ACHIEVEMENTS IN MECHANICAL & MATERIALS ENGINEERING

Influence of the heat treatment on a CrN coatings, deposited on a steel

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CrN coatings have been deposited by DC unbalanced magnetron sputtering of a sintered chromium target on a X12M steel substrates in a single-chamber vacuum furnace with a graphite heater and a heat-isolative chamber made of carbon wool. The heat treatment of the covered substrates is carried out in a two-chamber vacuum furnace. The chemical and phase composition of the coatings, the lattice parameter and texture coefficient are determined by XRD and GDOES analyses. Their micro-hardness and effective Young's modulus also have been investigated.

1. INTRODUCTION

The coatings of the type CrN having an appropriate structure, properties and at the same time a good adhesion to the substrate are usually obtained in the temperature range from $350^{o}C$ to $550^{o}C$. That is way in the most of the investigations, as substrates for these coatings are used heat-resistant or corrosion-resistant austenite steels [1,2,9], and the metallization process is usually carried out as a final heat treatment, after the hardening heat treatment – quenching and tempering. In practice this fact means, that in the case of the non heat resistant steels which are usually tempered between 180 - $220^{o}C$, the deposition of Cr and Ti based nitrides and carbides is an impossible process due to the unallowable changes in the substrate structure and properties. There exists in essence a very small amount of investigations about the above- mentioned problem and they mainly concern the resistively of the Cr and Ti based carbides and nitrides during an annealing [1, 3]. The obtaining of the coatings at temperatures above 550 – $600^{o}C$ and as well the possibility they to be subject to a thermal shock as the quenching are not explored area of steels.

The facts mentioned above poses some problems, which determine the aim of the present work:

1. To want extent the substrate temperature can be increased during the deposition of CrN coatings without a transformation of the process from a vacuum metallization into a vacuum diffusive metallization when the coating structure is formed mainly through a diffusive mechanism and the coefficient of diffusivity of the coating K_{Dc} is above 0,3-0,5 [5].
2. What changes in the coating structure and properties will occur during a following quenching and tempering depending on the steel chemical composition and its specificity of heat treatment.
3. Is it possible the deposition of these hard and wear-resistant coatings to be transformed from a final treatment into an initial one, which will create a possibility to improve this way the working properties of a large number of non heat-resistant and semi-heat-resistant steels.

2. EXPERIMENTAL PROCEDURE

The coatings have been deposited in a single-chamber vacuum furnace with a built-in DC unbalanced magnetron [5]. After reaching initial vacuum of $6\text{-}8.10^{-4}$ mbar, before depositing the films, the substrates have been heated to the corresponding metallizing temperature T_m, ranging between 450-850°C. Reaching the vacuum of $4\text{–}6.10^{-4}$ mbar, cleaning is carried out under the conditions of glow discharge in Ar flow at $1,5.10^{-1}$ mbar for 5 min at 900 V. A sintered pure 99,998% chromium target has been sputtered at a pressure $6 - 8.10^{-3}$ mbar in a flow gas mixture of Ar 2,6 sccm and N_2 26 sccm, for 60 min at a sputtering power of 2,3 kW (I_{sp}= 5A), providing condensation rates of 0,035–0,070 µm/min for a target-to-substrate distance $L_{t\text{-}s}$ = 70 and 95 mm. The substrate bias voltage have been   0 V, except the experiments at 500 ^{o}C, which had been carried out at substrate potentials U_s of 0, -50, -100 and -200 V respectively. Samples of steel according to the Bulgarian State Standard steel X12M (1,45-1,65%C, 11-12,5%Cr, 0,15-0,30%V, 0,40-0,60%Mo, 0,15-0,40%Mn, 0,15-0,35%Si, 0-0,03%S, 0-0,03%P) [7] have been used for substrates. The pressure and the gas flows have been controlled by an ionization vacuum meter and a mass-flow controller [5]. After the deposition, the coated substrates have been heat treated in a two-chamber vacuum furnace together with real parts at a technological process standard for the given substrate material. The heating up process to temperature of hardening (840±10°C) includes an intermediate keeping at 650°C for 60 min. After the hardening the tempering on 200°C was made.

The chemical composition of films has been determined by Ar glow discharge optical emission spectroscopy (GDOES) using a LECO 750GDS$^®$ instrument. The crystallographic structure and axial texture of the films have been analyzed by X-Ray diffraction (XRD) using CoK$_α$ radiation. The microhardness has been measured by a Vickers Nanoindentation tester FISCHERSCOPE$^®$ H100 using a load force of 50 mN at 60 sec. The thickness of the films has been determined on a cross section using a NIKON$^®$-OPTIPHOT metallographic microscope.

3. RESULTS AND DISCUSSIONS

According to their appearance the coatings can be separated into two groups. The first group includes the coatings obtained in the interval T_m = 450-600°C and having a gray or milk-gray color. The second one includes the coatings obtained at 650 and 850°C and having a dark gray color. In this group it is possible the coating to be oxidized or because of its

diffusive interaction with the substrate to be transformed into a diffusive one having a different phase composition. In X-ray and GDOES results the oxygen is not detected and that proves the second explanation.

The exploring of the coatings topography at magnifications x400 and x1000 show significant changes occurring at $T_m = 600 - 650^o$C. The coatings obtained up to T_m 600^oC fit to the IInd Zone of the Thornton's Zone Model, while those obtained between 650 and 850^oC fit to the IIIrd Zone. The boundary between the zones is in essence the recrystallization temperature of the condensate material. For nitrides and carbides this temperature is about $(0,7-0,8)$ T_m [8] and in the given case for CrN it corresponds to $600-650^o$C. The re-crystallization process means an intensive volume diffusion and a possibility for a diffusive interaction with the substrate if the latter has an appropriate chemical composition [10].

The influence of the L_{s-t} and U_s is not essential. There is a weakly-expressed tendency to a smoothening of the surface relief, probably due to a lessening of the condensation to diffusion rates ratio which proves more complete running of the coalescence and recrystallization.

The microstructure investigations on a cross section prove and add to the above said. Till to $T_m = 600^o$C the coatings are extremely disperse having a columned structure while at a negative bias to the substrate the dispersion increases and at $T_m = 500^o$C, $U_s = -100, -200$ V it is not columned but sooner consists of equi-axed grains. This fact shows that the overheating of the condensate owing to the increased bombardment has lead to a developing of a recrystallization process. In all cases the coatings of the first group are monolayered.

The coatings of the second group, obtained at $Tm = 650 - 850^o$C contain intermediate layers which is an evidence for their diffusive interaction with thesubstrate. The intermediate layers obtained at 650^oC and 850^oC are respectively $\sim0,3$ μm and $\sim0,5$ μm thick.

The heat treatment of the coatings obtained at 650^oC and 850^oC causes no changes in the topography, but the intermediate layer in the coatings already takes $\sim60\%$ of the total thickness of the film. Except for this, the coatings deposited at 850^oC contain three underlayers. The inner layer has appeared as a result of the additional diffusive interaction with the substrate when being heated during the heat treatment. When increasing L_{t-s}, the condensation rate decreases and the relative part of the diffusively obtained underlayers increases too, which approaches the process to the classical diffusive metallization. In the both temperatures of the depositing it is observed decreasing of the quantity of nitrogen, which at 850^oC is stronger.

The dependence between the coating thickness and Tm also has two zones. In the first one (450 - 600oC) there is not tendency to a decreasing. In the second one there is a weakly-expressed tendency to a decreasing from about $5,0(2,5)$ μm at 650^oC to about $4,0(1,0)$ μm at 850^oC for $L_{t-s} = 70(95)$ mm respectively, which proves too that above 600^oC a diffusive interaction with the substrate has occurred and it increases when enhancing T_m. The applying of a negative bias also leads to a decreasing of the thickness due to an enhanced back sputtering of the growing condensate.

The GDOES analyses show that the coatings obtained up to $T_m = 600^o$C are condensates with a microdiffusive bond to the substrate [6]. The depth profile outlines four zones (Fig.1):

The I^{st} zone is up to about $0,5$ μm thick and contains an increased amount of the metalloids at the expense of the metal content. This zone is due first- to the interaction between the condensate and the residual atmosphere in the furnace after switching off the magnetron, and second- to an adsorption of gas molecules on to the coatings surface (mainly O_2 and C) and their separation in the beginning of the GDOES analyses.

The IInd zone is the real part of the coating, in which the contents of the main elements Cr, N$_2$, O$_2$ and C remain constant. An important feature is that the N$_2$ quantity reaches about 53 at. % when increasing the L$_{t-s}$ from 70 to 95 mm. The bias has an analogous effect at −100 − 200 V. The N$_2$ content reaches 50 %. This facts means that the back sputtering from the coating surface due to the bombardment by Ar ions affects predominantly on the metal atoms.
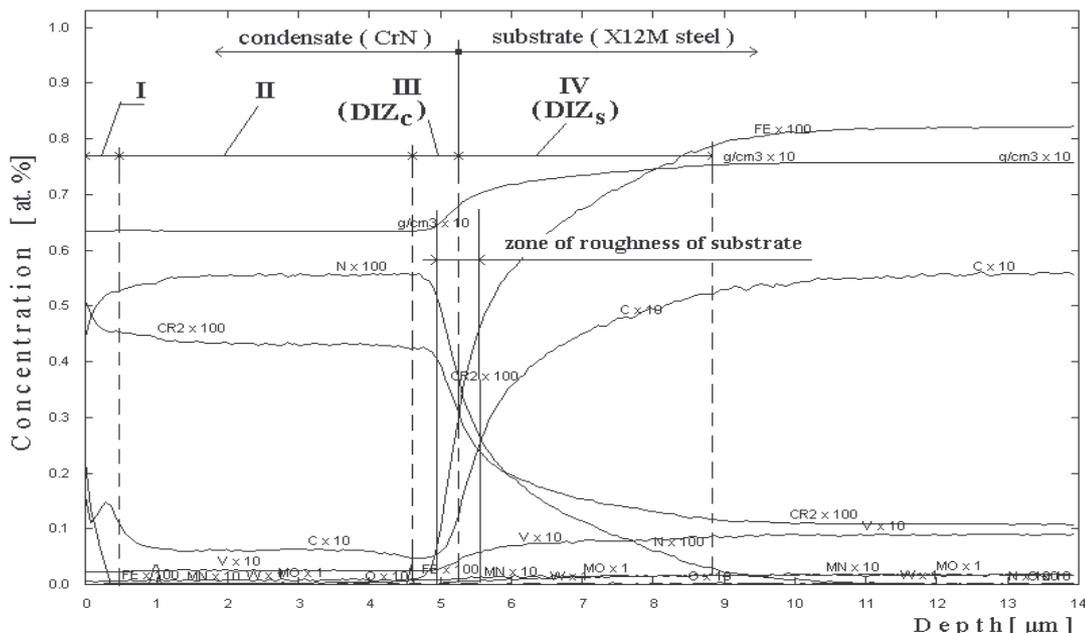

Fig. 1. GDOES profile of a CrN coating on a X12M steel, obtained at T$_m$ = 450°C, L$_{t-s}$ = 70 mm and U$_s$ = 0 V.

The IIIrd zone is situated at the inner side of the condensate, to the substrate, and can be named a Diffusive Influence Zone in the condensate (DIZ$_C$) [6]. It is characterized with a lowering of the Cr and N$_2$ amount and an increase of the Fe, and C content.

The IVth zone is the Diffusive Influence Zone in the substrate (DIZ$_S$) and is fully situated in it. Here it is obvious a saturation with Cr and N from the condensate and a lessening of the elements contained in the substrate.

If we take in a view the zone of roughness of the substrate surface, so the presence of the IIIrd and IVth zones may be considered as symbolical, the coatings in this group can be sorted to the vacuum condensates with an adhesive bond to the substrate [6].

The coatings of the second group (obtained at 650°C and 850°C) are characterized with more intensive redistribution of the elements between the substrate and condensate. In this coatings the IIIrd and IVth zones are very good showed, as the DIZ$_C$ reaches respectively 0,3 µm and 0,5 µm at 650°C and 850°C. This confirms, by indirection, that above 600-650 ^{o}C the volume diffusion has a practical significant velocity. The coatings of this group can be sorted to condensates with microdiffusive bond to the substrate [6].

The heat treatment of the coatings in this case leads to a significant redistribution of the elements of the condensate and the substrate, and also leads to forming, by a phase recrystallization, of the transitive diffusive layer consisted of two underlayers $\delta_{idl} = (\delta_{s \rightarrow c} + \delta_{c \rightarrow s})$ [6]. The first of them $(\delta_{c \rightarrow s})$ is situated in the substrate (Fig.2) and its ingredients are equal to the phase $(Cr,Fe)_{23}C_6$, and the other one $(\delta_{s \rightarrow c})$ is a part of the condensate, where the

transformation CrN→(Cr,Fe)$_2$CN is done. The coating is transformed from a condensate to a vacuum-diffusive coating with a residual condensate (RC$_t$) [6].

The results from the X-ray diffraction analyses prove the interpretation of the information from the GDOES investigation. Up to $T_m = 600^oC$ the coatings contain the phase CrN. The peaks of the phases (CrFe)$_2$CN and (Cr,Fe)$_{23}$C$_6$ appear in the X-ray patterns of the coatings after their heat treatment.
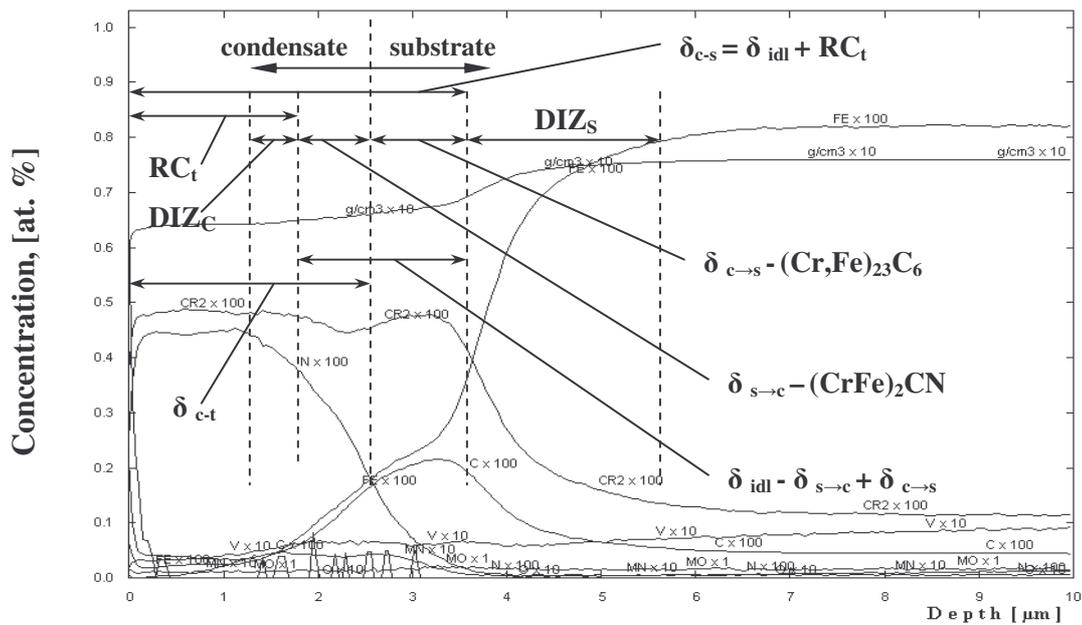

Fig. 2. GDOES profile of CrN coating on X12M steel, obtained at $T_m = 850^oC$, $L_{t-s} = 70$ mm and $U_s = 0$ V after heat-treatment.

The crystal lattice of the CrN is strongly deformed in the interval $T_m = 450 - 850^oC$ and the lattice parameter is less than the theoretical one. When increasing T_m it increases and the deformations tends to a decreasing. This result is in relation with the lessening of the N$_2$ on one hand and increase of the Cr on the other hand.

The increase of the substrate bias to a negative direction increase the deformations which according to <311> tends to $4,23.10^{-3}$ nm at Us = -200 V

On the X-ray patterns the coatings have a well-expressed texture. By increasing the T_m without applying a bias voltage, it is observed a moving from preferred orientation <311> at 450°C to mixed orientation <311> and <200> at 500°C , <111> and <311> at 650°C, and which is changed to monoaxis orientation <111> at 850°C. This is explained with increasing of the surface movement of adsorbed atoms when increasing the substrate temperature, which helps for their closer arrangement. The affection of the substrate Us is similar to the increasing of the temperature. At Us= -50 V the coating is textured on direction <311>, at -100 V the orientation becomes mixed <311> and <200>, and at -200 V is changed to <200>, which is the thicker direction than <311>. The variation of the texture from less compactness to more compactness orientation when increasing the temperature (respective bias-voltage) has been observed and confirmed by other scientists [4].

The coating obtained at $L_{t-s} = 70$ mm in the temperature interval 450-850^oC have a hardness H$_C$ and effective Young's modulus $E^* = E / (1 - v^2)$, measured on a plane,

diminishing from 9620 MPa to 7660 MPa and 267 GPa to 231 GPa, respectively. The result is in connection with the lowering of the internal stresses and also with the increase of the N content. Generally the not so far high hardness is due in addition to the significant axial texture according <200>. The coatings obtained at 850^oC have the lowest hardness. In this case not only the recrystallization has finished, but in addition due to the diffusive interaction with the substrate, the main phase is $(Cr,Fe)_{23}C_6$.

4. CONCLUSIONS

- the coatings obtained in the interval 450 - 600^oC are light gray and have a topography and microstructure corresponding to the IInd Zone of The Thornton's Zone model. These obtained at 650 ^oC and especially at 850 ^oC are dark gray and correspond to the III^{rt} Zone of Thornton's model.
- up to 850^oC the coatings are built mainly of the phase CrN. Four zones can be distinguished in them: the I^{st} one is situated at the surface and has an increased content of Cr, C and O_2 at the expense of the N_2; the IInd one is the main part of the coating with a constant ratio among the elements; the IIIrd and IVth zones are zones of a diffusive influence, in the condensate and substrate respectively.
- the coatings, obtained to 600^oC are condensates with an adhesive bond to the substrate, and these at 650^oC and 850^oC are with microdiffusive bond to the substrate.
- the quenching and tempering processes of steel X12M, covered with a coating of CrN, turn the latter into a double-layered or triple-layered vacuum-diffusive coating with a residual condensate, the transitive diffusive layers of which are made of phases $(Cr,Fe)_2CN$ and $(Cr,Fe)_{23}C_6$.

In conclusions it can be said that the deposition process of vacuum coatings – condensates built only of CrN on the steel X12M or another steel of this group, can not be using as a preliminary process.

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