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Corrosion resistance of multilayer coatings deposited by PVD techniques onto the brass substrate

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Abstract: The paper presents investigation results of the structure and corrosion resistance of the CuZn40Pb2 brass deposited by PVD process with the thin multilayer Ti/CrN, Ti/ZrN, Ti/TiAlN, TiAlN/Mo coatings. The corrosion tests were made in a 1 M HCl solution. It was found out that coatings deposited by PVD method on the brass substrate improve significantly its corrosion resistance. It has been demonstrated that the increase of the number of layers results in a significant increase of the corrosion resistance. The best results were obtained for the multilayer Ti/ZrN and Ti/CrN coatings.

Keywords: PVD, Multilayer coatings, Corrosion

1. INTRODUCTION

Deposition of hard coatings (transition metal nitrides, carbides or oxides) on material surface by PVD processes (physical vapour deposition) features one of the most intensely developed directions of improvement of the working properties of materials [1-3]. This technology makes it possible to modify their surface by shaping their physical and chemical properties. Employing the PVD techniques for the deposition of coatings (namely multilayer coatings) ensures high corrosion and wear resistance. Besides, the ceramic nitrides, carbides present interesting colours which allow them to be used in decorative components (e.g., golden or a polished brass-like) [4-5]. One of the general reasons for depositing by PVD techniques is developing the protective coating presenting corrosion resistance higher than the substrate [6-9]. Ceramic hard coatings increase of the life of the coated components, not only due to the protection against aggressive environments, but also during operation involving mechanical contact with abrasive surfaces. This effect results of high hardness resulting from the smaller grain size of the coatings' structure [10-12]. Ceramic hard coatings, in general, are usually chemically resistant at moderate temperatures, provided that they have relevant thickness, be tight, and reveal a compact microstructure. However, most coatings developed in the PVD processes have high defect density in the form of pores and columnar

microstructure enabling penetration of the aggressive agents through the coating allowing them to reach the substrate [13].

The goal of this work is to investigate corrosion resistance of coatings deposited by PVD techniques onto brass substrate.

2. EXPERIMENTS

The coatings were produced by reactive dc magnetron sputtering using metallic pure targets. They were deposited on CuZn40Pb2 brass substrates. The nitride coatings or nitride layers of the multilayer coatings were deposited when the substrates were static in front of the target in an Ar and N_2 atmosphere. The metallic layers of the multilayer coatings were deposited when the substrates were static in front of the target in an Ar atmosphere. Some deposition conditions are summarized in Table 1. Targets containing pure metals (Ti, Cr, Mo, Zr) and the 50% Ti - 50% Al alloy, were used for deposition the coatings. Experimental methodology was presented in [14].

3. DISCUSSION OF RESULTS

It was found out, as a result of the electrochemical corrosion investigations, that the coatings deposited in the PVD process onto the brass substrate may be an effective substrate material protection against corrosive agents. Analysis of the polarisation curves (Fig. 1) and of the corrosion rate, confirm the better corrosion resistance of the coated specimens compared to the pure brass ones (Table 1).

Table1.
Summary results of the electrochemical corrosion investigation

Coating type	Current density i_{cor}, $\mu A/cm^2$	Corrosion potential E_{cor}, mV	Corrosion rate, mm/year	Resistance polarization R_p, $k\Omega cm^2$	Thickness, μm
Ti/CrN × 1	2.2	- 220	0.027	2.4	5.8
Ti/CrN × 15	1.0	- 208	0.013	9.2	4.5
Ti/CrN × 150	0.6	- 202	0.008	7.8	3.1
Ti/ZrN × 1	0.6	- 238	0.008	7.1	2.1
Ti/ZrN × 15	0.4	- 211	0.005	12.7	1.6
Ti/ZrN × 150	0.2	- 191	0.003	12.9	1.9
Ti/TiAlN × 1	5.1	- 297	0.063	0.6	2.3
Ti/TiAlN × 15	3.4	- 268	0.032	1.4	2.7
Ti/TiAlN × 150	1.1	- 243	0.014	1.1	2.2
TiAlN/Mo × 1	5.4	- 220	0.066	2.9	6.2
TiAlN/Mo × 15	2.1	- 228	0.025	4.9	6.5
TiAlN/Mo × 150	1.3	- 194	0.015	4.1	5.9
Substrate	12.4	- 254	0.167	2.2	–

Current density, during anode scanning, is always lower for the uncoated specimen (12,4 $\mu A/cm^2$), which indicates to a good protection effect. The shape of the polarisation curves

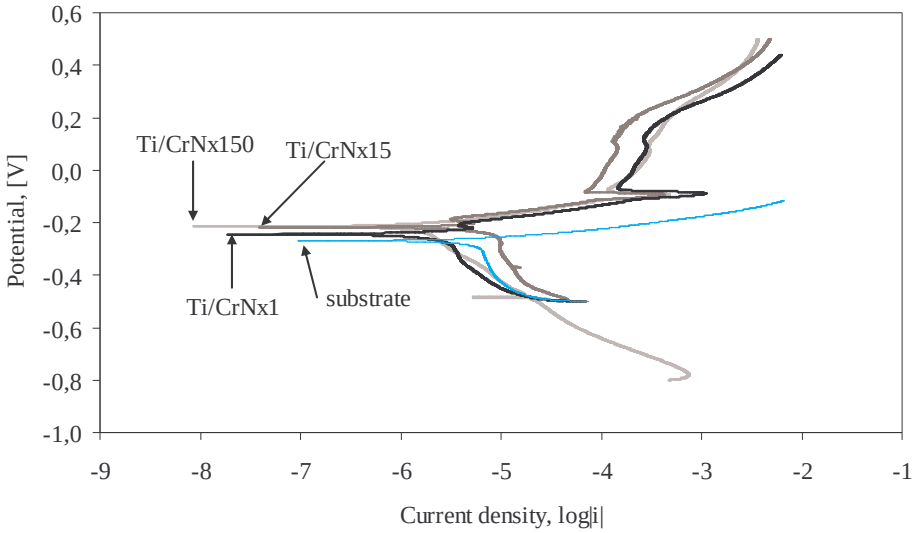

Figure 1. Potentiodynamic polarization curves of the Ti/CrN samples in 1 M HCl solution.

attests to the active dissolving of the CuZn40Pb2 brass surface, which is not protected with any coating. The lowest corrosion current density i_{cor}; and therefore, the lowest anode dissolving of the coating and the best corrosion protection properties are obtained for the coating with the number of layers 150 and 15. This may be explained by the fact that the multilayer coating deposition system gives better possibility to prevent corrosion causes, like scratches or crevices. Small pores and cracks in the coating and the difference between the big cathode area (coating) and the small anode surface (bottom of pores) decreases the corrosion protection of coatings. Defects and failures occurring in a single layer in the deposition process may be neutralised or "masked" by the successively deposited coating layers. Therefore, the corrosive agent path is extended or blocked. That is why with 150 layers the corrosive agent needs more time to penetrate through coating defects into the substrate material, than in case of 1 or 15 layers. The current density of monolithic coatings is much higher than that one obtained for multilayer coatings. The shape of the curves in the cathode range indicates to the strong slowing down of reactions occurring on the coated samples. The behaviour of the investigated system in the anode range may attest to their porosity or coating failures. Many coatings in the anode range got spontaneously passivated; however, the passive state occurs in the narrow potential range. The anode current growth connected with trans-passivation was observed in the 0,2 to 0,4 mV potential range. The results are presented in table 2, and the better behaviour corresponds to the coatings with ZrN ceramic layers.

Impedance measurement values (Table 1) confirm the higher corrosion resistance of the coated brass. Charge transfer resistance is higher for coated specimens. This attests that the coatings play role of the diffusion barrier. The multilayer coatings have the best protective properties, which are also confirmed by the polarisation examination results.

Changes of the coating colour and increase of their roughness caused by the intensive dissolving of their surface were observed during the aggressive agent action. Microscope observations make it possible to state that the coating damage process due to electrochemical corrosion proceeds in double way. In the first case the coating damage develops in many places; whereas the area of these damages is small. In the second case, however, the coating damage caused by the aggressive agent action comprises a big area, leading to changes in its appearance or delamination of the coating parts from the substrate material.

4. CONCLUSION

Corrosion current density – corrosion rate - was determined by analysis of the potentiodynamic polarization curves. This confirms the better corrosion resistance of specimens with coatings deposited by PVD technique, compared to the uncoated brass (12,4 $\mu A/cm^2$). The corrosion current density for the Ti/ZrN × 150, Ti/ZrN × 15, and Ti/CrN × 150 coatings deposited in the PVD process is within 0,2÷0,6 $\mu A/cm^2$, which attests to good anticorrosion properties of the PVD coatings, especially of the multilayer ones. This is connected with better possibilities of corrosion prevention, due to the employment of the multilayered coating deposition in the PVD process. Failures, like pores, crevices or columnar structure occurring in case of the single layer put down in the deposition process may be neutralized or "masked" by the successively deposited coating layers. In this way, the corrosion agents' path is longer or blocked. It was found out in the investigations that the increase of the number of layers in a coating results in decreasing the value of current density, demonstrated by reduction of corrosion rate. Impedance measurement results show that the charge transfer resistance is higher for coated specimens, which attests to their role as a diffusion barrier.

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