistry, material transfer between surfaces, film roughness, and the size and hardness of any debris in contact [96]. Generally, nitrides exhibit a higher coefficient of friction compared to their corresponding carbides [23]. In line with this, our carbonitride samples exhibit a higher coefficient of friction compared with the carbide samples with the same carbon content. The most significant difference is observed between the samples C3 and CN3, both containing 30% carbon relative to metallic constituents, with CN3 having a coefficient of friction twice as large, while the wear rate values are comparable. We note that the large difference in tribological behavior between samples C3 and CN3 was predicted through the analysis of H/E and H³/E² ratios in Section 3.5, which showed that the C3 sample exhibits much higher H/E and H³/E² values compared to those of the CN3 sample, while for other concentrations of carbon, they present comparable values (Figure 6d,e).

With a μ = 0.43 and K = 7.7 × 10⁻⁶ mm³/Nm, the *CN*3 sample presents the best characteristics for applications requiring a low wear rate and medium-to-high coefficient of friction.

With increasing carbon concentration, the coatings become less corrosion-protective, characterized by lower charge transfer resistance during EIS tests. This reflects a clear influence of the higher carbon concentration on impedance magnitude. The electrochemical behavior is induced by structural changes that can be attributed to differences in chemical compositions and the formation of new diffusion channels for electrolyte ingress, caused by carbide precipitates or inter-columnar void formation during the columnar growth of the coatings. The corrosion mechanism can be explained by the increase in grain boundaries and inter-columnar voids which can create pathways for aggressive electrolyte ingress. Indeed, the AFM-calculated surface porosity and cross-sectional SEM investigations represent a clear indication of the previous statement.

The evolution of dielectric properties over an extended period can be attributed to the protective nature of the coatings. It appears that amorphous coatings or those of low crystallinity can have a beneficial effect on their long-term protective properties. As the carbon content increases, a porous internal structure forms, due to favored columnar growth with larger columns terminated with spherical grains, as shown by AFM and XRD results and confirmed by cross-sectional SEM investigations. Consequently, these structural changes significantly influence the electrochemical behavior, leading to a sharp decrease in impedance data over longer immersion periods. As observed, these decreasing tendencies are proportional with the calculated crystallite sizes and surface porosity. That explains the higher impedance drop in the case of carbonitride coatings compared to carbide coatings with the same carbon content.

5. Conclusions

High-entropy coatings of $(TiCrAl_{0.5}NbCu)C_xN_y$ were fabricated through the cosputtering of elemental targets in an Ar + CH₄ + N₂ reactive atmosphere using a hybrid HiPIMS/DCMS technique. Two sets of samples were fabricated:

(a) high-entropy carbides, (TiCrAl_{0.5}NbCu)C_x;

(b) high-entropy carbonitrides, $(TiCrAl_{0.5}NbCu)C_xN_{0.13}, 0 \le x \le 0.48$.

The structural, mechanical, tribological, and corrosion resistance properties were investigated. The metallic sample exhibited a single BCC structure. The addition of C or N to the film's composition induced a crystallographic phase transition from BCC to FCC via an intermediary amorphous phase, occurring at low C (9%) or N (13%) elemental concentrations. As the carbon fraction within the films was further increased, up to 48%, the crystallinity of the FCC phases progressively enhanced, and a columnar growth type was stimulated, resulting in a gradual decrease in the density of the films to approximately 5.5 g/cm³ and a gradual increase in the surface roughness and surface porosity. The hardness and wear resistance progressively improved, while the corrosion resistance gradually declined. The samples with x = 0.48 exhibit the highest hardness of about 16.9 GPa and the lowest wear rate of about 5.5×10^{-6} mm³/Nm. Generally, the carbonitride samples displayed superior mechanical and wear resistance properties but exhibited lower corrosion resistance when compared to carbide samples with the same carbon content. We found a very good agreement between the evolution of H/E and H^3/E^2 parameters with the carbon content of the films and the tribological behavior of coatings. Notably, the $(TiCrAl_{0.5}NbCu)C_{0.3}N_{0.13}$ sample exhibited the most favorable characteristics for applications requiring medium-tohigh friction and wear-resistant surfaces, with a coefficient of friction of about 0.43 and a wear rate of about 7.7×10^{-6} mm³/Nm. The best corrosion resistance was presented by the low-carbon carbonitride samples, showing a charge transfer resistivity of about $3 \times 10^8 \,\Omega \cdot cm$, which is more than three times larger than that of the metallic HEA.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13111565/s1, Figure S1: Cross sectional SEM images corresponding to (a) sample *M*, (b) sample *N*, (c) sample *C*4, (d) sample *C*N4.

Author Contributions: Conceptualization, N.C.Z., M.D., C.E.A.G., A.L.-O. and X.A.; methodology, C.E.A.G., A.L.-O., M.D., M.M., A.S., X.A. and N.C.Z.; formal analysis, M.D., N.C.Z., A.C.P., I.P., A.E.K. and A.L.-O.; investigation, A.C.P., A.L.-O., M.D., I.P., A.E.K., J.M.I., A.A.H. and J.C.R.; writing—original draft preparation, N.C.Z., M.D., C.E.A.G., A.L.-O. and I.P.; writing—review and editing, N.C.Z., M.D., C.E.A.G., A.L.-O., M.M., A.S., X.A., A.C.P., I.P., A.E.K., J.M.I., A.A.H. and J.C.R.; supervision, N.C.Z., M.M. and A.S.; project administration, N.C.Z., M.M., A.S., C.E.A.G. and X.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by a grant of the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project number ERANET-M.-TriboHEA, within PNCDI III, by the Basque Innovation Agency, INNOBASQUE, grant no. ZL-2019/00622, and by the Core Program within the Romanian National Research Development and Innovation Plan 2022-2027, carried out with the support of MCID, project no. PN 23 05 (id: PN11N-03-01-2023).

Data Availability Statement: The data presented in this study are available in the article.

Acknowledgments: The authors would like to express their gratitude to Bogdan Bita from the National Institute for Laser, Plasma, and Radiation Physics, Magurele, Romania, for providing cross-sectional SEM analysis of the samples.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Bouaziz, O.; Zurob, H.; Huang, M. Driving Force and Logic of Development of Advanced High Strength Steels for Automotive Applications. Steel Res. Int. 2013, 84, 937–947. [CrossRef]
- Chen, L.; Zhao, Y.; Qin, X. Some Aspects of High Manganese Twinning-Induced Plasticity (TWIP) Steel, a Review. Acta Metall. Sin. 2013, 26, 1–15. [CrossRef]
- 3. Zhao, J.; Jiang, Z. Thermomechanical Processing of Advanced High Strength Steels. Prog. Mater. Sci. 2018, 94, 174–242. [CrossRef]
- Grigorescu, C.E.A.; Zoita, C.N.; Sobetkii, A.; Iordache, A.M.; Iordache, S.M.; Stefan, C.R.; Rusu, M.I.; Tortet, L.; Tonetto, A.; Notonier, R. Multinary Metal Alloys of the Heusler, Half-Heusler, Dilute Magnetic Semiconductors, and High Entropy Families: How Would Spin Make a Choice? J. Optoelectron. Adv. Mater. 2020, 22, 647–652.
- Yeh, J.-W.; Chen, S.-K.; Lin, S.-J.; Gan, J.-Y.; Chin, T.-S.; Shun, T.-T.; Tsau, C.-H.; Chang, S.-Y. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes. *Adv. Eng. Mater.* 2004, *6*, 299–303. [CrossRef]

- Cantor, B.; Chang, I.T.H.; Knight, P.; Vincent, A.J.B. Microstructural Development in Equiatomic Multicomponent Alloys. *Mater. Sci. Eng. A* 2004, 375–377, 213–218. [CrossRef]
- 7. Yeh, J.W. Recent Progress in High-Entropy Alloys. Ann. Chim. Sci. Mater. 2006, 31, 633–648. [CrossRef]
- 8. Braic, M.; Balaceanu, M.; Vladescu, A.; Zoita, C.N.; Braic, V. Deposition and Characterization of Multi-Principal-Element (CuSiTiYZr)C Coatings. *Appl. Surf. Sci.* 2013, 284, 671–678. [CrossRef]
- 9. Sathiyamoorthi, P.; Kim, H.S. High-Entropy Alloys with Heterogeneous Microstructure: Processing and Mechanical Properties. *Prog. Mater. Sci.* 2022, 123, 100709. [CrossRef]
- 10. Zhang, R.-Z.; Reece, M.J. Review of High Entropy Ceramics: Design, Synthesis, Structure and Properties. J. Mater. Chem. A 2019, 7, 22148–22162. [CrossRef]
- Gild, J.; Zhang, Y.; Harrington, T.; Jiang, S.; Hu, T.; Quinn, M.C.; Mellor, W.M.; Zhou, N.; Vecchio, K.; Luo, J. High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics. *Sci. Rep.* 2016, *6*, 37946. [CrossRef] [PubMed]
- Barbarossa, S.; Orrù, R.; Cao, G.; Balbo, A.; Zanotto, F.; Sani, E. Optical Properties of Bulk High-Entropy Diborides for Solar Energy Applications. J. Alloys Compd. 2023, 935, 167965. [CrossRef]
- Chen, L.; Zhang, W.; Lu, W.; Wei, B.; Huo, S.; Wang, Y.; Zhou, Y. Low Thermal Conductivity of Dense (TiZrHfVNbTa)C_x High-Entropy Carbides by Tailoring Carbon Stoichiometry. J. Adv. Ceram. 2023, 12, 49–58. [CrossRef]
- 14. Braic, M.; Braic, V.; Balaceanu, M.; Zoita, C.N.; Vladescu, A.; Grigore, E. Characteristics of (TiAlCrNbY)C Films Deposited by Reactive Magnetron Sputtering. *Surf. Coat. Technol.* 2010, 204, 2010–2014. [CrossRef]
- 15. Su, W.; Chen, L.; Zhang, W.; Huo, S.; Wang, Y.; Zhou, Y. Insights into Grain Boundary Segregation and Solubility Limit of Cr in (TiZrNbTaCr)C. J. Mater. Sci. Technol. 2023, 139, 1–9. [CrossRef]
- Chen, T.K.; Shun, T.T.; Yeh, J.W.; Wong, M.S. Nanostructured Nitride Films of Multi-Element High-Entropy Alloys by Reactive DC Sputtering. *Surf. Coat. Technol.* 2004, 188–189, 193–200. [CrossRef]
- Pshyk, A.V.; Vasylenko, A.; Bakhit, B.; Hultman, L.; Schweizer, P.; Edwards, T.E.J.; Michler, J.; Greczynski, G. High-Entropy Transition Metal Nitride Thin Films Alloyed with Al: Microstructure, Phase Composition and Mechanical Properties. *Mater. Des.* 2022, 219, 110798. [CrossRef]
- Huang, Y.-S.; Chen, L.; Lui, H.-W.; Cai, M.-H.; Yeh, J.-W. Microstructure, Hardness, Resistivity and Thermal Stability of Sputtered Oxide Films of AlCoCrCu_{0.5}NiFe High-Entropy Alloy. *Mater. Sci. Eng. A* 2007, 457, 77–83. [CrossRef]
- Schweidler, S.; Tang, Y.; Lin, L.; Karkera, G.; Alsawaf, A.; Bernadet, L.; Breitung, B.; Hahn, H.; Fichtner, M.; Tarancón, A.; et al. Synthesis of Perovskite-Type High-Entropy Oxides as Potential Candidates for Oxygen Evolution. *Front. Energy Res.* 2022, 10, 983979. [CrossRef]
- Gild, J.; Braun, J.; Kaufmann, K.; Marin, E.; Harrington, T.; Hopkins, P.; Vecchio, K.; Luo, J. A High-Entropy Silicide: (Mo_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}W_{0.2})Si₂. J. Mater. 2019, 5, 337–343. [CrossRef]
- Kim, S.J.; Yoon, K.N.; Ko, W.-S.; Park, E.S. Entropy-Stabilized Silicides: Expanding the B20 Single-Phase Region from Mono-Silicide to High-Entropy Silicide. APL Mater. 2022, 10, 121105. [CrossRef]
- Shen, W.-J.; Tsai, M.-H.; Chang, Y.-S.; Yeh, J.-W. Effects of Substrate Bias on the Structure and Mechanical Properties of (Al_{1.5}CrNb_{0.5}Si_{0.5}Ti)N_x Coatings. *Thin Solid Films* **2012**, *520*, 6183–6188. [CrossRef]
- Braic, V.; Vladescu, A.; Balaceanu, M.; Luculescu, C.R.; Braic, M. Nanostructured Multi-Element (TiZrNbHfTa)N and (TiZrNbHfTa)C Hard Coatings. Surf. Coat. Technol. 2012, 211, 117–121. [CrossRef]
- 24. Lin, S.-Y.; Chang, S.-Y.; Huang, Y.-C.; Shieu, F.-S.; Yeh, J.-W. Mechanical Performance and Nanoindenting Deformation of (AlCrTaTiZr)NC_y Multi-Component Coatings Co-Sputtered with Bias. *Surf. Coat. Technol.* **2012**, *206*, 5096–5102. [CrossRef]
- Sarker, P.; Harrington, T.; Toher, C.; Oses, C.; Samiee, M.; Maria, J.-P.; Brenner, D.W.; Vecchio, K.S.; Curtarolo, S. High-Entropy High-Hardness Metal Carbides Discovered by Entropy Descriptors. *Nat. Commun.* 2018, *9*, 4980. [CrossRef]
- Lv, C.F.; Zhang, G.F.; Cao, B.S.; He, Y.Y.; Hou, X.D.; Song, Z.X. Structure and Mechanical Properties of A-C/(AlCrWTaTiNb)C_xN_y Composite Films. *Surf. Eng.* 2016, 32, 541–546. [CrossRef]
- 27. Dippo, O.F.; Mesgarzadeh, N.; Harrington, T.J.; Schrader, G.D.; Vecchio, K.S. Bulk High-Entropy Nitrides and Carbonitrides. *Sci. Rep.* **2020**, *10*, 21288. [CrossRef]
- 28. Wen, T.; Ye, B.; Nguyen, M.C.; Ma, M.; Chu, Y. Thermophysical and Mechanical Properties of Novel High-entropy Metal Nitride-carbides. J. Am. Ceram. Soc. 2020, 103, 6475–6489. [CrossRef]
- Chapala, P.; Acharyya, S.G.; Shariff, S.M.; Naik, G. Novel Ti-Nb Alloys with Improved Wear Resistance for Biomedical Implant Application. In Proceedings of the 2016 38th Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC), Orlando, FL, USA, 16–20 August 2016; pp. 4208–4211.
- Tada, K.; Fujiwara, T.; Hasunuma, M.; Kawai, M. Wear and Corrosion Resistance of Ni-Cr-Mo-Nb Alloys. J. At. Energy Soc. Jpn. 1992, 34, 174–180. [CrossRef]
- Alberdi, A.; Marín, M.; Díaz, B.; Sánchez, O.; Escobar Galindo, R. Wear Resistance of Titanium–Aluminium–Chromium–Nitride Nanocomposite Thin Films. *Vacuum* 2007, *81*, 1453–1456. [CrossRef]
- Guo, X.; Xiao, Z.; Qiu, W.; Li, Z.; Zhao, Z.; Wang, X.; Jiang, Y. Microstructure and Properties of Cu-Cr-Nb Alloy with High Strength, High Electrical Conductivity and Good Softening Resistance Performance at Elevated Temperature. *Mater. Sci. Eng. A* 2019, 749, 281–290. [CrossRef]

- Xiong, H.; Ma, Y.; Zhang, H.; Chen, L. Design of Cu–Cr Alloys with High Strength and High Ductility Based on First-Principles Calculations. *Metals* 2022, 12, 1406. [CrossRef]
- Abdou, S.; Elkaseer, A.; Kouta, H.; Abu Qudeiri, J. Wear Behaviour of Grey Cast Iron with the Presence of Copper Addition. *Adv. Mech. Eng.* 2018, 10, 168781401880474. [CrossRef]
- Obiegbu, M.-J.C.; Akinlabi, E.T.; Fatoba, O.S.; Akinlabi, S.A. The Effects of Silicon and Copper on the Microstructure and Wear Resistance Performance of Al-Si-Sn-Cu/Ti-6Al-4V Composite Coatings. In Proceedings of the 2019 IEEE 10th International Conference on Mechanical and Intelligent Manufacturing Technologies (ICMIMT), Cape Town, South Africa, 15–17 February 2019; pp. 20–25. [CrossRef]
- Li, W.Z.; Polcar, T.; Evaristo, M.; Cavaleiro, A. High Temperature Properties of the Cr Nb Al N Coatings with Increasing Al Contents. Surf. Coat. Technol. 2013, 228, 187–194. [CrossRef]
- Su, Y.L.; Kao, W.H.; Chen, B.Y. Mechanical and Tribological Properties of NbTiAl_x, NbTiAl_{0.5}N_y, and NbTiAl_{0.5}N₁₄-CHz Coatings with Various Aluminum Target Currents and Nitrogen and Acetylene Flow Rates. *J. Mater. Eng. Perform.* 2022, 32, 7928–7945. [CrossRef]
- Garshin, A.P.; Kulik, V.I.; Nilov, A.S. Braking Friction Materials Based on Fiber-Reinforced Composites with Carbon and Ceramic Matrices. *Refract. Ind. Ceram.* 2008, 49, 391–396. [CrossRef]
- Yi, G.; Yan, F. Mechanical and Tribological Properties of Phenolic Resin-Based Friction Composites Filled with Several Inorganic Fillers. Wear 2007, 262, 121–129. [CrossRef]
- Kouznetsov, V.; MacÁk, K.; Schneider, J.M.; Helmersson, U.; Petrov, I. A Novel Pulsed Magnetron Sputter Technique Utilizing Very High Target Power Densities. Surf. Coat. Technol. 1999, 122, 290–293. [CrossRef]
- Chistyakov, R.; Abraham, B.; Sproul, W.D. Advances in High Power Pulse Reactive Magnetron Sputtering. In Proceedings of the 49th Society of Vacuum Coaters Annual Technical Conference, Washington, DC, USA, 22–27 April 2006; pp. 88–91.
- Zoita, N.C.; Dinu, M.; Kiss, A.E.; Logofatu, C.; Braic, M. A Comparative Investigation of Hetero-Epitaxial TiC Thin Films Deposited by Magnetron Sputtering Using Either Hybrid DCMS/HiPIMS or Reactive DCMS Process. *Appl. Surf. Sci.* 2021, 537, 147903. [CrossRef]
- Bobzin, K.; Brögelmann, T.; Kruppe, N.C.; Engels, M. Influence of DcMS and HPPMS in a DcMS/HPPMS Hybrid Process on Plasma and Coating Properties. *Thin Solid Films* 2016, 620, 188–196. [CrossRef]
- 44. Komiya, H.; Shimizu, T.; Teranishi, Y.; Morikawa, K.; Yang, M. Variation of Local Chemical Compositions of (Ti, Al)N Films on Inner Wall of Small Hole Deposited by High-Power Impulse Magnetron Sputtering. *Thin Solid Films* **2017**, *644*, 99–105. [CrossRef]
- 45. Paulitsch, J.; Schenkel, M.; Zufrass, T.; Mayrhofer, P.H.; Muenz, W.-D. Structure and Properties of High Power Impulse Magnetron Sputtering and DC magnetron sputtering CrN and TiN films deposited in an industrial scale unit. *Thin Solid Films* **2010**, *518*, 5558–5564. [CrossRef]
- 46. Fujii, Y. Improvement of X-Ray Reflectivity Analysis on Surface and Interface Roughness Estimation. *Am. J. Phys. Appl.* **2015**, *3*, 21–24. [CrossRef]
- Braic, M.; Zoita, N.C.; Danila, M.; Grigorescu, C.E.A.; Logofatu, C. Hetero-Epitaxial Growth of TiC Films on MgO(001) at 100 °C by DC Reactive Magnetron Sputtering. *Thin Solid Films* 2015, *589*, 590–596. [CrossRef]
- Zoita, N.C.C.; Braic, V.; Danila, M.; Vlaicu, A.M.M.; Logofatu, C.; Grigorescu, C.E.A.E.A.; Braic, M. Influence of Film Thickness on the Morphological and Electrical Properties of Epitaxial TiC Films Deposited by Reactive Magnetron Sputtering on MgO Substrates. J. Cryst. Growth 2014, 389, 92–98. [CrossRef]
- 49. Nečas, D.; Klapetek, P. Gwyddion: An Open-Source Software for SPM Data Analysis. Open Phys. 2012, 10, 181–188. [CrossRef]
- 50. AlMarzooqi, F.A.; Bilad, M.R.; Mansoor, B.; Arafat, H.A. A Comparative Study of Image Analysis and Porometry Techniques for Characterization of Porous Membranes. *J. Mater. Sci.* 2016, *51*, 2017–2032. [CrossRef]
- 51. Menk, J. Uncertainties and Errors in Nanoindentation. In *Nanoindentation in Materials Science*; InTechOpen: Houston, TX, USA, 2012. [CrossRef]
- 52. ISO 14577-1:2015; Metallic Materials—Instrumented Indentation Test for Hardness and Materials Parameters. ISO: Geneva, Switzerland, 2015.
- Chen, J.; Bull, S.J. On the Factors Affecting the Critical Indenter Penetration for Measurement of Coating Hardness. *Vacuum* 2009, 83, 911–920. [CrossRef]
- Guo, S.; Ng, C.; Lu, J.; Liu, C.T. Effect of Valence Electron Concentration on Stability of Fcc or Bcc Phase in High Entropy Alloys. J. Appl. Phys. 2011, 109, 103505. [CrossRef]
- 55. Guo, S. Phase Selection Rules for Cast High Entropy Alloys: An Overview. Mater. Sci. Technol. 2015, 31, 1223–1230. [CrossRef]
- Guo, S.; Liu, C.T. Phase Stability in High Entropy Alloys: Formation of Solid-Solution Phase or Amorphous Phase. Prog. Nat. Sci. Mater. Int. 2011, 21, 433–446. [CrossRef]
- 57. Senkov, O.N.; Scott, J.M.; Senkova, S.V.; Miracle, D.B.; Woodward, C.F. Microstructure and Room Temperature Properties of a High-Entropy TaNbHfZrTi Alloy. *J. Alloys Compd.* **2011**, *509*, 6043–6048. [CrossRef]
- 58. Senkov, O.N.; Wilks, G.B.; Miracle, D.B.; Chuang, C.P.; Liaw, P.K. Refractory High-Entropy Alloys. *Intermetallics* 2010, 18, 1758–1765. [CrossRef]
- Yao, J.Q.; Liu, X.W.; Gao, N.; Jiang, Q.H.; Li, N.; Liu, G.; Zhang, W.B.; Fan, Z.T. Phase Stability of a Ductile Single-Phase BCC Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr Refractory High-Entropy Alloy. *Intermetallics* 2018, 98, 79–88. [CrossRef]

- 60. Zhang, H.; Zhao, Y.; Huang, S.; Zhu, S.; Wang, F.; Li, D. Manufacturing and Analysis of High-Performance Refractory High-Entropy Alloy via Selective Laser Melting (SLM). *Materials* **2019**, *12*, 720. [CrossRef] [PubMed]
- 61. Senkov, O.N.; Miller, J.D.; Miracle, D.B.; Woodward, C. Accelerated Exploration of Multi-Principal Element Alloys with Solid Solution Phases. *Nat. Commun.* 2015, *6*, 6529. [CrossRef]
- 62. Löbel, M.; Lindner, T.; Mehner, T.; Lampke, T. Microstructure and Wear Resistance of AlCoCrFeNiTi High-Entropy Alloy Coatings Produced by HVOF. *Coatings* **2017**, *7*, 144. [CrossRef]
- 63. Gates-Rector, S.; Blanton, T. The Powder Diffraction File: A Quality Materials Characterization Database. *Powder Diffr.* 2019, 34, 352–360. [CrossRef]
- Zhang, Y.; Yan, X.-H.; Liao, W.-B.; Zhao, K. Effects of Nitrogen Content on the Structure and Mechanical Properties of (Al_{0.5}CrFeNiTi_{0.25})N_x High-Entropy Films by Reactive Sputtering. *Entropy* 2018, 20, 624. [CrossRef]
- Yalamanchili, K.; Wang, F.; Schramm, I.C.; Andersson, J.M.; Johansson Jöesaar, M.P.; Tasnádi, F.; Mücklich, F.; Ghafoor, N.; Odén, M. Exploring the High Entropy Alloy Concept in (AlTiVNbCr)N. *Thin Solid Films* 2017, 636, 346–352. [CrossRef]
- Ren, B.; Yan, S.Q.; Zhao, R.F.; Liu, Z.X. Structure and Properties of (AlCrMoNiTi)N_x and (AlCrMoZrTi)N_x Films by Reactive RF Sputtering. *Surf. Coat. Technol.* 2013, 235, 764–772. [CrossRef]
- 67. Ren, B.; Liu, Z.X.; Shi, L.; Cai, B.; Wang, M.X. Structure and Properties of (AlCrMnMoNiZrB_{0.1})N_x Coatings Prepared by Reactive DC Sputtering. *Appl. Surf. Sci.* 2011, 257, 7172–7178. [CrossRef]
- Cheng, K.-H.; Weng, C.-H.; Lai, C.-H.; Lin, S.-J. Study on Adhesion and Wear Resistance of Multi-Element (AlCrTaTiZr)N Coatings. *Thin Solid Films* 2009, 517, 4989–4993. [CrossRef]
- 69. Waseem, O.A.; Ryu, H.J. Powder Metallurgy Processing of a WxTaTiVCr High-Entropy Alloy and Its Derivative Alloys for Fusion Material Applications. *Sci. Rep.* 2017, *7*, 1926. [CrossRef] [PubMed]
- 70. Patterson, A.L. The Scherrer Formula for X-Ray Particle Size Determination. Phys. Rev. 1939, 56, 978–982. [CrossRef]
- 71. Moskovskikh, D.; Vorotilo, S.; Buinevich, V.; Sedegov, A.; Kuskov, K.; Khort, A.; Shuck, C.; Zhukovskyi, M.; Mukasyan, A. Extremely Hard and Tough High Entropy Nitride Ceramics. *Sci. Rep.* **2020**, *10*, 19874. [CrossRef] [PubMed]
- Lewin, E. Multi-Component and High-Entropy Nitride Coatings—A Promising Field in Need of a Novel Approach. J. Appl. Phys. 2020, 127, 160901. [CrossRef]
- 73. Wang, Y. Processing and Properties of High Entropy Carbides. Adv. Appl. Ceram. 2022, 121, 57–78. [CrossRef]
- 74. Gorsse, S.; Nguyen, M.H.; Senkov, O.N.; Miracle, D.B. Database on the Mechanical Properties of High Entropy Alloys and Complex Concentrated Alloys. *Data Br.* **2018**, *21*, 2664–2678. [CrossRef]
- 75. Liang, S.-C.; Tsai, D.-C.; Chang, Z.-C.; Sung, H.-S.; Lin, Y.-C.; Yeh, Y.-J.; Deng, M.-J.; Shieu, F.-S. Structural and Mechanical Properties of Multi-Element (TiVCrZrHf)N Coatings by Reactive Magnetron Sputtering. *Appl. Surf. Sci.* 2011, 258, 399–403. [CrossRef]
- Wade, K. Metal-Metal and Metal-Carbon Bond Energy Terms for the Rhodium Carbonyl Clusters Rh₄(CO)₁₂ and Rh₆(CO)₁₆. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 71–74. [CrossRef]
- 77. Chen, L.; Li, W.; Liu, P.; Zhang, K.; Ma, F.; Chen, X.; Zhou, H.; Liu, X. Microstructure and Mechanical Properties of (AlCrTiZrV)Nx High-Entropy Alloy Nitride Films by Reactive Magnetron Sputtering. *Vacuum* **2020**, *181*, 109706. [CrossRef]
- Leyland, A.; Matthews, A. On the Significance of the H/E Ratio in Wear Control: A Nanocomposite Coating Approach to Optimised Tribological Behaviour. Wear 2000, 246, 1–11. [CrossRef]
- 79. Musil, J.; Novák, P.; Čerstvý, R.; Soukup, Z. Tribological and Mechanical Properties of Nanocrystalline-TiC/a-C Nanocomposite Thin Films. J. Vac. Sci. Technol. A Vac. Surf. Film. 2010, 28, 244–249. [CrossRef]
- Pshyk, A.V.; Coy, L.E.; Yate, L.; Załęski, K.; Nowaczyk, G.; Pogrebnjak, A.D.; Jurga, S. Combined Reactive/Non-Reactive DC Magnetron Sputtering of High Temperature Composite AlN–TiB₂–TiSi₂. *Mater. Des.* 2016, 94, 230–239. [CrossRef]
- 81. Oses, C.; Toher, C.; Curtarolo, S. High-Entropy Ceramics. Nat. Rev. Mater. 2020, 5, 295–309. [CrossRef]
- 82. Mehmood, M.; Akiyama, E.; Habazaki, H.; Kawashima, A.; Asami, K.; Hashimoto, K. The Degradation of the Corrosion Resistance of Sputter-Deposited Chromium-Titanium Alloys by Nanoscale Heterogeneity. *Corros. Sci.* **1999**, *41*, 1871–1890. [CrossRef]
- Shao, T.; Ge, F.; Pei, C.; Huang, F.; Sun, D.; Zhang, S. Effects of Si Content on Tribo-Corrosion Behavior of Cr1-XSixN Coatings Prepared via Magnetron Sputtering. *Surf. Coat. Technol.* 2018, 356, 11–18. [CrossRef]
- 84. Yang, Y.; Zhang, C.; Peng, Y.; Yu, Y.; Liu, L. Effects of Crystallization on the Corrosion Resistance of Fe-Based Amorphous Coatings. *Corros. Sci.* **2012**, *59*, 10–19. [CrossRef]
- 85. Hirschorn, B.; Orazem, M.E.; Tribollet, B.; Vivier, V.; Frateur, I.; Musiani, M. Determination of Effective Capacitance and Film Thickness from Constant-Phase-Element Parameters. *Electrochim. Acta* **2010**, *55*, 6218–6227. [CrossRef]
- 86. Córdoba-Torres, P. Relationship between Constant-Phase Element (CPE) Parameters and Physical Properties of Films with a Distributed Resistivity. *Electrochim. Acta* 2017, 225, 592–604. [CrossRef]
- 87. Shi, Y.; Yang, B.; Liaw, P. Corrosion-Resistant High-Entropy Alloys: A Review. Metals 2017, 7, 43. [CrossRef]
- Cheng, K.-H.; Lai, C.-H.; Lin, S.-J.; Yeh, J.-W. Structural and Mechanical Properties of Multi-Element (AlCrMoTaTiZr)N_x Coatings by Reactive Magnetron Sputtering. *Thin Solid Films* 2011, 519, 3185–3190. [CrossRef]
- Mendizabal, L.; Bayón, R.; G-Berasategui, E.; Barriga, J.; Gonzalez, J.J. Effect of N₂ Flow Rate on the Microstructure and Electrochemical Behavior of TaN_x Films Deposited by Modulated Pulsed Power Magnetron Sputtering. *Thin Solid Films* 2016, 610, 1–9. [CrossRef]

- Cavaleiro, A.J.; Ramos, A.S.; Martins, R.M.S.; Fernandes, F.M.B.; Morgiel, J.; Baehtz, C.; Vieira, M.T. Phase Transformations in Ni/Ti Multilayers Investigated by Synchrotron Radiation-Based X-ray Diffraction. J. Alloys Compd. 2015, 646, 1165–1171. [CrossRef]
- 91. Lipowsky, P.; Hedin, N.; Bill, J.; Hoffmann, R.C.; Ahniyaz, A.; Aldinger, F.; Bergström, L. Controlling the Assembly of Nanocrystalline ZnO Films by a Transient Amorphous Phase in Solution. *J. Phys. Chem. C* 2008, 112, 5373–5383. [CrossRef]
- Vieira, M.T.; Ramos, A.S.; Castanho, J.M.; Oliveira, J.C.; Cavaleiro, A. From Ti–Al- to Ti–Al–N-Sputtered 2D Materials. J. Mater. Sci. 2007, 42, 9145–9153. [CrossRef]
- 93. Zhao, L.; Zong, H.; Ding, X.; Sun, J.; Ackland, G.J. Commensurate-Incommensurate Phase Transition of Dense Potassium Simulated by Machine-Learned Interatomic Potential. *Phys. Rev. B* 2019, 100, 220101. [CrossRef]
- 94. Tangstad, M. Phase Transformation in Quartz at Elevated Temperatures. Asp. Min. Miner. Sci. 2021, 6, 691–699. [CrossRef]
- 95. Wu, H.; Baker, I.; Liu, Y.; Wu, X. Dry Sliding Tribological Behavior of Zr-Based Bulk Metallic Glass. *Trans. Nonferrous Met. Soc. China* **2012**, *22*, 585–589. [CrossRef]
- 96. Matthews, A.; Leyland, A.; Holmberg, K.; Ronkainen, H. Design Aspects for Advanced Tribological Surface Coatings. *Surf. Coat. Technol.* **1998**, *100–101*, 1–6. [CrossRef]

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