STUDY OF SOME MECHANICAL PROPERTIES OF THIN HARD COATING CHROMIUM CARBIDES

Abstract

In the present work, some mechanical properties of chromium carbides coating on steel substrates were studied. The samples were prepared by d.c. magnetron sputtering of a pure Chromium (Cr) layer on steel substrates containing 1%wt of Carbon. The system (substrate/coating) was then annealed in vacuum at a temperature at which the carbon of the substrate may diffuse into the Cr metallic film. This fact leads to the formation of chromium carbides, which are identified by X-ray diffraction as Cr_7C_3, $Cr_{23}C_6$ and $(Cr,Fe)_7C_3$. The study by nanoindentation shows that the microhardness decreases with increasing of annealing temperature until 800°C, then increases rapidly to reach a maximum ($\approx$2800 Kg.mm^{-2}) at 1000°C. The internal stresses, measured by X-ray diffraction, are compressive at 900°C and tensile at 1000°C in the chromium coating. Nevertheless, they are tensile in the substrates regardless the temperature. The sign change of the stresses in the coating is probably due to the phase transformation ($Cr_7C_3 \rightarrow (Cr,Fe)_7C_3$).

Keywords: *Chromium, carbides, hard coating, nanoindentation.*

Résumé

Dans le présent travail, nous avons étudié quelques propriétés mécaniques des revêtements durs de carbures de chrome sur des substrats d'acier (100C6 norme AFNOR), contenant ~ 1% en poids de carbone.

Les échantillons, préparés initialement sous forme de couches minces de chrome déposées par pulvérisation cathodique magnétron sur des supports d'acier 100C6, ont subi des recuits thermiques entre 200 et 1060°C sous vide, puis caractérisés par diffraction des rayons X, et nanoindentation. L'analyse par DRX révèle la présence de carbures Cr_7C_3, $Cr_{23}C_6$ et $(Cr,Fe)_7C_3$. La microdureté mesurée décroît avec l'élévation de la température, puis croît à partir de 800°C, pour atteindre son maximum à 1000°C (HV = 2800 Kg.mm^{-2}). Enfin, les contraintes résiduelles dans les revêtements, mesurées par diffraction des X, sont de compression à 900°C et de traction à 1000°C. Le changement de signe des contraintes est probablement dû à la transformation de phases ($Cr_7C_3 \rightarrow (Cr,Fe)_7C_3$).

Mots clés: *Chrome, carbures, revêtement dur, nanoindentation.*

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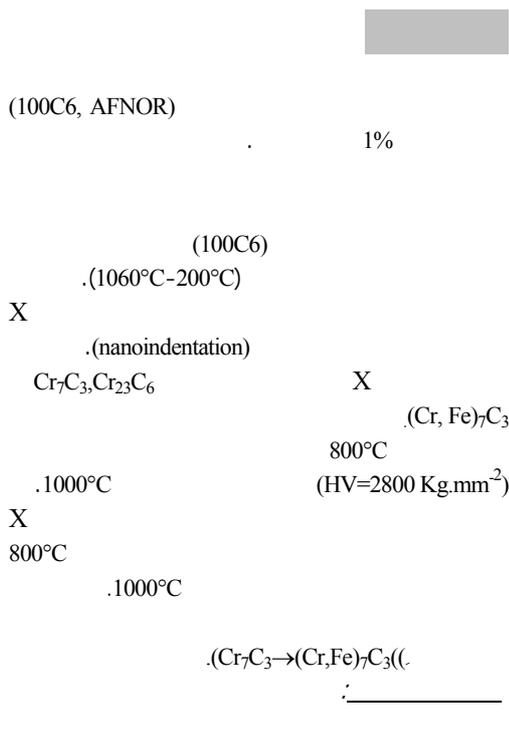
The resistance of pieces working under mechanical, thermal or chemical solicitations depends on the superficial layer of the constituent materials. To improve the surface properties, the pieces are often coated by some metallic or ceramic deposits [1].

The carbides and nitrides of transition metals are the most frequently used for their exceptional refractoriness and remarkable mechanical properties (an extreme hardness). Several processes, as the physical and chemical deposition (PVD and CVD), allow to produce these coatings on thin films or multi-layer forms [2, 3].

In the present work we study some mechanical properties of chromium carbides coatings prepared from a film of chromium deposited by magnetron sputtering on steel substrates and annealed in the temperature range 200-1060°C.

EXPERIMENTAL DETAILS

Chromium layers (~3µm thickness) were deposited by dc magnetron sputtering onto high carbon steel (100C6, according to AFNOR norms) substrates kept at 200°C during the deposition process. The samples were subjected to high vacuum annealing at a temperature between 400 and 1000°C for 30 min.

The qualitative phase analysis (formation and growth of chromium carbides) of the samples was performed on a Siemens D5000 diffractometer and the residual stresses were calculated with the use of a computer program and the $sin^2\psi$ method [4].

The microhardness and Young modulus of the films are determined using the ultramicroindentation system, NANOINDENTERTMII with a

(100C6, AFNOR)

. 1%

(100C6)

.(1060°C-200°C)

X

.(nanoindentation)

Cr_7C_3, $Cr_{23}C_6$ X

.$(Cr, Fe)_7C_3$

800°C

.1000°C   (HV=2800 Kg.mm^{-2})

X

800°C

.1000°C

.($Cr_7C_3 \rightarrow (Cr,Fe)_7C_3$)
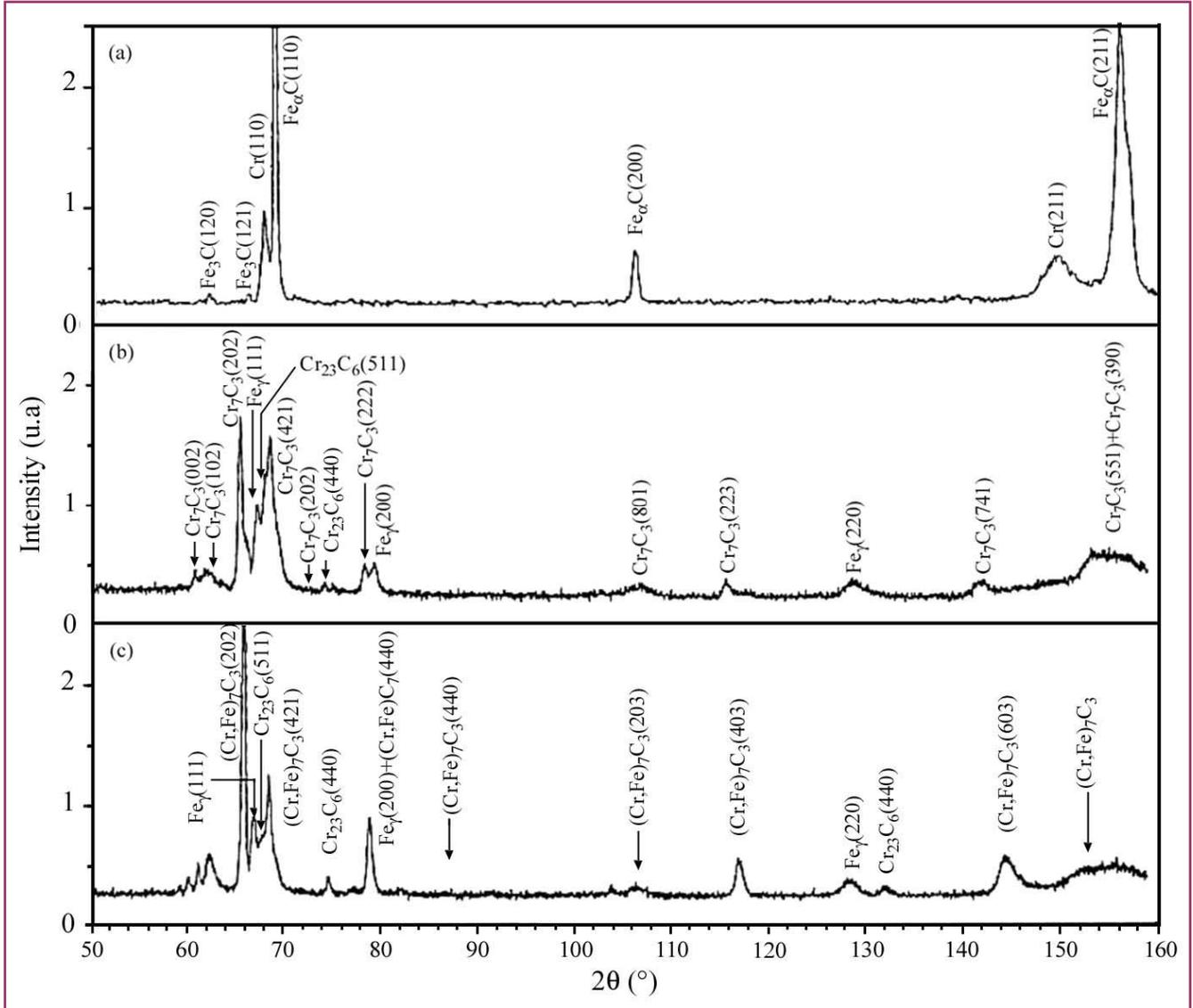
Figure 1: X-ray diffraction spectra of the samples [Cr(3μm)/100C6 steel] before **(a)** and after annealing during 30 min at 900°C **(b)** and 1000°C **(c)**.

trigonal indenter equivalent to the Vickers indenter in the "area versus depth" behaviour.

RESULTS AND DISCUSSION

Qualitative analysis

Figure 1-a shows a spectrum of coated substrate with chromium thin film, before annealing. It appears clearly that the deposited films are constituted of pure chromium. In addition to α-Fe peaks, we notice a number of reflections of Fe_3C. After heat treatment of the samples in the considered temperature range, we find that the binary carbide Cr_7C_3 forms at 700°C and grows when the temperature increases (Fig. 1-b). It transforms then at 1000°C into ternary carbide $(Cr, Fe)_7 C_3$ thanks to iron diffusion from substrate into coating films (Fig. 1-c). On the other hand, the $Cr_{23}C_6$ phase is revealed only at T ≥ 900°C. However, the Cr_3C_2 compound has not been observed. It is also established by X-ray microanalysis that the diffusion

of carbon from the substrate is responsible of these carbides formation [5].

Mechanical properties

Hardness

Figure 2 illustrates the results of the measurements done by nanoindentation. The general shape of indentation curves are globally the same. For the unannealed and annealed samples at 600°C, the curves show that the hardness is constant until a depth of ~ 4000Å, and then it decreases monotonously. For the treated samples at 800°C, the hardness stays also constant until ~ 4000Å, and then grows progressively with the depth. This fact owes, presumably, to the diffusion of carbon from the substrate, which leads to the formation of the chromium carbides in the layers near the interface coating/substrate. This phenomenon agrees with the X-ray diffraction measurement which revealed the presence of the Cr_7C_3 carbide. For the sample annealed at

1000°C, we observe a very important rise of the hardness which reaches a value of about 2800 Kg.mm^{-2} at the depth of 1100Å, (Fig. 2-a). This result explains the very clear increase of the resistance to the penetration (Fig. 2-b). It results then an improvement of the mechanical properties of the composite.
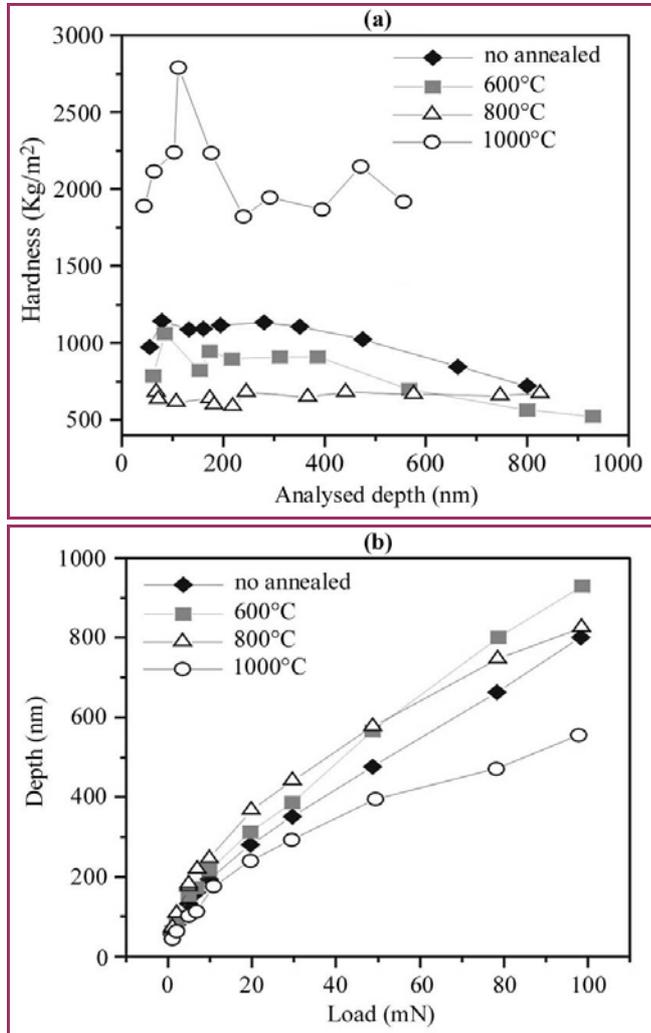
Figure 2: Nanoindentation measurements.

Elasticity Modulus

The variation of Young modulus with the analyzed depth for different annealing temperatures is shown on figure 3. We will notice that the relative curve to the sample annealed at 600°C is situated beneath of the one of the no annealed sample. The curves, in practice, present the same evolution. Thermal treatment leads, indeed, to the reduction of the structure defects and therefore to the reduction of elasticity modulus [6].

One will note, besides, that the Young modulus of the sample annealed at 800°C remains lower to the one of previous samples, and this, until 450 nm. We expect, from there, an increase of the elasticity modulus because of the probable presence of carbides induced by the diffusion of carbon from substrate.

On the other hand, in the case of the sample annealed at 800°C the evolution of Young modulus is different due to the complete transformation of the structure.
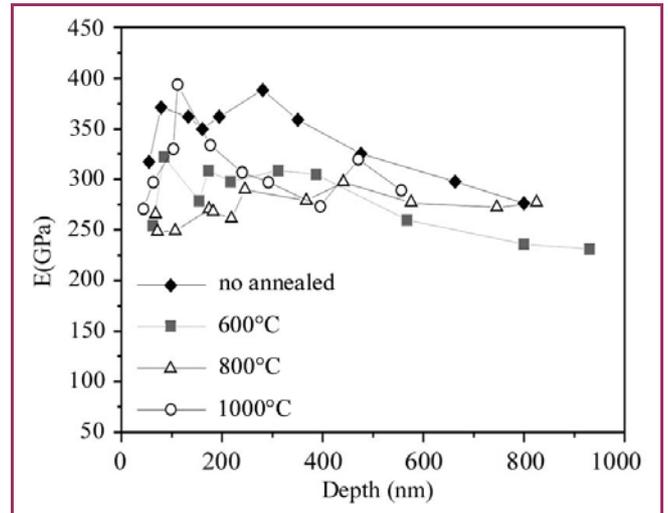
Figure 3: Evolution of Young modulus with analysed depth.

Residual stresses analysis

In order to determine the residual stress in Cr_7C_3 carbide and austenite γ phases, the selection of the employed tube and X-ray reflection were governed by the peak resolution and its diffraction angle. We have used a chromium radiation ($\lambda_{k\alpha} = 2.29$Å), the (220) reflection of austenite ($2\theta = 128°$) and the (223) line of Cr_7C_3 compound ($2\theta = 115°$). The Young modulus of the Cr_7C_3 carbide is determined by nanoindentation. However, the other radiocrystallographic elastic constants are extracted from the literature [7, 8]:

$$\tfrac{1}{2} S_2(\gamma) = 6.05 \; 10^{-6} \; MPa^{-1}$$
and $\quad \tfrac{1}{2} S_2(Cr_7C_3) = 3.85 \; 10^{-6} \; MPa^{-1}$

The carried out measurements are achieved in one direction $\varphi = 0$ and 7 values of ψ angle. The obtained results are listed in table 1. It was found that the $2\theta(\varphi,\psi)$ versus $\sin^2\psi$ plots can be represented by a simple linear relationship with a light curvature. The slight opening of ψ^+ and ψ^- branches indicates the probably presence of shearing with a least intensity. The total absence of sinusoidal variation of these curves shows that there is no texturation in our samples.

Table 1: Some residual stresses values determined by X-ray diffraction.

Sample	T (°C)	Phase	Peak	σ_ϕ (MPa)	$\Delta\sigma_\phi$ (MPa)
Cr(3μm)/(100C6) Steel	900	Cr_7C_3	(223)	- 734	± 323
	900	γ Austenite	(220)	+ 332	± 212
	1000	(Fe, Cr)$_7$C$_3$	(403)	+ 127	± 38

The internal stresses in Cr_7C_3 carbide phase from the coating are compressive, $\sigma_\varphi \cong -734$ MPa. This compressive nature of stresses which generally appears in PVD deposits [9, 10] favours the mechanical behaviour of films on the substrates and can confer to the coating a good resistance

against wear and corrosion.

The measurement carried out on austenite phase from the substrate (sample annealed at 900°C) gives a positive value of the stress $\sigma_\varphi \cong +332$ MPa. This is an expected value, because system equilibrium naturally requires response to any causal solicitation. In the same way, the measurement realized on $(Fe, Cr)_7 C_3$ phase gives a tensile stress, but with a lower intensity (+ 127 MPa). We try to think that the origin of stress sign change is due to iron atoms diffusion which takes certain substitutional positions firstly occupied by chromium atoms in the lattice of the Cr_7C_3 carbide. Also, the transformation of binary Cr_7C_3 carbide into ternary $(Cr, Fe)_7 C_3$ carbide is accompanied by an increase of volume of about 4%.

CONCLUSION

Chromium carbide coatings are obtained from a film of chromium deposited by d.c. magnetron sputtering on steel substrates (~1% wt of carbon content) and annealed in vacuum at different temperatures. Mechanical characteristics of coating supplant those of pure chromium film and, by far those of substrates.

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