POLISH ACADEMY OF SCIENCES - COMMITTEE OF MATERIALS SCIENCE
SILESIAN UNIVERSITY OF TECHNOLOGY OF GLIWICE
INSTITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS
ASSOCIATION OF ALUMNI OF SILESIAN UNIVERSITY OF TECHNOLOGY
Conference Proceedings
12th INTERNATIONAL SCIENTIFIC CONFERENCE
ACHIEVEMENTS IN MECHANICAL & MATERIALS ENGINEERING

Investigation of CrN coatings, deposited on a stainless steel under high temperatures

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

CrN coatings have been deposited on a 0Ch18N9T stainless steel substrates by DC unbalanced magnetron sputtering of a sintered chromium target in a single-chamber vacuum furnace with a graphite heater and a heat-isolative chamber, made of carbon wool. Four working substrate temperatures were used Ts= 450, 550, 650 and 850 °C. The surface morphology, chemical and phase composition of the coatings are determined by GDOES and XRD analyses. The micro-hardness, Young's modulus and energy of plastic deformation of the coatings also have been investigated. The influences of the deposition conditions on a mechanical characteristics, chemical and phase composition are discussed.

1. INTRODUCTION

The coatings of the type CrN having an appropriate structure, properties and at the same time a good adhesion to the substrate is usually obtained in the temperature range from 350°C to 550°C. That is the reason in the most of the investigations as substrates for these coatings to be used heat-resistant or corrosion-resistant austenite steels [1,4,6,7,9] and the metallization process to be carried out usually as a final treatment. There exists a very small amount of investigations on the problem of deposition of Cr and Ti based nitrides and carbides at higher temperatures. The process is impossible due to the unallowable changes in the substrate structure and properties and the existing works oncern the stability of the Cr and Ti based carbides and nitrides during an heating above 550°C [1,4,7]. The deposition of the coatings at temperatures above 550 - 600°C is insufficiently investigated area.

The facts mentioned above poses some problem, which determine the aim of the present work: to what 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 between 0,3-0,5 [10].

2. EXPERIMENTAL PROCEDURE

The coatings have been deposited in a single-chamber vacuum furnace with a built-in DC unbalanced magnetron. After reaching initial vacuum of 6 - 8.10^{-4} mbar, before depositing the films, the substrates have been heated to the corresponding metallizing temperature Ts= 450, 550, 650 and 850^{o}C. Reaching the vacuum of 6.10^{-4} mbar, cleaning is carried out under the conditions of glow discharge in Ar flow at 1- 1,5.10^{-1} mbar for 10 min at 900 V. A sintered pure 99,998% chromium target has been sputtered at a pressure 6 - 7.10^{-3} mbar under a flow mixture of Ar - 2,6 sccm and N_2 - 26,5 sccm, for 60 min at a sputtering power of 3,2 kW (Isp= 8A), providing condensation rates of 80- 96 nm/min for a target-to-substrate distance Lt-s = 70 mm. Samples of stainless steel according to the Bulgarian State Standard stainless steel 0Ch18N9T with chemical composition <0,08%C, 17-19%Cr, 8-11%Ni, <2,0%Mn, <0,3%Mo and ~0,7%Ti (in Euronorm X10CrNiTi18-10) have been used for substrates. The chemical composition has been determined by Ar glow discharge optical emission spectroscopy (GDOES) using a Leco 750GDS® instrument and by JXA 733 on the SEM (JEOL SUPERPROBE 733). The crystallographic structure of the films has been analyzed by X-Ray diffraction (XRD) using Co-Kα radiation. A Vickers nanoindentation tester FISCHERSCOPE® H100 using a load 50 mN has measured the micro-hardness, Young's modulus and energy of plastic deformation of the films. The morphology and thickness of the coatings has been determined on a cross section, using a NIKON-OPTIPHOT® metallographic microscope.

3. RESULTS AND DISCUSSIONS

The coatings, according to their appearance, can be separated into two groups. *The first group includes the coatings,* obtained in the temperatures of substrate Ts = 450, 550 and 650^{o}C and having a light-gray color.

The exploring of the coatings topography at magnifications x1000 shows significant changes occurring at Ts = 650^{o}C. The coatings obtained up to Ts=650^{o}C fit to the II^{-nd} Zone of the Thornton's Zone Model, while those, obtained at 650 and especially obtained at 850^{o}C fit to the III^{-rd} Zone [12,13]. 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 [5,12,13] and in the given case for CrN it corresponds to ~650^{o}C. The recrystallization process means intensive volume diffusion and a possibility for a diffusive interaction with the substrate if the latter has an appropriate chemical composition [10,11].

The microstructure investigations on a cross section prove and add to the above said. Till Ts = 650^{o}C the coatings 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 [10].

The depth GDOES profile outlines four zones (Fig.1):

The Ist zone is up to 0,3 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 GDOES analyses

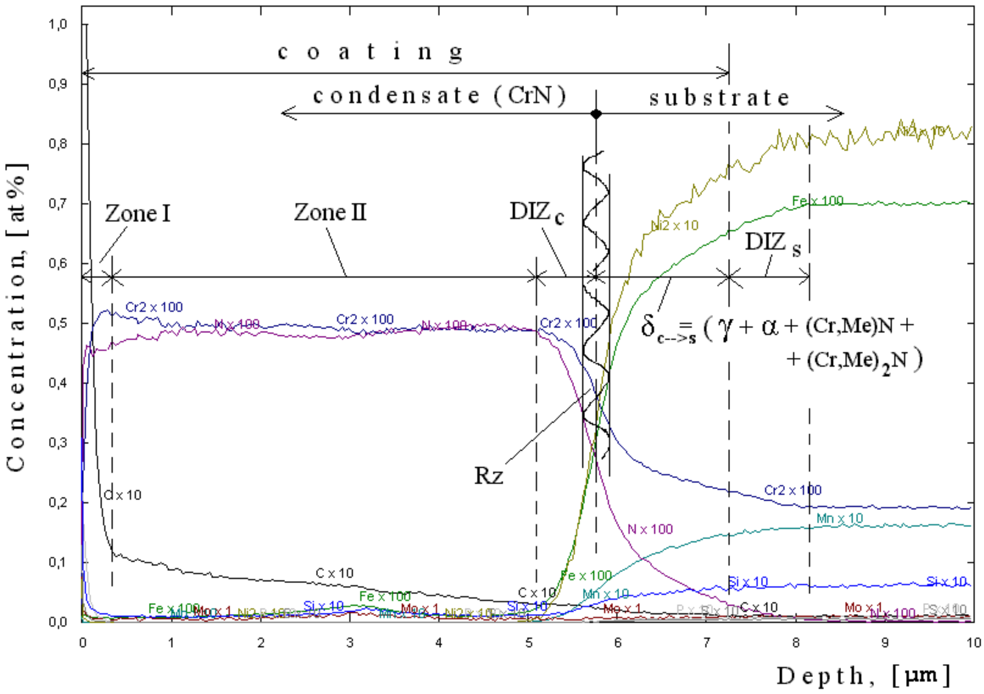

Fig.1. GDOES profile of CrN coating on a 10Ch18N9T stainless steel, obtained at Ts = 650°C, Lt-s = 70 mm and Us = 0 V.

The IInd zone is the essential part of the coating, in which the contents of the main elements Cr, N_2, Fe, Si, and Mn remain constant. It is a fact of interest that there is no presence of O_2, whereas the C quantity is about 0,3 ÷ 1,0 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.

The IIIrd zone situated at the inner side of the condensate to the substrate can be named a Diffusive Influence Zone (DIZc) in the condensate [10]. It is characterized with a lowering of the Cr and N_2 amount and an increase of the Fe, Ni, Mo and Si content.

The IVth zone is the DIZs in the substrate and is fully situated in it. Here there is an obvious saturation with Cr and N_2 from the condensate and a lessening of the elements contained in the substrate.usually

After the XRD and GDOES analyses in the substrate at the side to the condensate between the IIIrd and IVth zones there exists a Transitional Diffusive Layer (TDL). It consists of one underlayer $\delta_{c\rightarrow s}$ (Fig.1). Most probably its phase composition is (γ-$Fe_{(Cr)}$+ α-$Fe_{(Cr)}$+ (Cr,Me)N +$(Cr,Me)_2N$), where the additional elements (mainly Fe and Ni, Ti, Si, Mo,V) are signed with the symbol “Me”.

The reason for this phase composition of the TDL is the diffusive mechanism of its forming, and can be explained as follows: in the triple diagram Cr-Fe-Ni the composition of the stainless steel 10Ch18N9T is at the borderline of the one-phase zone γFe and two-phase zone (γFe + αFe) [2,3,8]. The entering of Cr atoms in the substrate decreases on one hand the quantity of Ni atoms provokes on the other hand the transformation γFe→ αFe. In this case by calculating the coefficient of Cr and Ni by structural diagram of the stainless steels it is defined the quantity of αFe which is about 30-40% at the border with the condensate and reaches 5-10% at the border with DIZs. When the Cr concentration reaches 22-23% it should start a detachment of σ-phase. This does not happen because the entering of the N_2 in the substrate outstrips the entering of the Cr leads to the forming of an alloyed chromium nitrides (Cr,Me)N and $(Cr,Me)_2N$. Their quantity decreases in depth of the substrate . Thereby it is forming TDL, consisted of $\delta_{c\rightarrow s}$ (TDL = $\delta_{c\rightarrow s}$) with phase composition γ-$Fe_{(Cr)}$+ α-$Fe_{(Cr)}$+ (Cr,Me)N +$(Cr,Me)_2N$ [2,3,8]. The thickness of the TDL in comparison with the total thickness of the coating defines the coefficient of diffusion of the coating K_{DC}, and with it and the type of the last one.

The higher temperatures start the recrystallization processes accompanied by strong diffusion which according to the conception of the General Model for vacuum and vacuum-diffusive coatings (GM) for defining the thickness of TDL change significantly the situation [10].

The coatings of the second group, obtained at Ts=850°C contain a large intermediate layer, which is an evidence for their diffusive interaction with the substrate (Fig.2).

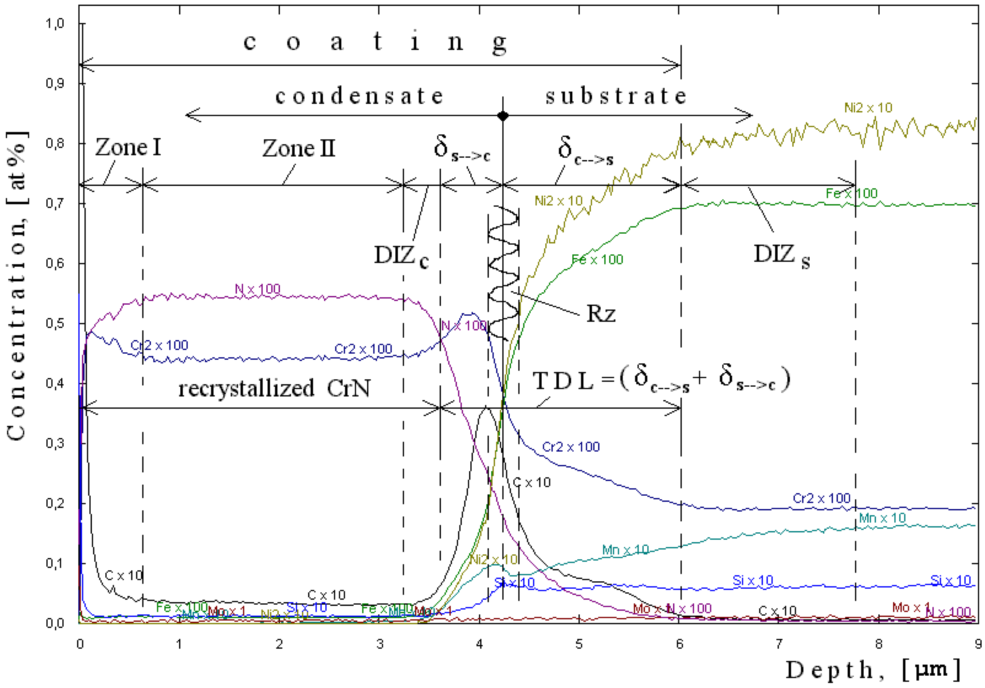

Fig.2. GDOES profile of a CrN coating on a 0Ch18N9T stainless steel, obtained at Ts = 850°C, Lt-s = 70 mm and Us = 0 V.

At Ts=850°C the type of the coating is already completely changed. First, TDL consists of two underlayers: TDL = $\delta_{s\rightarrow c}$ + $\delta_{c\rightarrow s}$. The underlayer in the coating $\delta_{s\rightarrow c}$ has a chemical composition equal to phase structure $\delta_{s\rightarrow c}$=$(Cr,Me)_2CN$ + α-$Cr_{(Fe)}$, whereas the underlayer in the substrate $\delta_{c\rightarrow s}$ is the same as that obtained at lower temperatures. Second, TDL is 2,6 µm thick and its color is dark grey. 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 oxygen is not detected in X-ray and GDOES results which proves the second explanation.

Because the thickness of TDL is about 2,5 µm (and K_{DC}~4,0), the coating belongs to vacuum-diffusive coatings with a residual condensate (VDC with RC). In the case of Ts = 850°C the coating is completely recrystallized which is confirmed by the measured values of universal hardness HU, Young's modulus E and energy of plastic deformation Wr (Fig.3). If take for instance the conception of GM, the recrystallized RC has a structure and properties close to these created with a classical thermo-chemical treatment of the steels (diffusive metallizing by plasma-vacuum method under the reaction scheme (PVDM-R) [11]), which belongs to TDL. So the coating created at Ts = 850°C belongs to the vacuum-diffusive coatings without a residual condensate (VDC without RC).

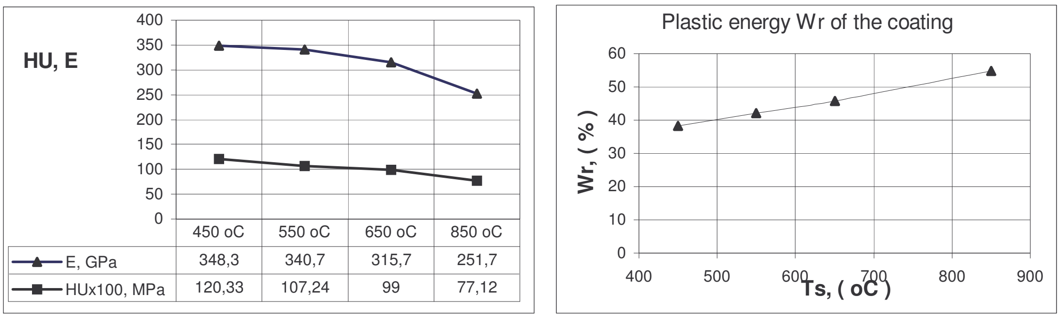

Fig.3. Dependence of the coating properties on the substrate temperature Ts:
a/ Young's modulus E and universal hardness HU; b/ energy of plastic deformation Wr.

A decrease of the mechanical characteristics of the CrN coatings deposited at high temperatures on a stainless steel substrate is due to the following reasons: a developing of the recrystallization processes in the coatings, and a partial transformation of the CrN film in the underlayer $\delta_{c\rightarrow s}$ containing $(Cr,Me)_2CN + \alpha\text{-}Cr_{(Fe)}$.

CONCLUSIONS

- The coatings obtained in the temperature interval 450 ÷ 650 °C are light-gray, resistant against etching and have topography and microstructure corresponding to the IInd Zone of The Thornton's Zone model. These obtained at 850 °C are dark-gray and correspond to the IIIrd Zone of Thornton's model.
- Up to 650°C the coatings are built mainly of the phase CrN. Four zones can be distinguished in them: the Ist one, to 0,2-0,3 µm thick, is situated at the surface and has an increased content of metalloids (C, N_2, O_2) 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 850 °C are double-layer with a recrystallization CrN phase and changed phase composition due to the diffusive interaction with the substrate and built of the phases $CrN + (Cr,Me)_2CN + \alpha\text{-}Cr_{(Fe)} + \gamma\text{-}Fe_{(Cr)} + \alpha\text{-}Fe_{(Cr)} + (Cr,Me)N + (Cr,Me)_2N$.
- The mechanical characteristics of the CrN coatings obtained at 850 °C - Young's modulus E and universal hardness HU decreases with 30% and 35% respectively, whereas their plasticity increases with 35%.
- During the deposition at temperatures higher than 650 °C the CrN coatings turn from vacuum condensates with a micro-diffusive bond to the substrate into plasma vacuum-diffusive coatings without a residual condensate.

In conclusions it could be said that vacuum coatings - this is condensates, built of CrN, that can be obtained on substrates of stainless steel 0Ch18N9T up to T_s=650°C. At higher temperatures they turn into plasma vacuum-diffusive coatings without a residual condensate during the deposition.

REFERENCES

1. Broszeit E., C.Friedrich, G.Berg, Surf. and Coat.Technology, 115 (1999), 9-16.
2. Doubinin G. N., Diffusive chromising of alloys, Moscow, Machine building, 1964 (in Russian)
3. Gaulliaev A. P., Metal-science, Moscow, Metallurgia, 1977 (in Russian)
4. Gautier C., J.Machet, Thin Sold Films, 295 (1997), 43 – 52
5. Gorelik S. S., Crystallization of the metals and alloys, Moscow, Metallurgia,1978 (in Russian)
6. Heinke W., Leyland A., Matthews A., Berg G, Friedrich C.,Broszeit E., Thin Solid Films, 270 (1995) 431-438
7. Hirai M., Ueno Y., Suzuki T., Jiang W., Grigoriu C., Yatsui K., Jpn.J.Appl.Phys., 40 (2001) 1052-1055
8. Ponomarenko E. P., Metallizing of steels and alloys in vacuum, Kiev, Technika, 1974 (in Russian)
9. Rutkowska A., Dabrowski M., Zeszyty naukowe-Mechanika 38 (1995) 191-198 (in Polish)
10. Shishkov R., E. Lisichkova, Vacuum, 46, 11 (1995), 1337-1346
11. Shishkov R., Vacuum, 46, 12 (1995), 1357-1360
12. Thornton J. A., Ann. Rev. Mater. Sci., 7 (1977) 239-260
13. Thornton,J., Thin J., Thin Solid Films, 54 (1978) 23