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Heat treatment of (Cr,Me)N coatings deposited on a low-alloy steel

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(Cr,Me)N coatings are deposited on substrates of steel 9XC by magnetron sputtering of a FeCrC200 target 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 substrate is carried out in a double-chamber vacuum furnace. The chemical and phase composition of the coatings, the lattice parameter and texture coefficient are determined by XRD and GD-OES analyses. Their micro hardness also have been investigated.

1. INTRODUCTION

The coatings of the type (Cr,Me)N 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°C to 650 ^{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, 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 heat resistant Cr and Ti based nitrides and carbides is an impossible process due to the unallowable changes in the substrate structure and properties. Simultaneously, it can be noted that the scientific information about the possibility such coatings to be used in practice at high temperatures is poor. There exists in essence a very small amount of investigations about the above-mentioned problem and they mainly concern the stability of the Cr and Ti based carbides and nitrides during an annealing [1,5]. 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 steel explored.

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

Ist: To want extent the substrate temperature can be increased during the deposition of (Cr,Me)N coatings without a transformation of the process from a vacuum metallization

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which forms vacuum condensates having an adhesive or micro diffusive bond to the substrate 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 $0,3 \div 0,5$ [3].

IInd: What changes in the coating structure and properties will occur during a following quenching and tempering carried out in dependance on the steel chemical composition and its specificity of heat treatment.

IIIrd: 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 steels.

2. EXPERIMENTAL PROCEDURE

The coatings have been deposited in a single-chamber vacuum furnace with a built-in DC unbalanced magnetron [3]. After reaching an initial vacuum of $6 - 8.10^{-4}$ mbar, before depositing the films, the substrates have been heated to the corresponding metallizing temperature T_m, ranging between $450 - 850$ ^{o}C. Reaching the vacuum of $4 - 6.10^{-4}$ mbar, cleaning is carried out under the conditions of glow discharge in Ar flow at 2.10^{-1} mbar for 5 min at 900 V. A ferrochromium alloy target of the type FeCrC200 (60%Cr, 34%Fe, 2%Si, 2%C, impurities) has been sputtered at a pressure $6 - 8.10^{-3}$ mbar in a flow mixture of Ar– 3.5 sccm and $N_2 - 26$ sccm for 60 min at a sputtering power of 3kW(I_{sp}=7A. The condensation rates have been $0,06 - 0,14$ µm/min for a target-to-substrate distances $L_{t-s} = 70$ and 95 mm. The substrate bias U_s has been 0 V, except the experiments at 500 ^{o}C, which have been carried out at substrate potentials of 0, -50, -100 and -200 V respectively. Samples of steel 9XC according to the Bulgarian State Standard ($0,85 - 0,95$%C, $0,3 - 0,6$%Mn, $1,2 - 1.6$%Si, $0.95 - 1,25$%Cr) have been used for substrates. The pressure and the gas flows have been controlled by an ionization vacuum meter and a mass-flow controller [4]. After the deposition, the coated substrates have been heat treated in a double-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 ($840 \div 850$ ^{o}C) includes an intermediate keeping at 650 ^{o}C for 60 min.

The chemical composition has been determined by Ar glow discharge optical emission spectroscopy (GD-OES) using a Leco 750GDS instrument. The crystallographic structure and axial texture of the films have been analyzed by X-Ray diffraction (XRD) using Fe K_α radiation. The micro hardness has been measured by a Vickers micro-indentation tester using a load 0,3 N. The thickness of the films has been determined on a cross section.

3. RESULTS AND DISCUSSIONS

Microstructure and topography

According to their appearance the coatings can be separated into two groups. The first group includes the coatings obtained in the interval $T_m = 450 \div 600$ ^{o}C and having a light gray or milk-gray color, corresponding to this of CrN. The second one includes the coatings obtained at 650 and 850 ^{o}C and having 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. The X-ray and GD-OES results proves the second explanation.

The exploring of the coatings topography at magnifications x500 and x1000 and, as well, the processing of the digital image by the program IMAGE PRO PLUS show significant changes occurring at $T_m = 600 \div 650^oC$. 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 $(0,7 – 0,8)\, T_m$ [6] and in the given case for (Cr,Me)N it corresponds to 600 – 650 ^oC. The recrystallization process means an intensive volume diffusion and a possibility for a diffusive interaction with the substrate if the latter has an appropriate chemical composition.

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 ratio between the condensation and diffusion rates 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 $T_m = 600$ ^oC the coatings are extremely disperse having a columned structure while at a negative bias to the substrate the dispersion increases and at $T_m = 500$ ^oC, $U_s = $ -100, -200 V it is not columned but sooner consists of equal axial grains. This fact shows that the overheating of the depositing 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 single-layer.

The coatings of the second group, deposited at $T_m = 650 \div 850$ ^oC contain intermediate layers which is an evidence for a diffusive interaction between the condensate and substrate. The intermediate layers obtained at 650 ^oC are thin, whereas those, obtained at 850 ^oC take the half thickness of the coatings.

The heat treatment of the coatings deposited at 650 ^oC and 850 ^oC causes no changes in the topography, but the intermediate layer in the coatings obtained at 650 ^oC already takes 1/3, while in these obtained at 850 ^oC– 2/3 of the total thickness. Except for this, the coatings deposited at 850 ^oC contain three underlayers. The inner one has appeared as a result of the additional diffusive interaction with the substrate when being heated during the heat treatment.

Chemical composition

The GD-OES analyses show that the coatings obtained up to $T_m = 600$ ^oC are condensates (Fig.1) with a micro diffusive bond to the substrate [4]. The depth profile outlines four zones:

The Ist zone is up to 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 their separation in the beginning of the GD-OES analyses

The 2nd zone is the real part of the coating, in which the contents of the main elements Cr, Fe, N, Si, W and C remain constant. It is a fact of interest that there is no presence of O, whereas the C quantity is about $0,5 \div 1$ at. % and corresponds to that of the target. This fact proves that the oxidizing potential of the residual atmosphere in the vacuum furnaces with graphite components is lower than this of the vacuum metallizing chambers. According to the scientific information it corresponds to a vacuum deeper two or more times. Another feature is the increase of the N from about 40 at. % to 50 at% when increasing the L_{t-s} from 70 to 95 mm respectively. The negative bias has an analogous effect at –100 and –200 V. The N

content reaches 50 %. This facts means that the back sputtering from the coating surface owing to the bombardment by Ar ions affects predominantly on the metal atoms.

The IIIrd zone lies at the inner side of the condensate to the substrate and can be named a Diffusive Influence Zone (DIZ) in the condensate [4]. It is characterized with a lowering of the Cr and N amount and an increase of the Fe, Si and C content.
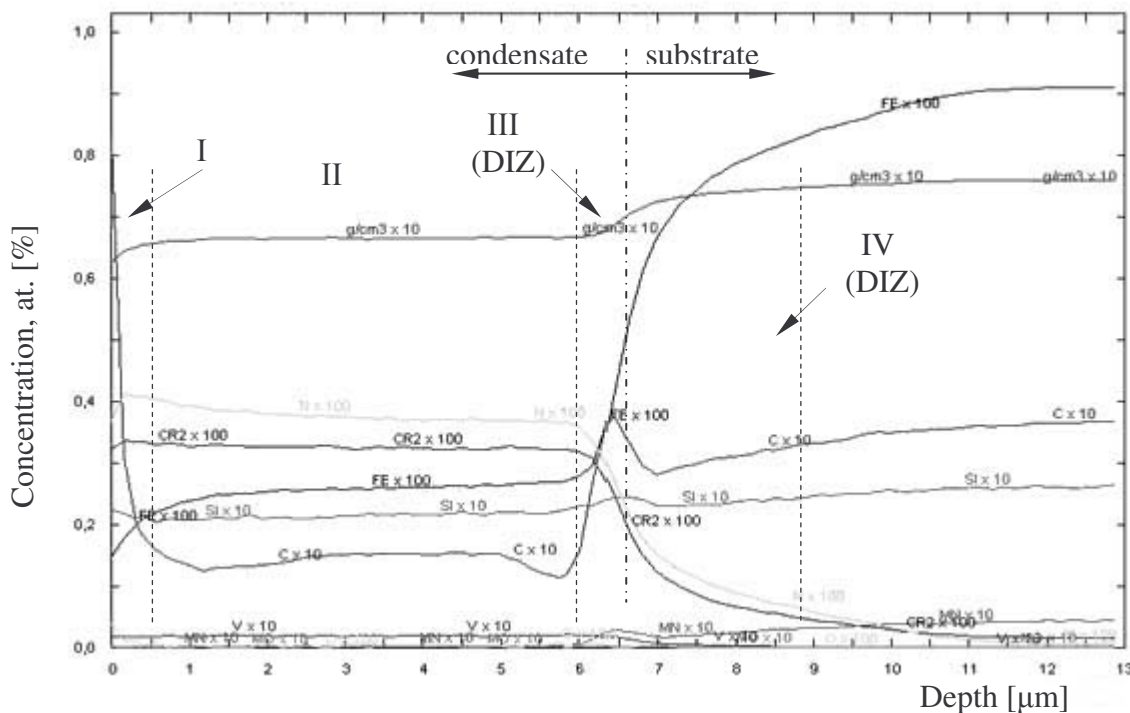

Fig. 1. GD-OES profile of a (Cr,Me)N coating on 9XC steel,obtained at T_m = 450 ^{o}C, L_{t-s} = 70 mm and U_s = 0 V

The IVth zone is the DIZ in the substrate 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.

The second group coatings (obtained at 650 ^{o}C and 850 ^{o}C) are characterized with an intensive redistribution of the elements between the substrate and condensate. At 650 ^{o}C the formation of an intermediate transition diffusive layer drops behind due to the slower redistribution of the Cr and Fe in comparison with that of the N and C, whereas at 850 ^{o}C (Fig.2) this result is not well expressed. It is seen that the outer underlayer corresponds by a composition to $(Cr,Me)_2CN$, but the inner one to the substrate - to $(Cr,Me)_{23}C_6$.

This result permits to conclude that at T_m > 600 ÷ 650 ^{o}C in parallel with the condensate growth an intensive diffusive interaction between it and the substrate runs and causes structural changes in the condensate. They are in connection with a phase transformation occurring in the following sequence: $(Cr,Me)N \rightarrow (Cr,Me)_2N \rightarrow (Cr,Me)_2CN \rightarrow (Cr,Me)_{23}C_6$. The saving of the outer underlayer of $(Cr,Me)_2CN$ shows that the inner underlayer $(Cr,Me)_{23}C_6$, arose for once, serves as a barrier against the further redistribution of the C and N between the condensate and substrate.

Phase composition and lattice parameter

The results from the X-ray diffraction analyses prove the interpretation of the information from the GD-OES investigation. Up to $T_m = 600$ ^{o}C the coatings contain mainly the phase (Cr,Me)N, whereas at the lower temperatures there is a presence of (Cr,Me)$_2$N. The peaks of the phases (Cr,Me)$_2$CN and (Cr,Me)$_{23}$C$_6$ appear mainly in the X-ray patterns of the coatings obtained at $T_m > 600$ ^{o}C and after their heat treatment.
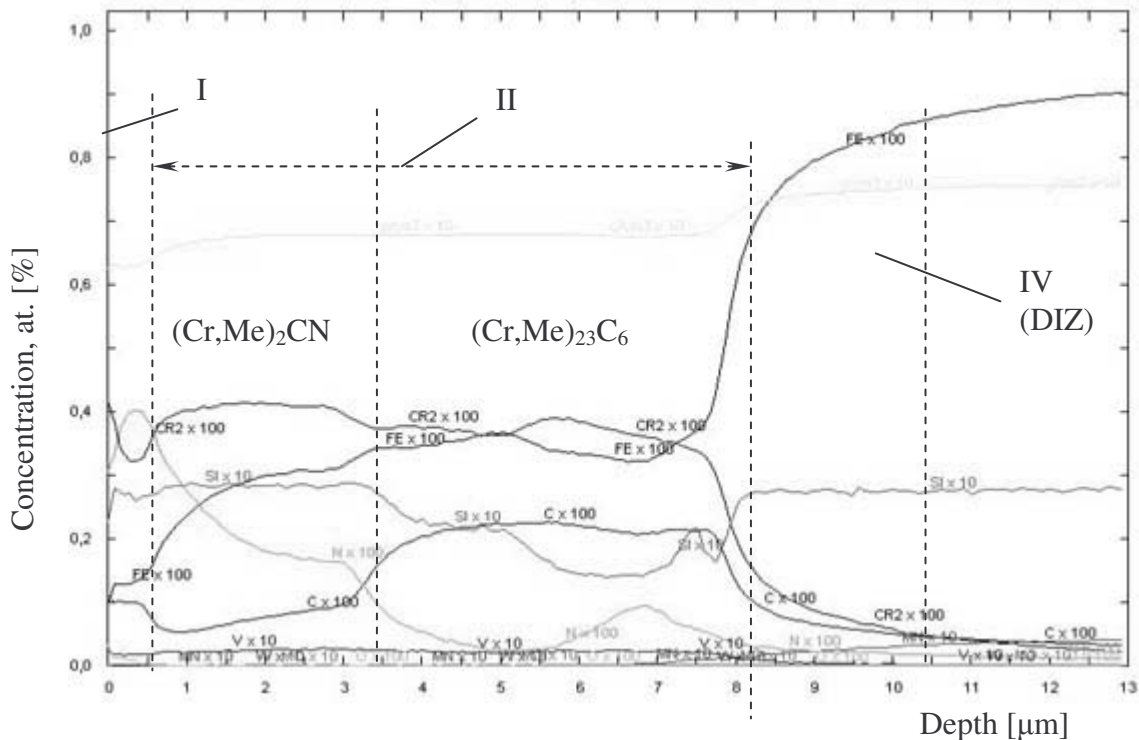

Fig. 2. GD-OES profile of (Cr,Me)N coating on 9XC steel, obtained at $T_m = 850$ ^{o}C, $L_{t-s} = 70$ mm and $U_s = 0$ V

The crystal lattice of the (Cr,Me)N is strongly deformed in the interval $T_m = 400 \div 600$ ^{o}C and the lattice parameter is less than the theoretical one. When increasing T_m it increases and the deformations tend to a zero level. This result is in relation with the lessening of the Fe and Si on one hand and increase of the Cr on the other hand. At the same time, the N content enhances to 50%.

Micro hardness and texture

After the X-ray patterns the coatings have a well-expressed texture. In all cases up to $T_m = 600^o$C there exists a predominant axial orientation according to <200>. The texture coefficient [2] decreases from 0,8 to 0,4 when rising temperature and increases when enhances U_s, having the highest value of 1 at $U_s = -100$ V.

The coatings obtained at $L_{t-s} = 70$ mm in the interval $450 \div 600$ ^{o}C have a hardness, measured on a plane, diminishing from 1400HV to 850HV. The result is in connection with the lowering of the internal stresses and also with the increase of the N content which leads to a lessening of the harder phase (Cr,Me)$_2$N and to a running of a coalescence processes. Generally the not so far high hardness is due, in addition, to the significant axial texture

according <200>. The jump of the hardness up to 1600HV at 650 ^{o}C is due to the commented diffusive interaction with the substrate of the C and N and the turning of (Cr,Me)N consecutively into (Cr,Me)$_2$N and to a lower degree – into (Cr,Me)$_2$CN, which phases have a higher hardness. The coatings obtained at 850 ^{o}C 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,Me)$_{23}$C$_6$. Its hardness is lower than that of the Cr-based nitrides. More over, a certain amount of the phase αCr$_{(Fe)}$ is formed according the GD-OES and X-ray analyses and taking into account the diagram Cr – Fe – C.

4. CONCLUSIONS

- The coatings obtained in the interval 450 ÷ 600 ^{o}C are light (or milk) gray, resistant against etching and have topography and microstructure corresponding to the IInd Zone of The Thornton's Zone model. These obtained at 650 ^{o}C and especially at 850 ^{o}C are dark gray and correspond to the IIIrd Zone of Thornton's model.
- Up to 600°C the coatings are built mainly of the phase (Cr,Me)N. Four zones can be distinguished in them: the Ist one, to 0,5 μm thick, is situated at the surface and has an increased content of metalloids (C, N, O) at the expense of the metals (Cr, Fe); 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.
- Coatings obtained at 650 and 850 ^{o}C are double-layer with a changed phase composition due to the diffusive interaction with the substrate, respectively: (Cr,Me)N + (Cr,Me)$_2$N + (Cr,Me)$_2$CN at 650 ^{o}C, but at 850 ^{o}C the main phases are (Cr,Me)$_2$N + (Cr,Me)$_2$CN + (Cr,Me)$_{23}$C$_6$.
- The quenching and tempering processes of steel 9XC covered with a coating (Cr,Me)N turn the latter into a double-layer or triple-layer one built of the phases (Cr,Me)$_2$N, (Cr,Me)$_{23}$C$_6$ and αCr$_{(Fe)}$ with no residual condensate.
- In conclusions it could be said that vacuum coatings – condensates, built of (Cr,Me)N can be obtained on substrates of low-alloy tool steel up to T$_m$ = 600 ^{o}C. At temperatures higher than 600 – 650 ^{o}C and during heat treatment (hardening and tempering) they turn into plasma vacuum-diffusive coatings built mainly of the phases (Cr,Me)$_2$CN and (Cr,Me)$_{23}$N$_6$. The result means that the deposition process of vacuum coatings – condensates built only of (Cr,Me)N on the steel 9XC can not be run as a preliminary process.

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