PVDM-R of Ch12M steel by magnetron deposition of CrN coatings and next heat treatment*

R. Shishkov[a], M. Jordanov[b], W. Kwaśny[c]

[a] Material Science and Technology of Materials Department, University of Russe; 8, Studentska Street, 7017 Russe, Bulgaria

[b] Departament of Engineering and Pedagogy, Technical University of Sofia, Burgasko shose 59, 8800 Sliven, Bulgaria

[c] Division of Materials Processing Technology and Computer Techniques in Materials Science Institute of Engineering Materials and Biomaterials, Silesian University of Technology ul. Konarskiego 18a, 44-100 Gliwice, Poland

The CrN coatings have been deposited on Ch12M steel substrates by sputtering of a sintered chromium target at metallizing temperatures T_m, ranging between 450-850°C and a bias voltage Us, ranging from 0 to -200V by the method of "Plasma Vacuum Diffusive Metallizing - Reactive scheme" (PVDM-R) in a single-chamber vacuum furnace with a graphite heater and a heat-isolative chamber made of carbon wool. The covered samples are hardened at temperature 1020 ±10°C and tempered at 200°C. The kinetics and mechanism of the structure forming of the coatings are investigated. 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 Young's modulus also have been investigated. The microstructure and type of the coatings before and after tempering have been determined.

1. INTRODUCTION

The chromium based protective wear-resistant and decorative coatings have a structure and properties analogous to those of the TiN coatings and even exceed them in some aspects [1,3,5,8,9]. They possess a higher corrosion-resistance [1,2,7] and a lower friction coefficient etc. [1,3,4,6].

In last years investigations for developing of a new and perspective method for "Plasma Vacuum Diffusive Metallizing" (PVDM) have been carried out. After the method a condensate is deposited in vacuum furnace on heated metal substrates by magnetron sputtering. The diffusive interaction condensate-substrate creates a coating of diffusive type. The character and the type of the coating are defined by the coefficient of diffusion - K_{DC} [11], which is the relation between the thickness of the intermediate diffusive layer, created on the borderline layer/substrate and the total thickness of the coating.

The aim of the present work is to study the possibility to obtain CrN coatings at high temperatures in a vacuum furnace by PVDM-R process using a sintered chromium target and the effect of the next heat treatment. It also takes an interest to turn the coating deposition 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.

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2.   EXPERIMENTAL PROCEDURE

The coatings have been deposited in a single-chamber vacuum furnace with a built-in DC unbalanced magnetron. After reaching an initial vacuum of $6\text{-}7.10^{-4}$ 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 7.10^{-4} mbar, cleaning is carried out under the conditions of glow discharge in Ar flow at 1.10^{-1} mbar for 10 min at 900 V. A sintered pure 99,998% chromium target has been sputtered at a pressure $8 - 9.10^{-3}$ mbar in a flow gas mixture of Ar - 2,6 sccm and N_2 - 26 sccm, for 60 min at a sputtering power of 3,2 kW (I_{sp}= 8A), providing condensation rates of 40-85 nm/min for a target-to-substrate distance $L_{t\text{-}s}$ = 70 mm. The substrate bias U_s has been 0 V, except the experiments at 500°C, which have been carried out at substrate potentials of 0, -50, -100 and -200 V. Samples of steel Ch12M have been used for substrates. After the deposition, on the coated substrates a vacuum heat treatment (VHT) is made in a two-chamber vacuum furnace together with real parts at a technological standard process for the given substrate material. The heating up process to temperature of hardening (1020±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 (GDOES) using a LECO 750GDS® instrument. The phase composition, crystallographic structure and axial texture of the films have been analysed by X-Ray diffraction (XRD) using CoK_α radiation. The microhardness and Young's modulus have been determined by a Vickers Nanoindentation tester FISCHERSCOPE® H100 using a load of 50 mN. The morphology and thickness of the films has been investigated on a cross section using a NIKON®-OPTIPHOT metallographic microscope.

3.   RESULTS AND DISCUSSIONS

Microstructure and topography
The exploring of the coatings topography separates them into two groups. The coatings from the first group, obtained up to Ts=600°C fit to the II[-nd] Zone of the Thornton's Zone Model, while those from second group, obtained at 650°C and especially obtained at 850°C fit to the III[-rd] Zone of the Thornton's Zone Model. 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). Ts and in the given case for CrN it corresponds to 600-650°C. The recrystallization process means an intensive volume diffusion and a possibility for a diffusive interaction with the substrate [11,12].

The microstructure investigations on a cross section shows that till T_m=600°C the coatings are mono-layered and are extremely disperse having a columned structure. They do not change their type and belong to the vacuum condensates with micro-diffusive bond to the

substrate [11]. In the coatings at 650^oC it is difficult to be observed, but at 850^oC a condensate CrN and a thin underlayer between the coating and the substrate can be seen.

The microstructure of the CrN coatings, deposited on Ch12M substrates at 650^oC and 850^oC, after VHT is a VDC without RC of CrN. They consist of two basic underlayers: an outer one having a gray color built of alloyed $Cr_2N + Cr_2CN$ and an innerone which is more dense and lighter consisting of alloyed chromium carbides.

Phase composition and texture

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. 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

According to the XRD analysis till 650^oC the coatings consist of one phase - CrN. Because of the low thickness of the coatings ($2,13 \div 5,74$ µm) in the X-ray patterns it appear also lines of the ferrite in the substrate. According to the X-ray patterns the coatings have a well-expressed texture. The level of the texture is defined by calculating the coefficient of texture $\delta_{<hkl>}$ by a method, which often is used for vacuum condensates [3]. The increase of T_m without a bias voltage changes the preferred orientation <311> at 450°C into a mixed orientation <311> and <200> at T_m=550 - 600°C and then into <200> 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 disposition. The effect of the bias is similar to that when increasing the temperature. At Us= -50 V the coating is textured according the direction <311>, at -100 V the orientation becomes mixed <311> and <200>, and at -200 V is changed to strongly mono-axis orientation <200>, which is more dense 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 [2,3,4].

The coatings deposited at 850^oC have two-phase composition - CrN and $(Cr,Me)_2CN$. This speaks of a diffusive interaction between the condensate and substrate (the carbon from the substrate and the nitrogen from the condensate) at the explored conditions. As a result the phase $(Cr,Me)_2CN$ is formed. It is showed a little displacement of the X-ray patterns due to the diffusion of other elements (mainly Fe and also W, Mo, V, Ti, Si), which are signed with "Me". This is confirmed by the GDOES analysis.

A considerable modification in phase composition is showed of the coatings deposited at 650^oC and 850^oC after VHT. The level of the diffusion interaction between the condensate and substrate defines the phase composition of the coatings. In this case the temperature of metallization and the composition of the substrate are of a great interest. The phase transformations occur according the following sequence:

1) For the *condensate*: $CrN \rightarrow Cr_2N \rightarrow (Cr,Me)_2N \rightarrow (Cr,Me)_2CN \rightarrow (Cr,Me)_{23}C_6 \rightarrow (Cr,Me)_7C_3$ and respectively 2) For the *substrate*: $(Cr,Me)_2CN \rightarrow (Cr,Me)_7C_3$.

The ways of obtaining the phase $(Cr,Me)_2CN$ in the condensate and the substrate are different and depends on the velocity of diffusion of the different elements, or on the variation of the chemical compositions after the triple diagrams Cr-CrN-CrC и Cr-Fe-C.

After VHT in the coatings deposited at 650^oC the phase CrN is missing. It transforms first into a nitride Cr_2N, then into a carbonitride $(Cr,Me)_2CN$ and finally into a carbide $(Cr,Me)_{23}C_6$. The coatings, deposited at 850^oC after VHT are transformed from a mono-phase (CrN) to a three-phase composition ($Cr_2N + (Cr,Me)_2CN + (Cr,Me)_{23}C_6$). At the both temperatures it is observed patterns

of the phase $(Cr,Me)_7C_3$ coming from the substrate. The specificity of the coatings deposited at 650^oC after VHT, is the phase $(Cr,Me)_{23}C_6$ which eighter is missing or is in very small quantity. This shows a stronger diffusion in comparison with the coatings deposited at 850^oC.

Chemical composition

All the coatings deposited in T_m between 450 and 600^oC have the same structure and arrangement of the elements in depth. According to the General Model the coatings are VC with diffusion bond [11]. Until 850^oC the coatings are classified as transitional ones depending on their total thickness. The depth profile outlines four zones [10], but in the coating deposited at 650^oC and 850^oC after VHT additional underlayers appear.

The heat treatment of the coatings in this case leads to a significant redistribution of the elements of the condensate and the substrate. This causes a forming, by a phase recrystallization, of a transitive diffusive layer consisted of two underlayers $\delta_{tdl} = (\delta_{s \to c} + \delta_{c \to s})$. After VHT, the deposited at 650^oC and at 850^oC coatings on Ch12M are transformed into VDC without RC. In the coatings deposited at 650^oC the first underlayer $\delta^1_{s \to c}$ is equal by chemical composition to the $(Cr,Fe,Me)_2CN$ phase from the diagram Cr-CrN-CrC [4], while the second underlayer $\delta^2_{s \to c}$ is equal to $(Cr,Fe,Me)_{23}C_6$ from the diagram Cr-Fe-C [4] - Fig.1. In the substrate it is formed an underlayer $\delta_{c \to s}$ with chemical composition equal to the phases $(Cr,Me)_7C_3 + \alpha\text{-(Fe,Cr)}$.
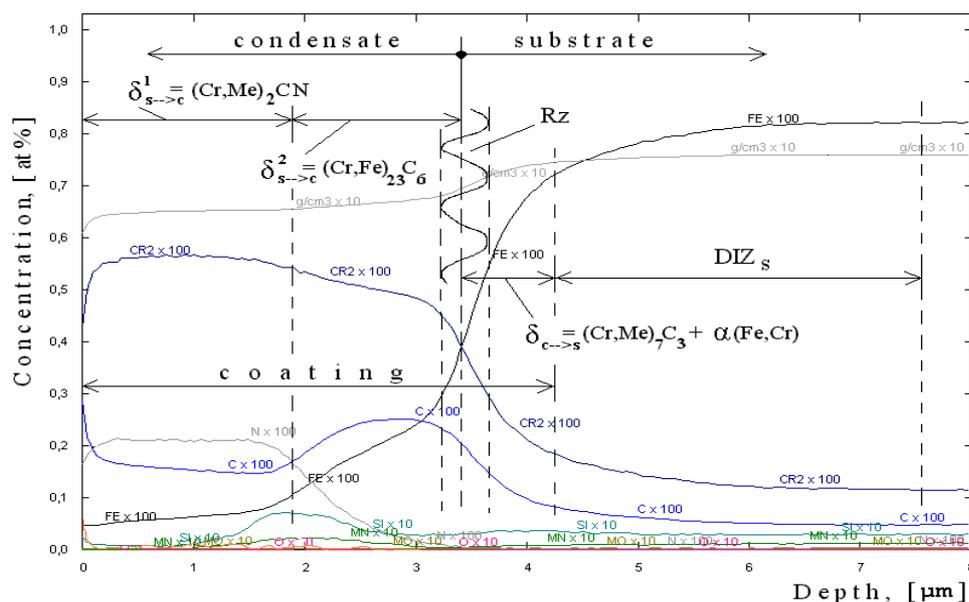

Fig.1. GDOES profile of CrN coating on Ch12M steel obtained at Tm = 650^oC, Lt-s = 70 mm and Us = 0V after heat treatment.

Its phase composition is the same as the steel, but the difference is only in the quantity of the phases. Actually the underlayer $\delta_{c \to s}$ is gradually transformed in a Diffusive Influence Zone in the substrate (DIZ_S). It is due to the stopping role of the underlayer $\delta^2_{s \to c}$, which has a carbide structure.

In the coatings deposited at 850^oC , after VHT, the outer diffusive underlayer is with different chemical composition and has consists of phases $(CrN + Cr_2N)$ – Fig2. The underlayer $\delta_{c \to s}$ situated in the substrate at the side of the condensate is built of the phases

$(Cr,Me)_7C_3 + \alpha\text{-}(Fe,Cr)$. Obviously the second heating for hardening from 1020 ^{o}C has led to an extra reallocation of the elements in the condensate and the substrate.
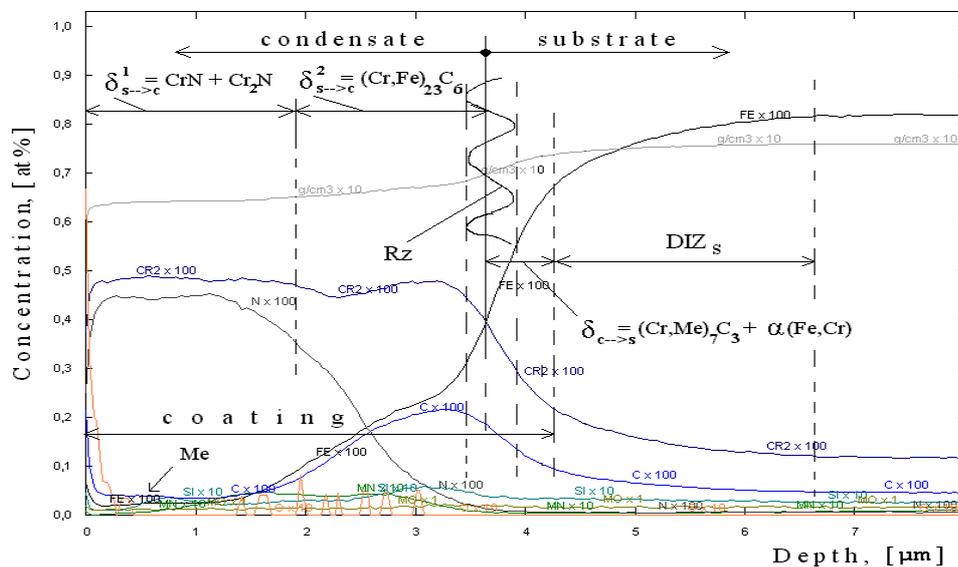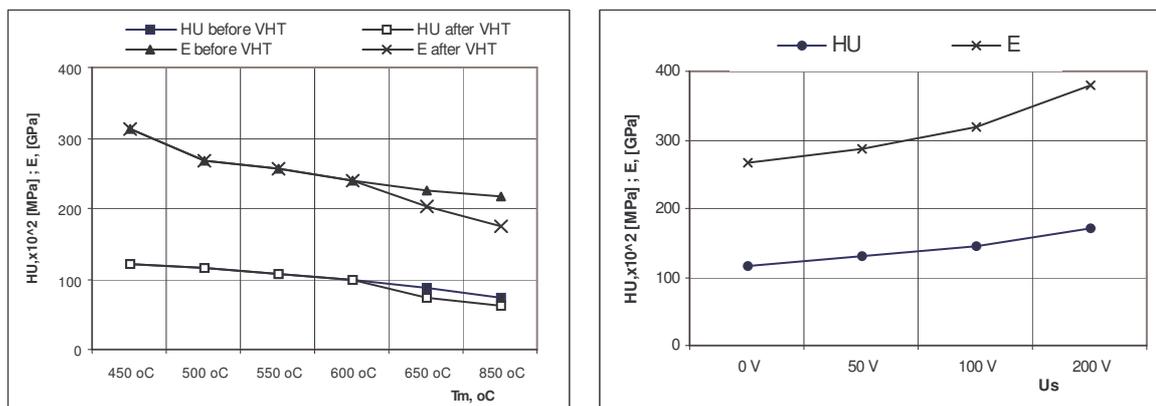

Fig.2. GDOES profile of CrN coating on Ch12M steel, obtained at Tm = 850°C, Lt-s = 70 mm and Us = 0V after heat treatment.

Micro hardness and Young's modulus

The coatings obtained in the interval $T_m=450\div850^oC$ (before and after VHT) and at a bias voltage $U_s=0\div\text{-}200V$ have a universal hardness HU and effective Young's modulus E, measured on a plane, as shown of Fig. 3.

a)   b)

Fig. 3. Vickers hardness of the coatings as a function
of the metallizing temperature T_m (a) and bias voltage U_s (b) of Ch12M substrates.

The result is in connection with the lowering of the internal stresses and also with the increase of the N_2 content. Generally the not so far high hardness is due in addition to the significant axial texture according <200>.

4. CONCLUSIONS

- The coatings obtained in the interval 450 - 600°C have a light gray color. Their topography and microstructure correspond to the IInd Zone of The Thornton's Zone model. These obtained at 650 °C and especially at 850 °C are dark gray and correspond to the IIIrd Zone of Thornton's model.

- Up to 850°C the coatings are with micro-diffusive bond to the substrate and 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 hardening heat treatment of the system CrN/Ch12M steel transform the type of the coating from a vacuum condensate with a micro-diffusive bond to the substrate into a vacuum-diffusive coating with or without residual condensate changing from chromium-carbonitride to chromium-carbide phase composition.

- The plasma-vacuum deposition process of vacuum condensates built only of CrN on the steel Ch12M or another steel of this group can not be used as a preliminary process, because the vacuum heat treatment (hardening and tempering) changes the type of the coatings and their phase composition.

- Chromium-carbide or chromium-nitride vacuum-diffusion coating with K_{DC}=1 can be obtained on Ch12M steel substrates by previous or accompanied deposition of condensate sputtering a chromium or ferro-chromium target for time 60 min (direct or indirect process) combined with a vacuum heat treatment

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