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COMPARATIVE INVESTIGATION OF CrN, CrCN AND CrSiCN COATINGS PREPARED BY MAGNETRON SPUTTERING

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CrN, CrCN and CrSiCN coatings were prepared by magnetron sputtering on Si and C45 steel substrates. The coatings were investigated for elemental and phase composition, surface morphology, mechanical properties and friction behaviour.

The X-ray diffractograms showed the formation of the hexagonal β-Cr_2N phase for the CrN coating and a mixture of fcc CrC and hexagonal Cr_2C phases for CrCN and CrSiCN. The research carried out demonstrated the superiority of the Cr-based complex systems (CrCN, CrSiCN) compared to the CrN coating in terms of hardness and friction performance, demonstrating the beneficial effects of C and Si presence in the film composition.

Keywords: CrN, CrCN and CrSiCN coatings, magnetron sputtering, structure, mechanical properties, friction

1. Introduction

Transition metal nitrides are widely used for protecting materials against wear, abrasion and corrosion, being successfully used in many applications to enhance the service life of a large variety of tools, mechanical components and devices [1], [2]. Among them, TiN coating is the best known and extensively used in industrial applications, being, besides its excellent qualities, cheaper and easier to be prepared. Compared to titanium nitride, chromium nitride exhibits superior fracture toughness and ductility, lower friction coefficient, higher hardness and corrosion resistance, and represents a potential candidate for TiN replacement in applications such as die casting tools and cutting tools for machining Al alloys or wood [3]-[14]. The subsequent development of binary CrN coatings focused on CrCN ternary coatings [15] and, more recently, on complex systems in which

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certain amounts of various metals (Ti, Zr, Ag) or non-metals (B, Si) were taken into account as additions to CrN to produce complex ternary (CrTiN [12], CrZrN [16], CrAgN [17], CrAlN [18]), quaternary (CrSiCN [19],[20]) or even quinternary (AlCrTiSiN [21]) structures. Over the last decade, this method of alloying simple binary compounds with different elements proved to be an effective approach to modify their composition, microstructure and morphology, with beneficial effects on film proprieties (for a recent review on binary carbides with alloying elements see Ref. [22]). Both CrN and multicomponent Cr based coatings were prepared so far by different PVD methods: magnetron sputtering (MS) [6], [14] or cathodic arc evaporation (CAE) [3], [4], [15] techniques.

The goal of the present work was to comparatively investigate Cr based hard coatings of different complexities (CrN, CrCN, CrSiCN). The constituent elements of the multicomponent Cr based coatings were chosen taking into account the existing studies which demonstrated that transition metals carbonitrides are superior to their corresponding nitrides in terms of hardness and tribological performance [1], while Si incorporation usually results in film amorphization and hardness enhancement [23].

2. Experimental procedure

2.1. Deposition method

The main deposition conditions for preparing CrN, CrCN and CrSiCN coatings by magnetron sputtering are given below.

Preliminary experiments were conducted to select the conditions for obtaining coatings with maximum hardness values and thicknesses of 3.2-3.5 µm. The CrN, CrCN and CrSiCN coatings were deposited on Si (100) wafers (20 x 20 mm) and polished (Ra =0.08 µm) C45 steel disc (25 mm in diameter), depending on the investigation carried out (R_a roughness of 0.08 µm) substrates, depending on the investigation carried out: Si for energy dispersive X-ray spectroscopy (EDS) and hardness measurements, while C45 for X-ray diffraction (XRD) analysis, surface topography examination, adhesion and friction tests. Uncoated C45 steel and CrN coatings were taken as reference.

The coatings were deposited by using an AJA ATC ORION system equipped with Cr and Si cathodes of 5 cm in diameter in a reactive gas mixture of CH_4, N_2 and Ar, at a total pressure of 0.67 Pa. The substrates (Si and C45 steel) were ultrasonically cleaned for 10 min in isopropanol. The base pressure in the deposition system was of 6×10^{-5} Pa. Prior to deposition, the samples, placed on a rotating holder (30 rpm) to ensure homogeneous compositions of the films, were sputter cleaned by applying a substrate bias of -1000 V for 5 min in an Ar atmosphere at 0.7 Pa. RF powers of 200 and 180 W were applied to Cr and Si cathode, respectively. The main deposition parameters are listed in Table 1. The substrate holder, of 7 cm in diameter, was positioned at 17 cm above the magnetron targets.

Table 1

Deposition parameters: N_2, CH_4 and Ar mass flow rates (F_R (N_2), F_R(CH_4) and F_R (Ar)), power applied to cathodes (P), substrate bias voltage (V_s), substrate temperature (T_s), deposition duration (t)

Coatings	F_R (N_2) (sccm)	F_R(CH_4) (sccm)	F_R (Ar) (sccm)	P (W) Cr cathode	P (W) Si cathode	V_s (V)	T_s (^0C)	t (min)
CrN	4	-	6	200	-	-60	300	140
CrCN	1	3	6	200	-	-60	300	180
CrSiCN	1	3	6	200	180	-60	300	110

2.2 Investigation methods

Elemental compositions of the coatings were obtained by energy-dispersive X-ray spectroscopy (EDS) using a scanning electron microscope (Table Top 3030PLUS-Hitachi) fitted with an EDS spectrometer. Phase composition, crystalline structure, texture and crystallite sizes were investigated by X-ray diffraction by means of Rigaku Miniflex II diffractometer operating in Bragg-Brentano configuration, with CuK_α radiation.

Surface morphology was examined using the scanning electron microscope mentioned above and a Dektak 150 surface profilometer. Film thickness and roughness were measured using the Dektak profilometer. Hardness measurements were conducted by using a Vickers microhardness tester (0.05 N load). Film adhesion on the C45 steel substrate was determined by the scratch test method, according to the EN 1071-3:2005 standard. The critical load (L_c) was determined by optical microscope analysis of the scratch scars.

Friction performance of the coating in dry atmosphere (22^0 C, 60% relative humidity) was evaluated by using a CSM ball-on-disc tribometer (sapphire ball of 6 mm in diameter, 0.15 m/s sliding velocity, 10 mm track diameter, 250 m sliding distance, 5 N load).

3. Results and discussions

3.1 Elemental composition

The atomic concentrations of the elements for the coatings deposited by MS method, as derived from the EDS analysis, are summarized in Table 2 ((C+N)/ (Cr+Si) and C/N ratios are also given). It should be noted that the non-metal/metal ratios were of 0.5-0.9, while C/N values for the carbonitride coatings were in the range from 2.7 to 3.2. This last finding is of particular interest and can partially explain the low friction behavior of the carbonitride coatings.

Table 2

Compositions of the magnetron sputtering deposited CrN, CrCN and CrSiCN coatings

Coatings	Elemental composition (at. %)				(C+N)/ (Cr+Si)	C/N
	Cr	Si	C	N		
CrN	64.7	-	-	35.3	0.5	0
CrCN	50.3	-	37.8	11.9	0.9	3.2
CrSiCN	51.1	3.5	33.1	12.3	0.8	2.7

3.2 X-ray structural analysis

The X-ray diffraction patterns of the CrN, CrCN and CrSiCN coatings are shown in Fig. 1.

The diffractogram for the CrN coating shows the formation of the β-Cr_2N phase (hexagonal structure), being detected the (110), (002), (200), (300) and (220) reflections, whose positions are close to those given in ICSD00-035-0803. It is to be noted that the coating has a (300) texture. A different situation can be observed for the CrCN and CrSiCN coatings. Both coatings, with similar diffraction patterns, exhibit a low degree of crystallinity, approaching amorphous. Only two broad and low intensity peaks are visible in each diffractogram and therefore the exact nature of the phases formed is more difficult to evaluate. The XRD data were refined by peak deconvolution using pseudo-Voigt functions (Fig.2), allowing a more detailed examination of the XRD patterns. A tentatively peak assignment was conducted as follows. The calculated peaks located at 37.6°, 44.6°, and 78.2° (for CrCN) and at 38.8°, 44.6° and 78.5° (for CrSiCN) can be assigned to CrC compound, with face-centered cubic (fcc) structure (ICSD 04-004-4288). The peaks at 42.9° (CrCN) and 43.5° (CrSiCN) might be attributed to hexagonal Cr_2C phase (ICSD 00-014-0519), for which the (101) peak situated at $2\theta=42.7^\circ$ is the most intense one. Peak assignment to Cr carbides was justified by the fact that carbon contents in the investigated coatings are significantly higher than nitrogen ones (Table 1). The shifts of the peak positions from those given in the quoted ISCDs are probably caused by both the presence of nitrogen in the carbon sub-lattice and the stress level in the coatings. It is interesting to notice that previous studies on Cr based hard coatings revealed the formation of different phases and structures, depending on the deposition method and working parameters: CrN (fcc) [24], Cr (hexagonal) and Cr_2N (hexagonal) [14], [12], Cr_2N and CrN [13] in CrN coatings, Cr_7C_3 (fcc) and $Cr_{23}C_6$ (hexagonal) [25] in CrCN coatings and CrN [19], [20] in CrSiCN coatings.

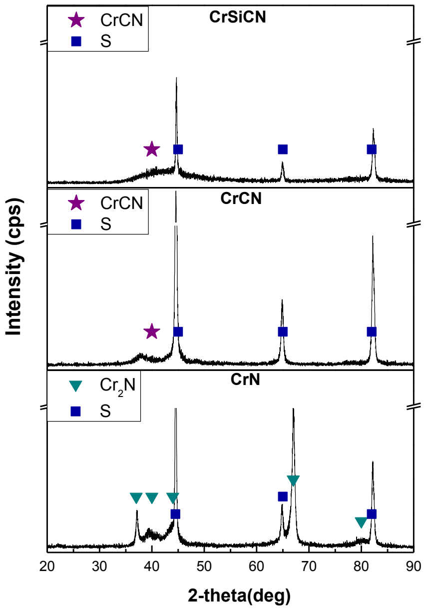


Fig.1. X-ray diffraction patterns of CrN, CrCN and CrSiCN coatings (S-substrate)

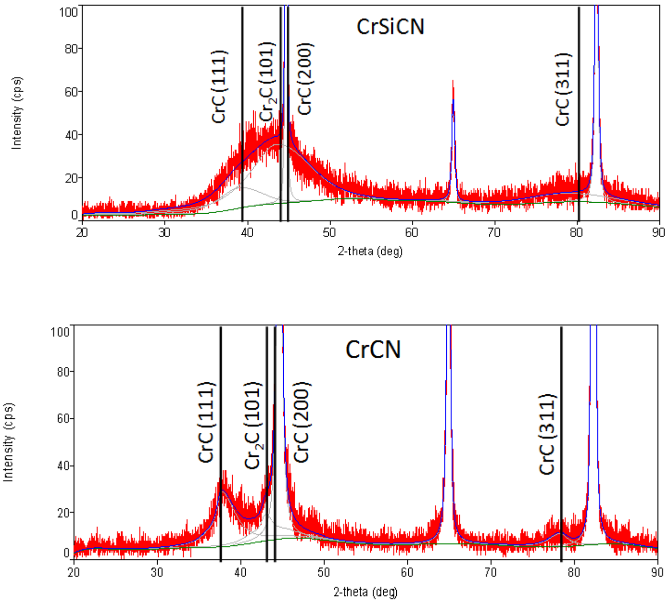
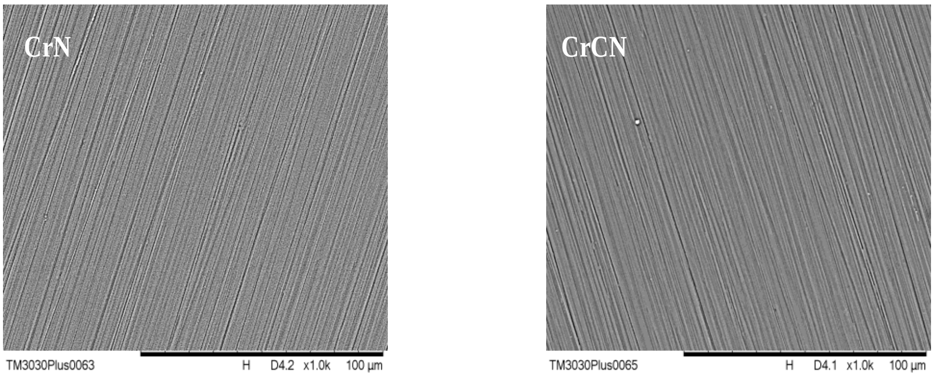


Fig.2. X-ray diffraction patterns of CrCN and CrSiCN coatings refined by peak deconvolution using pseudo-Voigt functions

3.3 Surface morphology

Fig. 3 shows SEM micrographs on surfaces of the coatings deposited on C45 steel substrates. As seen, the deposited films are roughly similar and exhibit very smooth surfaces, with no visible differences between various coatings.



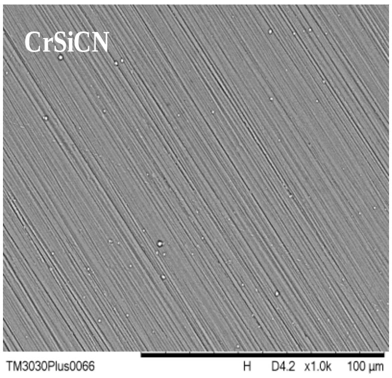


Fig. 3. SEM images for the surfaces of the coatings prepared by magnetron sputtering method

The surface topography of the coatings was also investigated by surface profilometry. Surface line profiles and R_a roughness of the CrN, CrCN and CrSiCN coatings are given in Fig. 4. The profilometry results show that the multicomponent coatings exhibit higher R_a roughness values compared with the CrN coating.

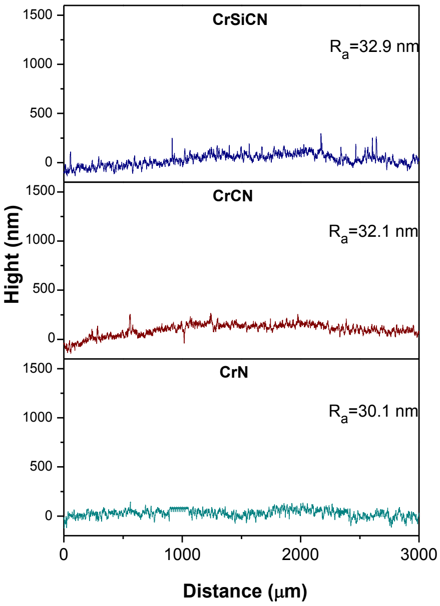


Fig. 4. Surface line profiles and R_a roughness of CrN, CrCN and CrSiCN coatings deposited by magnetron sputtering

3.4 Deposition rate and mechanical characteristics

The deposition rates and main mechanical characteristics of the coatings (hardness, adhesion strength) are summarized in Table 3.

Table 3

Deposition rate (D_R), hardness (H) and adhesion critical load (Lc) of the CrN, CrCN and CrSiCN coatings

D_R (nm/min)			H (GPa)			Lc(N)		
CrN	CrCN	CrSiCN	CrN	CrCN	CrSiCN	CrN	CrCN	CrSiCN
25.3±0.5	18.3±0.5	29.5±0.5	14.6±0.2	16.4±0.2	19.3±0.2	38.4±0.4	35.2±0.4	36.7±0.4

As revealed by the experimental data, the highest deposition rate was measured for CrSiCN.

Hardness measurements revealed that C and Si additions to CrN determined the increase in coating hardness. As mentioned above, transition metal carbonitrides are harder than the corresponding nitrides due to the covalent character of the carbon bonding [1]. Also, the presence of Si as alloying element determines the hardness increase due to the formation of amorphous Si-based phases (Si, SiCN) which decrease the grain boundary sliding process [23]. The highest value was obtained for the CrSiCN coating (about 19 GPa).

Concerning the results of the adhesion tests, the measured values of the critical load (Lc), ranging from about 35 to 38 GPa, demonstrated a good film adhesion to the C45 steel substrate.

3.5 Friction behavior

The friction experiments were conducted on coated and uncoated 25 mm C45 steel discs. To evaluate the friction performance of the coatings, the variation of the friction coefficient (μ) as a function of sliding distance (d) was determined (Fig. 5). For comparison, the results for an uncoated sample are also given.

Firstly, it is worth mentioning that all the deposited films exhibit lower coefficients of friction when compared to the uncoated steel specimen. The coatings with C and Si additions exhibited superior friction behavior than that of the CrN coatings.

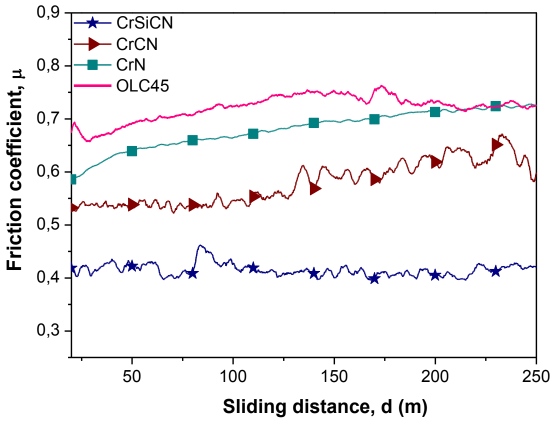


Fig. 5. Friction coefficients (μ) vs. sliding distance (d) for the substrate (C45 steel) and CrN, CrCN, and CrSiCN coatings deposited by magnetron sputtering. Testing conditions: open atmosphere, counterpart - 6 mm sapphire ball, 0.15 m/s, 250 m sliding distance, 5 N load

The friction coefficients (Fig. 4) have values between 0.39 to 0.58 (at the end of the test) and reveal a steady evolution in time, indicating a uniform wear process. The lowest friction coefficient was found for CrSiCN, demonstrating the beneficial effects of the presence of C and Si in the film composition. This result can be accounted by the high carbon content in the film composition (Table 2). As commonly admitted, in sliding contacts of carbide or carbonitride coatings with relatively high C concentrations, an amorphous carbon (graphite-like) layer is formed at coating-counterpart interface, which acts as a solid lubricant and determines friction reduction [26].

4. Conclusions

CrN, CrCN and CrSiCN coatings were prepared by magnetron sputtering technique. The following main conclusions can be drawn from the current study.

The X-ray diffraction patterns of the investigated coatings showed the formation of the β-Cr_2N phase (hexagonal structure) for the CrN coating and a mixture of CrC (fcc) and Cr_2C (hexagonal) for CrCN and CrSiCN coatings. These latest coatings exhibited a low degree of crystallinity, approaching amorphous.

As compared to CrN binary coating, the multicomponent CrCN and CrSiCN coatings showed enhanced hardness and improved friction performance. The highest hardness (H=19.3 GPa) and the lowest friction coefficient (μ=0.39) was found for CrSiCN, demonstrating the beneficial effects of the presence of C and Si in the film composition.

The experimental results revealed that the CrN based multicomponent coatings (CrCN and CrSiCN) can be considered promising candidates to be used as protective coatings on various components and parts for mechanical and tribological applications.

R E F E R E N C E S

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