

STRUCTURE AND PROPERTIES OF OXYNITRIDE LAYERS PRODUCED UNDER GLOW DISCHARGE CONDITIONS

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A b s t r a c t. The structure and chemical composition of composite multicomponent oxynitrided layers obtained in multiplex processes that combines electrochemical chromium deposition on AISI 1045 steel and glow discharge assisted oxynitriding are described. Quantitative X-ray microanalysis shows that the layers of type: $\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{O}_3 + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_2\text{N} + (\text{Cr,Fe})_7\text{C}_3$ formed. These layers have a diffusion character and show a good adhesion to the substrate. They show very high corrosion resistance, markedly greater than that of chromium coated and only nitrided steel.

K e y w o r d s: glow discharge oxynitriding, composite layers, corrosion resistance.

INTRODUCTION

Chromium nitride layers have a high hardness and good resistance to corrosion, erosion and frictional wear. For these reasons various PVD techniques as well as relatively new methods of their production, such as a combination of electrochemical chromium deposition with glow discharge assisted nitriding are being developed. Using of oxynitriding process instead of nitriding could increase the corrosion resistance of layers obtained [1-3]. The paper presents the results of the surface morphology and corrosion resistance of the composite layers, produced by glow discharge oxynitriding of the chromium precovered steel.

EXPERIMENTAL DETAILS

The samples were made of AISI 1045 steel covered electrochemically with chromium layer of 20 μm thick, and than subjected to glow discharge assisted oxynitriding at a temperature of 560°C in nitrogen/hydrogen ($\text{N}_2 : \text{H}_2 = 1 : 1$) atmosphere with an addition of approximately 2 vol.% of air. The pressure within the reaction chamber was 3 hPa and a duration time 15 min, 120 min and 240 min.

The layers, thus obtained, were examined metallographically and their phase contributions were determined using a Philips 1830 X-ray diffractometer with a CoK_α radiation (the wavelength $\lambda = 1.7902 \text{ \AA}$). The quantitative distribution of layer forming elements was determined with a CAMECA SEMPROBE SU-30 X-ray microanalyser. The thickness and the chemical composition of very thin layers formed in the first stage of oxynitriding (15 min) were examined using a special method for thin coatings [4, 5]. The intensity measurements of K_α lines of characteristic X-rays of oxygen and nitrogen and L_α line of chromium were performed at four accelerating voltages (7, 10, 12.5 and 15 kV) and a beam current of 20 nA. Andrardite, CrN and pure chromium were used as standards. The results thus obtained were corrected using CAMECA's correction program XTFML LAYERF, based on Pouchou-Pichoir's method [4] for stratified samples. Chemical composition of much thicker layers formed in 4 hours oxynitriding process was determined using CAMECA's correction program for bulk samples, based on Pouchou-Pichoir's method [6]. K_α lines of characteristic X-radiation of all analysed elements were measured at an accelerating voltage of 15 kV and a beam current of 20 nA. The surfaces of the samples were observed in a TESLA BS-300 scanning electron microscope and in a CAMECA SEMPROBE SU-30 X-ray microanalyser. The corrosion resistance was measured by the potentiodynamic method in a 0.5M NaCl solution at a temperature of 25°C. The samples were polarized from a potential of -1000 mV towards the anodic direction with a potential varying rate of 50 mV/min and 10 mV/min within the corrosion potential region. The potential was measured with the respect to that of a saturated calomel electrode. The potentiodynamic measurements were performed using an Atlas-Solich fully computerized system. Prior to the measurements, the samples were maintained in the test solution for 24 hours so as to let the corrosion potential stabilize.

RESULTS AND DISCUSSION

Figure 1 shows the microstructures of the sample surfaces after glow discharge assisted oxynitriding for 15, 120 and 240 min.

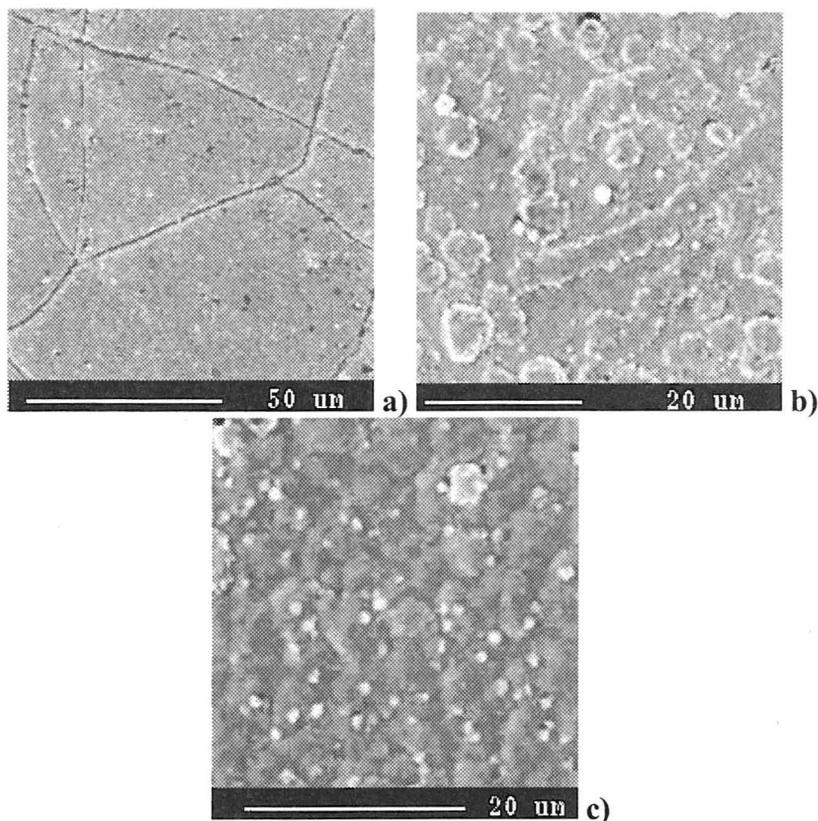


Fig. 1. Appearance of the surface of coatings produced by glow discharge assisted oxynitriding of AISI 1045 steel pre-coated with 20 μm chromium layer. Duration times: 15 min a), 120 min b), 240 min c).

After 15 min of oxynitriding the appearance of sample surface (Fig. 1a) does not differ from that before the process and X-ray diffractometry does not show any additional peaks on diffraction pattern. Yet, microanalysis shows the presence of oxygen and nitrogen on the sample surface. The chemical composition of the surface zone was analysed in smooth places between the crevices in the chromium coating, using a special method of quantitative microanalysis for thin coatings [4-6]. We have found that at the surface of the sample two different layers were formed. The top layer forms Cr_2O_3 phase of a mass thickness of $3.1 \mu\text{m}\cdot\text{cm}^{-2}$ and underneath layer forms Cr_2N phase with a $18.3 \mu\text{m}\cdot\text{cm}^{-2}$ mass thickness.

After two hours of oxynitriding, the regular "islets" in diameter of 5-6 μm and the oblong bands covering the crevices in the chromium coatings, were formed (Fig. 1b). With the increasing of the treatment time, the number of "islets"

increases so that they join one another and form larger agglomerates and finally a solid composite multilayer (Fig. 1c).

The microstructure of the multilayer formed in 4 hours oxynitriding process is shown on the cross section of the sample in the Fig. 2. The figure contains a BSE (back-scattered electrons) micrograph and X-ray maps of analyzed elements. In the BSE image bright areas corresponds to high atomic number phases and dark areas corresponds to the low atomic number ones.

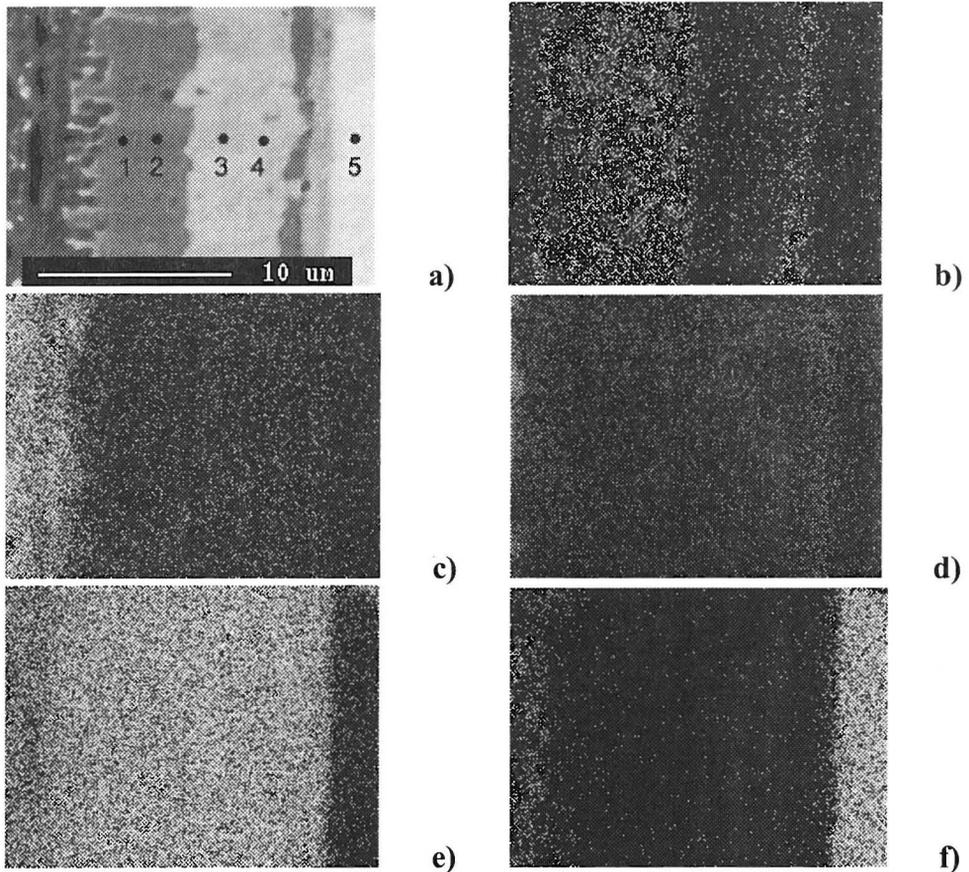


Fig. 2. Microstructure of a multilayer produced by 4 hours oxynitriding of AISI 1045 steel precovered with a 20 μm thick Cr layer. BSE image - a), and X-ray maps of: N K_{α} - b), O K_{α} - c), C K_{α} - d), Cr K_{α} - e), Fe K_{α} - f).

The concentrations of individual elements in selected microregions of the composite multilayer, marked in the Fig. 2a, are given in Table 1. The X-ray

diffraction pattern of the phases located in the near surface zone of the multilayer is shown in the Fig.3.

Table 1. Concentration of elements (at %) in selected microregions of the composite multilayer produced by oxynitriding on AISI 1045 steel precovered with a 20 μm thick Cr layer.

Place of analysis (Fig. 2a)	Distance from the surface [μm]	Concentration of elements [at %]			
		N	C	Cr	Fe
1	7	34.2	0.0	65.5	0.3
2	9	33.4	0.0	66.3	0.3
3	11	6.5	0.0	92.8	0.7
4	13	3.4	0.0	96.8	0.6
*	16.5	0.0	31.4	65.2	3.4
5	18	0.0	0.4	6.5	93.1
	30	0.0	0.4	2.1	97.4
	40	0.0	0.5	1.4	98.1

* analysis has been performed in a wider part of the layer, not visible in the Fig. 1a

One can find on the basis of these results, that the surface layer, about 2.5 μm thick, contains Cr_2O_3 oxides. Small amount of iron oxides is present in this layer. Beneath, a very thin layer (less than 1 μm thick) of CrN phase exists. Under this phase a second Cr_2O_3 layer was formed. Below, a layer of Cr_2N phase, about 7 μm thick, containing less than 1 at.% of iron, was found. Small islets of the mentioned above oxides are located in an ~ 2 μm thick zone of this layer, directly underneath of the oxide layer (internal oxidation zone). Underneath a layer of chromium, about 5 μm thick, was found. This layer contains dispersive nitrides. Between this zone and AISI 1045 steel substrate, two layers of type of $(\text{Cr}_x\text{Fe}_{1-x})_2\text{N}$ and $(\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3$, about 1 μm thick each, were identified [7]. These layers have a diffusion character and show good adhesion to the substrate.

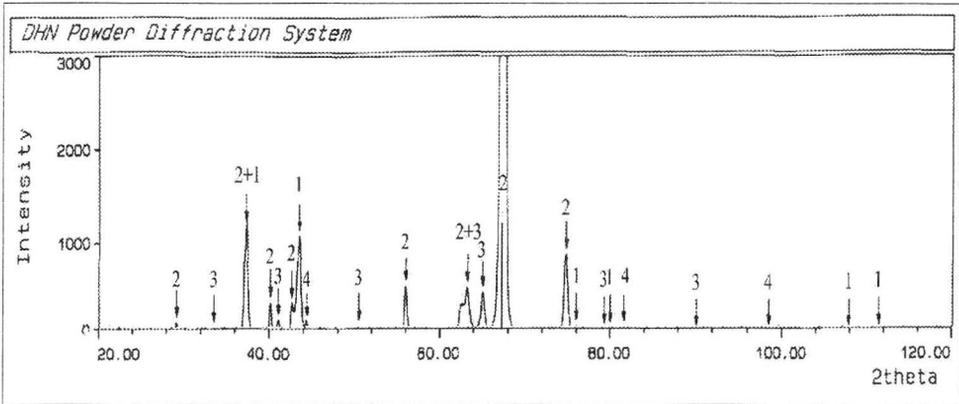


Fig. 3. X-ray diffraction pattern of a multilayer produced by oxynitriding of AISI 1045 steel precovered with a 20 μm thick Cr layer. Notations: 1 – CrN; 2 – Cr₂N; 3 – Cr, 4 – Cr₂O₃.

The formation of $(\text{Cr}_x\text{Fe}_{1-x})_2\text{N}$ layer can be explained by the presence of deep cracks in the chromium coating, through which nitrogen atoms penetrate towards the substrate, and then along the boundary between the chromium layer and the steel substrate (easy diffusion way).

The $(\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3$ sublayer formed as a result of mutual diffusion of chromium from the chromium coating and carbon and iron from the steel substrate during oxynitriding process. The hardness of the sublayer was of the order of 2600HV0.05.

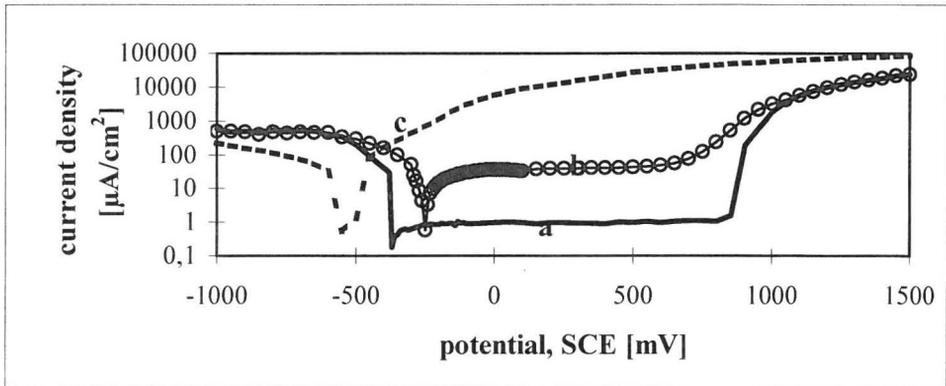


Fig. 4. Polarization curve of the $[\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{O}_3 + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_2\text{N} + (\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3]$ layers produced by glow discharge assisted oxynitriding of AISI 1045 steel precoated with 20 μm chromium layer compared with the polarization curves of the layers type of $[\text{CrN} + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3]$ produced by glow discharge assisted nitriding b) and for the only chromium coated steel c).

Figure 4 shows the polarization curve obtained for the composite layers of type $[\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{O}_3 + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_2\text{N} + (\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3]$ obtained in the oxynitriding process on AISI 1045 steel coated with chromium compared to those for the layers of type $[\text{CrN} + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3]$ obtained by glow discharge nitriding [3] and for only chromium coated steel. As can be seen from this figure, the best corrosion resistance is shown by the layers produced in oxynitriding process. Such good corrosion resistance of these samples can be explained by the presence of composite layers that contain $\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{N}$ phases within the near surface zone, and because the crevices present in chromium coating have been filled with chromium oxides and nitrides [2].

CONCLUSIONS

Glow discharge assisted oxynitriding of chromium precoated AISI 1045 steel permits the production of composite surface layers of type $[\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{O}_3 + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_2\text{N} + (\text{Cr}_x\text{Fe}_{1-x})_7\text{C}_3]$. These layers have a diffusion character and show good adhesion to the substrate. They show very high corrosion resistance thanks to the presence of the composite layers that contain Cr_2O_3 , CrN and Cr_2N within the near surface zone, and because the crevices present in the chromium coating have been filled with chromium oxides and nitrides. These advantages of the layers produced by glow discharge assisted oxynitriding of chromium precoated AISI 1045 steel open new possibilities for their application.

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REFERENCES

1. Collard S., Kupfer H., Hecht G., Hoyer W., Moussaoui H., Surface and Coatings Technology 112, 181-184, 1999.
2. Wierchoń T., Ulbin-Pokorska I., Sikorski K., Surface and Coatings Technology 130, 274-279, 2000.
3. Wierchoń T., Ulbin-Pokorska I., Precht W., Sikorski K., 12th Int. Federation for Heat treatment and Surface Engineering Congress, Melbourne, pp.31-35, 2000.
4. Pouchou J.L., Pichoir F., La Recherches Aérospatiale 5, 47-65, 1984.
5. Sikorski K., X-ray Microanalysis of Thin Coatings and Small Particles, Inżynieria Materiałowa z. 11, (in Polish), Publishing House of the Warsaw University of Technology, Warsaw 2000.
6. Pouchou J.L., Pichoir F., La Recherches Aérospatiale 3, 121-138, 1984.
7. Sikorski K., Wierchoń T., 10th Conf. on Electron Microscopy of Solids eds. Jezierska and Kozubowski, Printing Press of the Jagiellonian University, , pp. 343-346, Krakow 1999.

MIKROSTRUKTURA I WŁAŚCIWOŚCI WARSTW WYTWARZANYCH NA STALACH W PROCESIE TLENOAZOTOWANIA JARZENIOWEGO

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S t r e s z c z e n i e. Przedstawiono wyniki badań mikrostruktury i składu chemicznego wieloskładnikowych kompozytowych warstw wytworzonych w procesie tlenoazotowania w wyładowaniu jarzeniowym na stali AISI 1045 pokrytej elektrolitycznie warstwą chromu. Mikroanaliza rentgenowska wykazała powstawanie warstw typu : $\text{Cr}_2\text{O}_3 + \text{CrN} + \text{Cr}_2\text{O}_3 + \text{Cr}_2\text{N} + \text{Cr} + (\text{Cr}_x\text{Fe}_{1-x})_2\text{N} + (\text{Cr,Fe})_7\text{C}_3$. Warstwy te mają dyfuzyjny charakter, dobrą przyczepność do podłoża i b. wysoką odporność korozyjną.

S ł o w a k l u c z o w e : tlenoazotowanie jarzeniowe, warstwy kompozytowe, odporność korozyjna.