High-temperature solar-selective coatings based on Cr(Al)N. Part 1: Microstructure and optical properties of CrN_y and Cr_{1-x}Al_xN_y films prepared by DC/HiPIMS

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Abstract

In order to explore the potentialities of Cr_{1-x}(Al)_xN_y materials in multilayer-based solar selective coatings (SSC) for high temperature applications (T>500 °C), the optical behavior of Cr_{1-x}(Al)_xN_y films is studied in this work. Two sets of layers (CrN_y and Cr_{1-x}Al_xN_y) were prepared by direct current (DC) and high-power impulse magnetron sputtering (HiPIMS) technology. The deposition parameters: N₂ flux, HiPIMS frequency and aluminum sputtering power, were modified to get a wide variety of stoichiometries. The composition, morphology, phases and electronic structure of the films were characterized in depth. The optical behavior was determined by UV-Vis-NIR and FTIR spectroscopies, and the optical constants were obtained from the measured transmittance and reflectance spectra based on appropriate dielectric function models. Our results indicate that small changes in the layer composition influence the optical constant. In particular, a metallic-like behavior was obtained for CrN_y layers with N vacancies (CrN_{0.95} and CrN_{0.67} films) while a semiconductor-like behavior was observed for CrN_{1.08}. Thus, the CrN_y films can be used as effective absorber layer in multilayer-based SSC, and namely, the CrN_{0.67} film as an IR reflector/absorber layer too. Likewise, the optical properties of Cr_{1-x}Al_xN_y layers can also be tuned from metallic to semiconductor-like behavior depending on the chemical composition. Indeed, the absorption coefficients of Cr_{1-x}Al_xN_y films with optimized Al content and N-vacancies are comparable to those reported for state-of-the-art materials such as TiAlN or TiAlCrN. In addition, a Cr_{0.96}Al_{0.04}N_{0.89} film was found to be a suitable IR reflector/absorber layer.

1. Introduction

Concentrated solar power (CSP) technology is one of the most promising candidates for mitigating the future energy crisis. The extracted power from CSP is clean, reliable and environment friendly. The CSP systems use mirrors to concentrate sunlight onto a receiver, where the light is converted to heat, which drives a heat engine to generate electricity [1]. One of the ways to improve the efficiency of the CSP is by using solar selective coatings (SSC) on the receiver or absorber. These SSC must present high values of the solar absorptance (α) in the UV-Vis region and low values of thermal emittance

(ε) in the infrared (typically $\alpha > 95\%$, $\varepsilon_{25\text{ }^\circ\text{C}} < 15\%$) and need to be chemically and structurally stable within the range of operating temperatures (preferably, up to 500 °C in vacuum for linear systems and above 800 °C in air for point focus systems); durable (ideally 25 years) and with good adhesion to the receiver or absorber tube [1-3].

In recent years, transition-metal nitrides, oxides and oxynitrides have received significant attention for being used as SSC in the mid (300-400 °C) and high-temperature (> 500 °C) applications due to their excellent mechanical, chemical, thermal and optical properties [4-6]. A change in their stoichiometry (N and/or O content) modifies the density of free electrons in the “d band” and consequently in their optical and electrical properties [6-9]. As an example, Martinez et al. [10] reported that sub-stoichiometric CrN_y films present a metallic-like character, while over-stoichiometric films of CrN_y show semiconductor behavior. Moreover, the incorporation of an additional element, such as Al, changes the bonding structure (e.g. metallic to covalent), resulting in the variation of the optical properties and electrical resistivity [7, 8, 10-13], as well as improving their mechanical properties and oxidation resistance [14]. In this context, it has been reported that materials as TiNO_x (commercially available for mid-temperature SSC [5]) and others materials as TiAlN , TiAlNO , TiAlSiN or NbAlN , display low reflectance and high absorption coefficient in the UV-Vis spectral range, making them excellent candidates to be used as components in mid-and high-temperature SSC [15-21].

In the quest of alternative materials for high-temperature SSC, the *fcc*- CrAlN system could be an interesting candidate due to its superior thermal stability (above 900 °C) and oxidation resistance [22-23]. The results exploring this route are still few and under progress. Chen et al. [24] was the first showing that CrAlN (with low Al content ≈ 4.5 at. %) had similar reflectance and absorbance characteristics to those of TiN -based films in the solar spectrum region. A recent work published by Al-Rjoub et al. [25], about SSC based on CrAlSiN and CrAlSiON , doped with different amount of silicon, showed that the higher silicon content SSC present better selectivity, high solar absorptance, $\alpha = 95.9\%$, and low emissivity, $\varepsilon = 9.7\%$ (calculated for 400 °C), and thermal stability at 600 °C in vacuum for 650 h. In other hand, similar to Ti(Al)N , it is expected that the optical properties of Cr(Al)N could be tuned by controlling the chemical composition.

However, there is very little knowledge about the influence of N vacancies on phase stability, mechanical, and optical properties of CrN_y coatings [26-29]. Concerning $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films with variable stoichiometry, and according to our knowledge, the optical properties have not been previously reported. Further studies are needed for the establishment of the correlations between chemical composition, microstructure and optical properties in these compounds. The acquired knowledge will result very useful in the design of multilayered, gradient or composite materials for solar-selective absorption with improved efficiencies. In this sense, two set of films (CrN_y and $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$) with different stoichiometries have been prepared using DC/HiPIMS technology aiming to correlate chemical composition with the structure and the optical properties. In a previous paper [30], the influence of pulse parameters on the chemical composition, mechanical and oxidation resistances properties of the CrN_y films has been deeply

studied, while in this work we focus on the structure and optical properties of the CrN_y films, as well as on an exhaustive chemical, structural and optical characterization of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films. The determination of the optical constants of $\text{Cr}_{1-x}(\text{Al}_x)\text{N}_y$ films with variable metallic contents and metal/nitrogen ratios will serve as fundamental database to develop solar selective coatings.

2. Experimental

2.1. Coating preparation

The CrN_y and $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ layers were prepared by pulsed magnetron sputtering combining DC and HiPIMS power supplies connected to aluminum (99.5% purity) and chromium (99.5% purity) targets, respectively. Different type of substrates (silicon, 316L steel and quartz) were used depending on the employed characterization technique. Prior to the deposition of the coatings, the substrates were cleaned using a sequence of ultrasonic washing with alkaline detergents, rinsing with de-ionized water, cleaning with isopropanol and air-drying. Finally, they were subjected to Ar^+ sputtering to remove the native oxide and physisorbed layers on the surface. The base pressure of the vacuum chamber was $\sim 1 \times 10^{-4}$ Pa and the working pressure set at 1 Pa. The Ar flux was maintained to 20 sccm while the N_2 flux was varied from 1 to 8 sccm. The HiPIMS sputtering conditions of the chromium target were 300 W of applied power and 200 or 1000 Hz of pulse frequency. The corresponding pulse lengths were selected in order to keep constant the duty cycle at 2%. For aluminum target, DC pulses (frequency of 250 kHz and 88% of duty cycle) were applied at sputtering powers ranging from 20 to 150 W in order to change the Al concentration inside the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films. The samples are named following the measured stoichiometry.

2.2. Morphology, microstructure and chemical composition

Chemical composition of the samples was obtained by electron probe microanalysis (EPMA). The equipment was a JEOL JXA-8200 SuperProbe instrument equipped with four wavelengths detectors (WDS) and one energy-dispersive X-ray (X-EDS). Three measurements were carried out at 15 kV ($I=20$ nA) on different positions separated >500 μm with a spot size of 20 μm . With these conditions, the probe depth is about several microns depending on the excited element. Non-Rutherford backscattering (non-RBS) measurements were used to determine the N content more precisely and to verify the chemical composition of some of the coatings. Measurements were performed at the "Centro Nacional de Aceleradores" (CNA) [31] using an alpha particle beam at the energy of 3.7 MeV and a passivated implanted planar silicon detector positioned at a laboratory angle of 165° . At this energy the $\text{N}(\text{He},\text{He})\text{N}$ cross section presents a broad resonance that increases the sensitivity of the technique for the N detection. The obtained elemental compositions were quite similar to those obtained by EPMA, and both values will be indistinctly considered. The oxygen contamination was determined by EPMA.

The X-ray diffraction (XRD) patterns of the coatings deposited on 316L steel were obtained in an X'Pert Pro PANALYTICAL diffractometer and measured in grazing incidence at 1° , using Cu K_α radiation. The average crystal size was estimated using the position of the (111) peak and the Scherrer equation. The morphology and thickness of the as-prepared coating were observed by scanning electron microscopy (SEM). Cross-section views were obtained cleaving the coatings deposited on silicon substrates with a diamond tip and posterior examination with a high resolution field emission gun (FEG) microscope, HITACHI-S4800, equipped with and X-EDS detector (Bruker, XFlash-4010).

For the transmission electron microscopy (TEM) characterization of the as-prepared coatings deposited on silicon substrates, cross-sections were prepared following the conventional procedure of mechanical polishing followed by argon ion milling to electron transparency. To get microstructural and chemical information, two Jeol TEM microscopes were used: a 2100Plus and a JEM3000F, with an embedded ENFINA spectrometer (from GATAN) to get the electron energy-loss spectroscopy (EELS). The EELS spectra were recorded in TEM mode with a spectrometer collection angle of 9 mrad. Under these conditions, the energy resolution of the microscope/spectrometer system was ~ 1.2 eV. The N-K and Cr-L_{2,3} edges were measured separately. In order to compare the spectra, the N-K edges have been aligned to 395 eV, after background removal and normalization to the continuum after the edge. To obtain the area under the L₃ and L₂ white lines, the area under the L_{2,3} edges was removed and the spectra integrated using the same energy window.

The film stress was estimated by measuring the curvature on coatings deposited over silicon substrates using a profilometer and the Stoney's equation.

2.3. Optical properties

An UV-Vis-NIR Cary 5000 equipped with two accessories: universal measurement accessory (UMA) and integrating sphere were employed to measure specular and total reflectance, ballistic and total transmittance in the UV-Vis-NIR spectral range, i.e. from 250 nm to 2500 nm.

Measurements of the reflectance in the IR range were carried out with a Fourier transform infrared (FTIR) spectrometer Bruker Vertex 70. It is equipped with a DLaTGS detector and KBr beam splitter. The measurement range was 400 cm^{-1} to 4000 cm^{-1} ($2.5 - 25\text{ }\mu\text{m}$), and the resolution was 0.4 cm^{-1} . A specular "W-type" accessory is employed to measure IR-reflectance employing a gold-coated glass as reference.

The determination of the complex refractive index ($n-ik$) is based on the analysis of the light reflected and transmitted by the samples at three different incident angles (6° , 30° and 50°) for s- and p-polarized incident light. We use a generic algorithm to fit simultaneously the angular dependence of reflectance and transmittance spectra for both polarizations and a code based on the transfer matrix method to calculate the optical response of the films considering they are supported on a 1 mm-thick quartz substrate and air as the incoming and outgoing media for light, respectively. To account for the spectral dependence of the complex refractive index of semiconductor-like films

we use a Forouhi-Bloomer model in the new amorphous parametrization [32], whereas a Drude model is employed for those featuring a metal-like character [33].

3. Results and discussion

3.1. CrN_y films: structural and chemical characterization

A set of CrN_y films with different stoichiometries (from $y=0.67$ to 1.08) was prepared by HiPIMS changing the pulse characteristics and nitrogen fluxes. The synthesis parameters, film characterization (morphology, microstructure and chemical composition) and mechanical and oxidation resistance properties can be found elsewhere [30]. In this section, the structural and optical behavior of three selected coatings ($\text{CrN}_{1.08}$, $\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$) are presented. These stoichiometries correspond to samples D, A and C, respectively, in [30]. The films exhibited different crystalline composition and columnar morphology as can be seen in Fig. 4 and 6 from [30]. The *fcc*-CrN phase is found by XRD in all cases with a significant shift towards higher angles as the nitrogen content decreased. The deficiency of N atoms in *fcc*-CrN leads to a distorted lattice, where the Cr-Cr atoms become closer, causing a reduction in the lattice parameter. In the particular case of $\text{CrN}_{0.67}$ sample (cf. Fig. 4 in [30]), a secondary phase-hexagonal Cr_2N is formed in addition to stoichiometric *fcc*-CrN and sub-stoichiometric CrN_y phases. It has been reported previously that low nitrogen flow can result in the formation of *hcp*- Cr_2N [28, 34].

The presence of N vacancies affects the chemical bonding and induces changes in the electronic structure of the CrN coatings that can be revealed by electron energy-loss spectroscopy (EELS). The energy-loss near edge fine structure of the EELS spectra (ELNES) arises from the energy distribution of the unoccupied electronic states above the Fermi level. These being the final states of the electronic transition from the particular inner electron shell that is being ionized and can be used to extract structural and electronic information regarding phases, local charge distributions, coordination and binding characteristics from nanometric areas of a sample [35]. One approach to understand the ELNES features consists of the comparison of the spectra with those of similar compounds or environments and try to identify common features [36-39]. Fig. 1(a) depicts the near-edge fine structure of the N-K edge measured for our CrN_y films and for CrN and Cr_2N references (obtained from [38]). The N-K edge of *fcc*-CrN and *hcp*- Cr_2N phases show characteristic signatures (see inset of Fig. 1) that are explained in the work reported by Mitterbauer et al. [38]. The cubic CrN phase presents two peaks (A and B) with similar intensity and a broad peak at around 430 eV (C), while the hexagonal Cr_2N phase exhibits only one sharp peak (A) and a broad shoulder (C'). In our films, the spectrum of $\text{CrN}_{1.08}$ is similar to CrN, but when the N content decreases in the films ($\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$), the intensity of these peaks and their relative intensity change. The I_A/I_B ratios are included in Table 1 for a clearer comparison. Similar or comparable changes have been observed for CrN_x , [9], TiN_x [39] and VN_x , [40]. The peak A corresponds to the electronic transitions to unoccupied N 2p hybridized to Cr 3d states

[38], so a variation of its intensity would be expected when a change in the “formal oxidation state” occurs. On the other hand, a decrease in intensity of the B and C peaks is expected to occur when nitrogen is removed, because these peaks have their origin in inter- and intra-shell scattering from the first non-metal coordination shell respectively [40].

The $L_{2,3}$ edges of the transition metals include sharp and intense peaks known as “white lines” due to transitions of $2p_{1/2}$ (L_3) or $2p_{2/3}$ (L_2) core electron to the lowest state of the conduction band. Their energy position and intensities, as well as the L_3/L_2 ratio can offer insights about the valence state, formation of alloys, moment magnetic, etc. [41]. In the case of the CrN, the conduction band is mainly formed from Cr 3d and N 2p orbitals and slight differences appear in the $L_{2,3}$ spectra depending on CrN phase and stoichiometry. In the Fig. 1(b), the Cr- $L_{2,3}$ edges, normalized to the continuum after the edges, are plotted. The spectra from CrN and Cr₂N references are shown as insets and were obtained from [38]. The Cr- $L_{2,3}$ edges measured for our films manifest a chemical shift to lower energy positions and an increased L_2 intensity with respect to L_3 , with the decrease of the N content, as previously observed by Zhang et al. [9]. The chemical shift indicates a decrease in the chromium formal oxidation state, increased filling of the d band (i.e. fewer empty d states), which produces the decrease of the intensities of the $L_{2,3}$ edges and lower (L_3+L_2) and L_3/L_2 values, according to a more metallic character [37]. In Table 1, the values of (L_3+L_2) and L_3/L_2 are shown. A decrease in the L_3/L_2 ratio is observed when the N vacancies increase, indicating a lower ionicity of chromium and a change in the bonding character [9]. These results revealed a more metallic character in the defective CrN (substoichiometric CrN_y layers) as compared to the CrN reference film. The higher the N vacancy density, the more metallic character of the film.

Fig. 1. EELS spectra of the CrN_y films and CrN and Cr₂N references (as insets): (a) N-Kedge, and (b) Cr- $L_{2,3}$ edges.

Table 1. I_A/I_B (see the text) and L_3+L_2 , L_3/L_2 values obtained from the EELS spectra of the CrN_y films and from CrN and Cr_2N references [38]. The difference observed in L_3+L_2 (sum normalized to the continuum) and L_3/L_2 between CrN reference and $\text{CrN}_{1.08}$ can be explained considering the presence of some oxygen in the CrN reference [37]).

	CrN	$\text{CrN}_{1.08}$	$\text{CrN}_{0.95}$	$\text{CrN}_{0.67}$	Cr_2N
I_A/I_B	1.01 ± 0.01	0.99 ± 0.01	1.06 ± 0.01	1.46 ± 0.05	–
L_3+L_2	1.50 ± 0.01	1.39 ± 0.08	1.37 ± 0.09	1.21 ± 0.07	0.79 ± 0.02
L_3/L_2	1.61 ± 0.01	1.56 ± 0.03	1.54 ± 0.04	1.49 ± 0.05	1.47 ± 0.03

As a summary, the comparison of the EELS spectra of our films with CrN and Cr_2N references indicates that $\text{CrN}_{1.08}$ has a similar electronic structure than the cubic CrN phase with an ionic bonding, while a more metallic character is observed for $\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$. The spectra of $\text{CrN}_{0.67}$ resemble to Cr_2N , but taking into account the XRD results and the differences observed in the EELS spectra, it can be concluded that this film is formed by a mixture of phases: *fcc*-CrN (with and without N vacancies) and *hcp*- Cr_2N .

3.2. CrN_y films: Optical characterization

Fig. 2(a) and (b) show the reflectance spectra of the CrN_y layers as a function of the incident photon wavelength within the UV-Vis-NIR (250 - 2500 nm) and IR range (2500 - 25000 nm), respectively. It is clearly observed that $\text{CrN}_{1.08}$ shows the lowest fraction of reflected incident light throughout the UV-Vis-IR range. The optical response of this material features interference fringes above 1500 nm, which indicates a semi-transparent semiconducting behavior above this wavelength. The $\text{CrN}_{0.67}$ film exhibits the highest reflectance, with no oscillations in the spectra, indicating a metallic nature throughout the energy range under analysis. Finally, the optical behavior of $\text{CrN}_{0.95}$ is similar to $\text{CrN}_{0.67}$.

The optical properties of the films are dictated by their optical constants, i.e. their complex refractive index, which can be extracted from the transmittance and reflectance measurements using appropriate dielectric function models (semiconductor for $\text{CrN}_{1.08}$ and Drude for $\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$ films). Fig. 3(a) and (b) display the wavelength dependence of the complex refractive index, obtained from the fitting of the experimental data as discussed in the experimental section. For $\text{CrN}_{1.08}$, the n value increases continuously from $n=2.16$ at 350 nm to a maximum of 3.38 at ≈ 1800 nm, reaching a steady-state. The extinction coefficient “ k ” increases from 0.85 at 350 nm to 1.27 at 1100 nm, and then decreases with the wavelength until 0.54, characteristic of a semiconductor behavior [18, 26]. The optical constants match with the trend reported in the literature for a CrN reference [26], although smaller values of n and k are obtained in the whole energy range. This means that our $\text{CrN}_{1.08}$ film is optically less dense as

compared to the mentioned reference. A metallic-like behavior is observed for $\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$ with n and k values increasing with λ for all measured range (n varies from 0.9 to 1.5 for $\text{CrN}_{0.95}$ and from 1.6 to 2.6 for $\text{CrN}_{0.67}$) and $k > n$ (from 1.0 to 1.7 for $\text{CrN}_{0.95}$ and from 1.8 to 2.8 for $\text{CrN}_{0.67}$). It is clear that even small changes in the layer composition ($\text{CrN}_{1.08}$ vs. $\text{CrN}_{0.95}$) influence its optical constants. The presence of N vacancies in CrN_y increases the k value, and changes the behavior of the films from semiconductor to metallic-like as previously reported [9]. The optical behavior of $\text{CrN}_{0.67}$ is comparable to Cr_2N [26-27, 42], although smaller values of n and k are obtained, which can be attributed to the co-existence of *fcc*-CrN phase and the low crystallinity of both phases (CrN_y and Cr_2N). A decrease of the electrical resistivity (more metallic character) has been reported when metallic Cr_2N nanoinclusions are added to a CrN matrix [28]. The absorption coefficient α' calculated for the three films according to the expression $\alpha' = 4\pi k / \lambda$ is depicted in Fig. 3(c). A decrease with λ is observed for the three coatings, with the highest values for the $\text{CrN}_{0.67}$ film. Table 2 summarizes the values of n , k and α' at 550 nm for the three films. The obtained α' values are as good as the reported for TiAlN and TiAlCrN [5] suggesting that the three films could be used as absorber layers in multilayer-based SSC. Notice that $\text{CrN}_{0.67}$ film could also be used as IR reflector/absorber layers due to its high reflectance in the IR energy range (2.5 μm to 25 μm).

These results and those published previously [30], demonstrate that the presence of N vacancies in *fcc*-CrN leads to a microstructure modification (SEM observation), grain refinement (XRD data), lattice contraction (XRD data) and generation of additional phases: Cr_2N (XRD+EELS), alteration of the electronic structure and bonding states (EELS). All these structural factors influence significantly the absorption and scattering of the incident light and therefore, the overall optical properties of the CrN_y films, moving from a semiconductor ($y=1.08$) to a metallic-like behavior ($y=0.95$ and $y=0.67$) in the whole energy range (250 - 25000 nm).

Fig. 2. Reflectance spectra of CrN_y films: (a) UV-Vis-NIR energy range, and (b) IR energy range.

Fig. 3. (a) Refractive index n , (b) extinction coefficient k and (c) absorption coefficient α of the CrN_y films in the wavelength range of 350 nm to 2500 nm.

Table 2. Optical properties: refractive index n , extinction coefficient k , and absorption coefficient α' , obtained at $\lambda = 550$ nm for the CrN_y films

	n (550 nm)	k (550 nm)	$\alpha' \times 10^6 \text{ m}^{-1}$ (550 nm)
$\text{CrN}_{1.08}$	2.2	1.0	22
$\text{CrN}_{0.95}$	1.0	1.1	26
$\text{CrN}_{0.67}$	1.7	1.9	45

3.3. $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films: microstructural characterization

Table 3 shows the synthesis parameters, the chemical composition, the stoichiometry and the crystal size (obtained by XRD) of the deposited $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films. The oxygen contamination, measured by EPMA, is below 5 at.%. The Al content is influenced by the Al sputtering power and the N_2 flow. The appropriate selection of both parameters enabled the preparation of $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ layers with different stoichiometry (“ x ” from 0.47 to 0.04 and “ y ” from 0.89 to 1.13).

Table 3. Experimental conditions used to deposit the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ layers (Cr and Al sputtering power and N_2 flow), thickness, chemical composition and stoichiometry obtained by RBS, and crystal size obtained by XRD.

		Cr Power W	Al Power W	Power ratio	N_2 flow sccm	Thickness nm	N at. %	Al at. %	Cr at. %	Crystal size nm
$\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ ($y \geq 1$)	$\text{Cr}_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$	300	150	2	8	550	53 ± 4	25 ± 2	22 ± 2	52 ± 16
	$\text{Cr}_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$	300	75	4	3	340	50 ± 4	19 ± 2	31 ± 2	54 ± 20
	$\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$	300	50	6	8	350	53 ± 4	11 ± 1	36 ± 2	38 ± 13
	$\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$	300	20	15	2	272	52 ± 4	2 ± 1	46 ± 2	42 ± 11
$\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ ($y < 1$)	$\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$	300	50	6	1	450	48 ± 4	19 ± 2	33 ± 2	53 ± 22
	$\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$	300	20	15	1	110	47 ± 4	2 ± 1	51 ± 3	17 ± 3

The microcrystalline structure of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films deposited on 316L steel substrates was studied by grazing angle XRD (cf. Fig. 4). The corresponding diffractograms are consistent with a carlsbergite cubic structure (*fcc*-Cr(Al)N) but the peak positions appear to shift randomly. The analysis of the peak-shift is not straightforward as the result of the sum of different factors. If we consider negligible the effect of the film stress (very low values were measured, <1 GPa), a right-shift is observed when the Al content and/or N vacancies increase as a consequence of a lower lattice parameter. Conversely, the over-stoichiometric films ($y>1$) exhibit left-shift due to a lattice expansion. These films may have metallic vacancies and/or different Cr valences (from +III to +IV), necessary to conserve the charge neutrality of the material. The change in the Cr formal oxidation state will be analyzed later when EELS results will be presented. The largest right-shifts are observed for the $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ films. The counterbalance caused by the nitrogen incorporation can be observed by comparing them with $\text{Cr}_{0.63}\text{Al}_{0.38}\text{N}_{1.00}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$, respectively. In the remaining two samples, $\text{Cr}_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$ and $\text{Cr}_{0.76}\text{Al}_{0.23}\text{N}_{1.13}$, the influence of both factors is balanced and the position match better with the theoretical values of *fcc*-CrN (carlsbergite). The average crystal sizes, obtained from the Scherrer's equation using the (111) reflection, can be seen in Table 3. They ranged from 40 nm to 60 nm except for the film with the lowest x and y values ($\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$), whose higher concentration of nitrogen vacancies and lattice defects led to a significant diminution of crystal size. The films with higher Al content ($x>0.3$) exhibit higher crystal sizes (~55 nm).

Fig. 4. XRD diffractograms of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films measured in glancing angle configuration (1°).

The cross-section SEM images of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films (Fig. 5) reveal a columnar growth morphology, with column widths that increase with the Al content (from 20-30 nm for $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ to ~80 nm for $\text{Cr}_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$). The surfaces present a pyramidal morphology with feature size increasing with the aluminum content. The coatings with the same aluminum amount but lower N content (lower N flux) present wider columns.

Fig. 5. SEM cross-section and top views of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films under study.

In order to study the effect of the Al content and the presence of N vacancies in the electronic structure of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ layers, representative coatings with different Al and N contents ($\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$, $\text{Cr}_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$ and $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$) have been studied by EELS. The N-K and Cr-L_{2,3} edges are depicted in Fig. 6(a) and (b), respectively. Clear

changes are observed in the fine structure of the N-K edge in comparison to CrN_y films (cf. Fig. 1). A decrease of the A peak intensity and the I_A/I_B ratio (summarized in Table 4) are observed when aluminum is incorporated into the *fcc*-CrN lattice, as previously reported [39, 42-43]. This is a predictable trend due to the change from a transition metal (chromium) to a p-block element (aluminum). In addition, a slight increase of the I_A/I_B ratio due to a diminution of B intensity is observed when the N content decreases for similar Al contents (Cr_{0.62}Al_{0.38}N_{1.00} vs. Cr_{0.63}Al_{0.37}N_{0.92}), as we showed previously for CrN films. In the Cr-L_{2,3} spectra, (see Fig. 6b) a slight chemical shift to a lower energy position is observed for Cr_{0.63}Al_{0.37}N_{0.92} in comparison with Cr_{0.62}Al_{0.38}N_{1.00}. This corresponds to a lower chromium oxidation state, increased filling of the d band (i.e. fewer empty d states) and decreased L_2+L_3 and L_3/L_2 values (see Table 4), in agreement with a more metallic character [37]. In Table 4, as expected, it is also observed that the L_3+L_2 and L_3/L_2 values decrease with the Al content. All these changes observed in the electronic structure will have an effect on their optical properties.

Fig. 6. EELS spectra of the Cr_{1-x}Al_xN_y films: (a) N-K edge, and (b) Cr-L_{2,3} edges.

Table 4. I_A/I_B (see the text) and L_3+L_2 , L_3/L_2 values obtained from the EELS spectra of a selection of the Cr_{1-x}Al_xN_y layers.

	CrN	Cr _{0.77} Al _{0.23} N _{1.13}	Cr _{0.62} Al _{0.38} N _{1.00}	Cr _{0.63} Al _{0.37} N _{0.92}
I_A/I_B	1.01 ± 0.01	0.80 ± 0.02	0.65 ± 0.01	0.72 ± 0.02
L_3+L_2	1.50 ± 0.03	1.24 ± 0.06	1.20 ± 0.09	1.12 ± 0.07
L_3/L_2	1.61 ± 0.01	1.60 ± 0.04	1.58 ± 0.03	1.56 ± 0.02

3.4. $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films: optical properties

Fig. 7 shows the optical reflectance spectra of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ layers as a function of the wavelength within the UV-Vis-NIR (250 - 2500 nm) and IR range (2500 - 25000 nm). Two different behaviors are observed in the UV-Vis-NIR range: $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$, $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ show reflectivity curves characteristic of metallic-like materials, while $\text{Cr}_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$, $\text{Cr}_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$ and $\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$ show a non-metallic behavior above 600, 780 and 860 nm respectively. This change is noticed in the spectra as a periodic variation of the intensity, typical of semi-transparent semiconducting or dielectric materials. In the IR range, the sample $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ shows a metallic-like behavior throughout the spectral interval under analysis with high reflectivity, while the rest of layers present a semi-transparent semiconducting or dielectric behavior with oscillations in almost all range.

Fig. 7. Reflectance spectra of $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films: (a) UV-Vis-NIR energy range, and (b) IR energy range.

Fig. 8 depicts the wavelength dependence of the optical constants (n and k) obtained adjusting the experimental reflectance and transmitted spectra measured in the UV-Vis-NIR range using a semiconductor model, as discussed in the experimental section. It is worth mentioning that although the response of $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ coatings could be also fitted using a Drude model, a better agreement is found when a semiconductor model is employed. Likewise, two groups of samples with different optical behaviors are observed. 1) Semi-transparent coatings: $\text{Cr}_{0.53}\text{Al}_{0.47}\text{N}_{1.12}$, $\text{Cr}_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$ and $\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$ with n values almost constant throughout the spectral range considered, along with low values of the extinction coefficient that decrease slightly with λ . In particular, the response of the $\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$ layer presents an absorption band centered around 900 nm. This particular feature can be attributed to a defective CrN lattice with metal vacancies, as XRD analysis demonstrated. 2) Metallic-like coatings: $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$, $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$, feature highest k values and both n and k increase with λ for the complete UV-Vis-NIR range.

The n and k values obtained at 550 nm (see Table 5) for all the films analyzed are in the range of the reported ones for different hard nitride films: $n=1.83$ for TiN, 3.5 for CrN,

2.7 for TiAlN (measured at 620 nm); $k=2.6$ for TiAlN, 1.5 for TiAlCrN [5]. The absorption coefficient α' as a function of the wavelength is depicted in Fig. 9(a) and shows a decrease with λ for all the films. The α' values at 550 nm are plotted as a function of the aluminum content (x) in Fig. 9(b). The value of “ y ” (N content) is also given in the plot to be considered. Generally, the α' values decrease with the Al content, but a remarkable increase is observed for very low Al contents ($x=0.04$) and/or N contents below the stoichiometric value ($y<1$). Table 5 also summarizes the α' values at 550 nm for the films. The highest absorption coefficients are obtained for the films with the lower Al content ($x=0.04$) for both $y=1.08$ and 0.89 respectively. The values of the $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$, $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ films are in the range of reported for TiAlN and TiAlCrN [5], indicating its potential use as absorber layer in multilayer-based SSC. The $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ film, due to its high reflectance in the IR range (2500 to 25000 nm) could also be used as IR reflector/absorber layer.

Fig. 8. (a) Refractive index n and (b) extinction coefficient k of the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films.

Fig. 9. (a) Experimental calculated absorption coefficient (α') for the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films. (b) α' obtained at $\lambda = 550$ nm as a function of Al content (x) for the $\text{Cr}_{1-x}\text{Al}_x\text{N}_{y\geq 1}$ films.

Table 5. Optical properties: Refractive index n , extinction coefficient k , and absorption coefficient α' , obtained at $\lambda = 550$ nm for the $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films.

		n (550 nm)	k (550 nm)	α' ($\times 10^6 \text{m}^{-1}$) (550 nm)
$\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ ($y \geq 1$)	$\text{Cr}_{0.43}\text{Al}_{0.47}\text{N}_{1.12}$	2.4	0.23	5.6
	$\text{Cr}_{0.62}\text{Al}_{0.38}\text{N}_{1.00}$	3.2	0.55	12.7
	$\text{Cr}_{0.77}\text{Al}_{0.23}\text{N}_{1.13}$	3.2	0.49	11.3
	$\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$	2.8	1.75	40.4
$\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ ($y < 1$)	$\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$	1.7	1.29	29.9
	$\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$	3.1	1.53	35.1

4. Summary and conclusions

CrN_y and $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films have been prepared by magnetron sputtering combining HiPIMS and DC-pulsed sources. The appropriate selection of deposition conditions and Al sputtering power determined the presence of metal and nitrogen vacancies, modifying the morphology, crystallinity, electronic structure and optical properties. Both types developed a typical columnar growth with a predominant *fcc*-CrN structure whose lattice parameter changed depending on the film composition and stoichiometry. The formation of an additional hexagonal Cr_2N phase is observed for the lowest nitrogen content ($\text{CrN}_{0.67}$).

For the CrN_y films the electronic and optical properties varied accordingly, moving from a semiconductor ($\text{CrN}_{1.08}$) to a metallic-like behavior ($\text{CrN}_{0.95}$ and $\text{CrN}_{0.67}$) in whole UV-Vis-IR energy range. These films with high values of extinction (k) and absorption (α') coefficients could be used as absorber layer in multilayer-based solar selective coatings. The metallic $\text{CrN}_{0.67}$ film could also be used as IR reflector/absorber layer in SSC due to its high reflectance in the IR range.

The deposited $\text{Cr}_{1-x}\text{Al}_x\text{N}_y$ films (with $0.2 < x < 0.5$ and $y \approx 1$), present a semi-transparent semiconducting behavior in UV-Vis-NIR energy range, with small k values, while the layer with lower Al content ($x=0.04$) presents a metallic-like character. The presence of N vacancies ($y < 1$) also modify the optical properties from semiconductor to metallic-like behavior. The low Al-doped CrAlN samples ($\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{1.08}$ and $\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$) and the $\text{Cr}_{0.63}\text{Al}_{0.37}\text{N}_{0.92}$ demonstrated high absorption coefficients (at 550 nm) and good photon absorption capability in all UV-Vis-NIR energy range, and could be used as absorber components in multilayer-based high-temperature solar selective coatings. The film

$\text{Cr}_{0.96}\text{Al}_{0.04}\text{N}_{0.89}$ also evidenced a metallic-like character in the IR energy range, probing to be also suitable as IR reflector layer.

In this work it is demonstrated that DC/HiPIMS technology allows tailoring the chemical composition of Cr(Al)N films along with their electronic and optical properties. Varying the film stoichiometry $\text{Cr}_{1-x}(\text{Al})_x\text{N}_y$, the optical parameters can be tuned from semiconductor to metallic-like behavior. This detailed study allows the selection of the adequate preparation conditions to deposit multilayered stacks with absorption selective properties. Two solar-selective coating stacks based on these Cr(Al)N films with high absorptance ($\alpha > 95\%$) and low emissivity ($\varepsilon < 15\%$) values are presented in the companion paper (Part 2) [44].

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