

Structure and corrosion resistance of gradient and multilayer coatings

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Materials

ABSTRACT

Purpose: Investigation of the structure and corrosion resistance of the TiN, TiN+multiTiAlSiN+TiN, TiN+TiAlSiN+TiN, TiN+TiAlSiN+AlSiTiN coatings deposited by PVD process and TiCN+TiN, TiCN+Al₂O₃+TiN, TiC+TiCN+Al₂O₃+TiN, TiN+Al₂O₃ coatings deposited by CVD process.

Design/methodology/approach: The metallographic examinations (SEM), the examinations of thin foils (TEM), investigation of the electrochemical corrosion behavior of the samples in a PGP 201 Potentiostat/Galvanostat, in a three-electrode chamber was done.

Findings: Corrosion current density – corrosion rate - was determined by analysis of the potentiodynamic polarization curves. Relationships of structure and corrosion properties has been presented.

Research limitations/implications: Implication of the investigation results are researches of corrosion properties in high temperature.

Practical implications: Employment of the surface treatment technology for tools, made from tool materials, with the PVD and CVD methods, to obtain the high wear resistant coatings, makes it possible to improve the properties of these materials in the dry-cutting conditions, by – among others – decreasing their friction coefficient, microhardness increase, improvement of the tribological contact conditions in the cutting tool-machined workpiece zone, and also to improve protection against the adhesion and diffusion wear.

Originality/value: Original system of substrate/coating compositions.

Keywords: Tool materials; PVD; CVD; Coatings

1. Introduction

Hard coatings of the metal nitrides increase life of the elements coated by them. Also their abrasion wear is less in contact with hard materials, and also they are more resistant to chemically active environments compared with the uncoated metal materials [4]. This effect results from the smaller grain size and amorphous structure of the coatings. Hard coatings are usually chemically resistant at moderate temperature, provided they have the relevant thickness, are tight, and do not demonstrate the columnar structure. However, the majority of coatings deposited by the PVD and CVD processes have a high defect

density in the form of pores and the columnar microstructure enabling penetration of the aggressive agent into the material [5].

The dynamical development of the industry poses higher and higher demands, especially in the area of the adjustment of the properties of materials to their operation conditions or applications. This regards, first of all, constructional materials, tool materials, etc. Achievement of the required high working properties is connected, in most cases, with the necessity of improvement of their manufacturing technologies, employment of novel manufacturing technologies or modifications of the surface layer. Deposition of hard coatings (transition metal nitrides, carbides or oxides) on material surface by PVD and CVD

processes features one of the most intensely developed directions in improvement working properties of the materials.

Employment of the surface treatment technology for tools made from tool materials, with the PVD and CVD methods, to obtain the high wear resistant coatings makes it possible to improve the properties of these materials in the dry-cutting conditions, by – among others – decreasing their friction coefficient, microhardness increase, improvement of the tribological contact conditions in the cutting tool-machined workpiece zone, and also to improve protection against the adhesion and diffusion wear [1-3, 6-10].

The goal of this work is to investigate corrosion resistance of coatings deposited by PVD and CVD techniques.

2. Investigation methodology

The CAE method was employed in own research for depositing the hard, wear resistant PVD coatings. The coatings deposition process was carried out in the arc-vacuum chamber based on the arc evaporation method, so called Cathodic Arc Evaporation (Fig. 1). Just before the coating deposition process, the specimens were prepared applying the standard procedure of chemical cleaning using the multi-stage washing in ultrasonic cleaner, then they were ion-etched in the chamber to clean the surfaces in the atomic scale and to activate it. Conditions of coating deposition: substrate polarisation -200 V (for cermet), substrate temperature 550°C, pressure in the chamber 0,2 Pa, working atmosphere N₂.

The High Temperature – CVD process was employed for depositing Al₂O₃ and Ti(C,N) based CVD coatings.

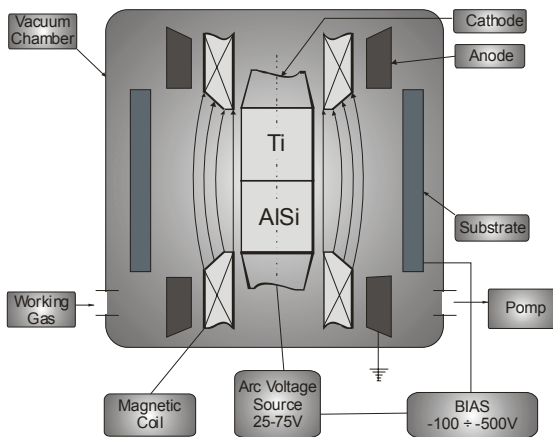


Fig. 1. Chamber for workplace gradient and multilayer coatings deposition in CAE process

Investigation of the electrochemical corrosion behaviour of the samples was done in a PGP 201 Potentiostat/Galvanostat, in a three-electrode chamber using a 1 M NaOH solution. The auxiliary and reference electrodes were platinum and calomel respectively. The following tests were performed:

- measurements of the polarization in the range of -500 (-700) mV to 500 mV at the scanning rate of 15 mV/min, to

determine the corrosion current i_{cor} on the substrate using the Tafel analysis method and VoltaMaster 4 software package;

- measurements of the corrosion potential E_{cor} during 60 minutes;
- measurement of the corrosion rate.

The examinations of thin foils were made on the JEOL 3010CX TEM at the accelerating voltage of 300 kV. The diffraction patterns from the TEM were solved using the computer program.

The metallographic examinations of the investigated materials (coatings and substrates) were made on the Philips XL-30 and JEOL JSM 5610 equipped with X-ray energy dispersive spectrometer.

3. Investigations results

It was found out, as a result of the electrochemical corrosion investigations, that 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 TiN+multiTiAlSiN+TiN and TiN+TiAlSiN+AlSiTiN coatings, deposited by PVD process and TiC+Ti(C,N)+Al₂O₃+TiN coatings deposited by CVD process. (Fig. 2, Table 1). 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 multilayers coating the corrosive agent needs more time to penetrate through coating defects into the substrate material, than in case of monolayers coating. The current density of monolayer coatings is much higher than one obtained for multilayer coatings. Corrosion currents and corrosion rate can be determined from the polarisation curves flow, as well as with the Volta Master software (Table 1).

Results of the corrosion potential E_{cor} confirm the high corrosion resistance of the coatings (Fig. 3, Table 1). The relatively high initial potential value for some coatings is explained by the need of longer time for reaching by the NaOH solution to the substrates of specimens by diffusion through small surface defects. Impedance measurement values (Table 1) shows, 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.

The fractographic examinations carried out give grounds to state that the coatings were deposited uniformly onto the investigated substrate materials and that they are characteristic of the depending on the coating type employed, and that the particular layers adhere tightly to themselves and to the substrate (Fig. 4a).

Examinations of the chemical compositions of the coatings carried out using the X-ray energy dispersive spectrograph EDS confirm presence of the relevant elements in the deposited coatings and their layers (Fig. 4b-4d).

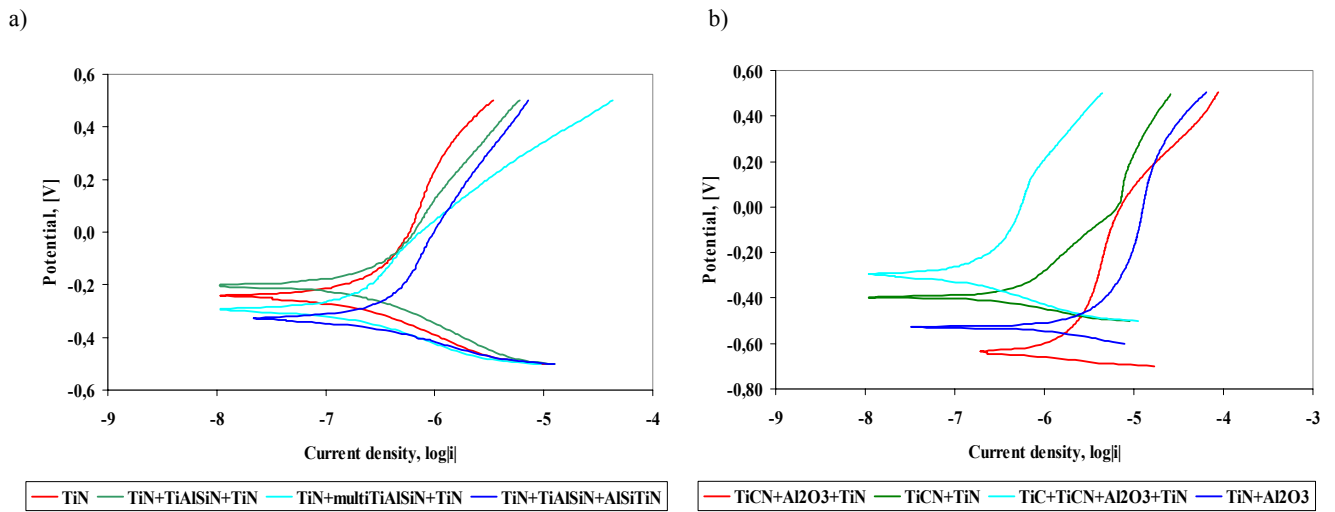


Fig. 2. a) b) Potentiodynamic polarization curves of the coatings deposited by PVD process in 1 M NaOH solution.

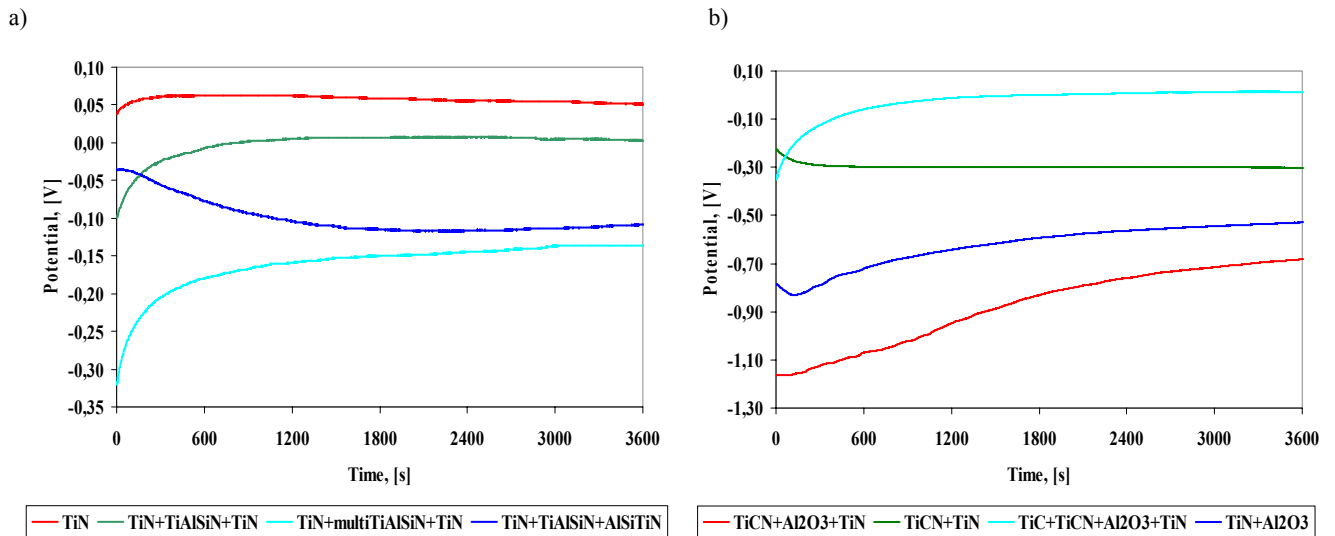


Fig. 3. a) b) Open circuit potential curves of the coatings deposited by PVD process in 1 M NaOH solution.

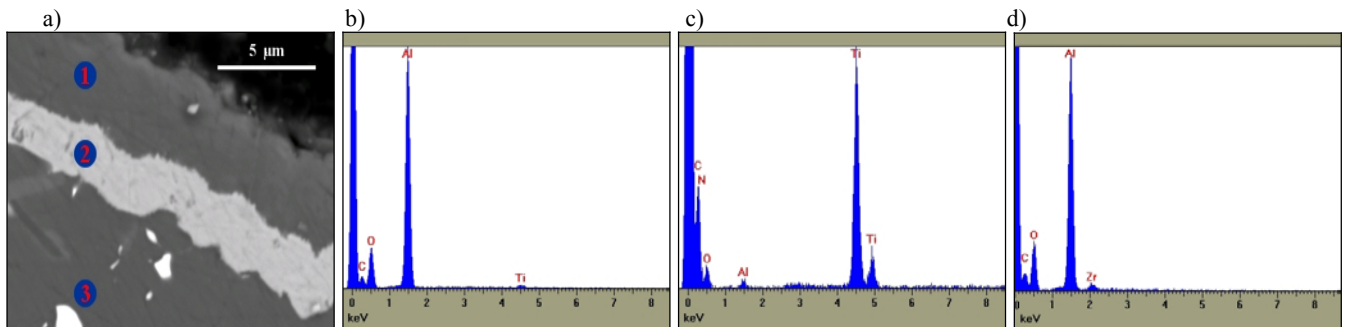


Fig. 4. a) Fracture surface of the TiN+Al₂O₃ CVD coating, b) X-ray energy dispersive plot the area 1 as in figure a, c) X-ray energy dispersive plot the area 2 as in figure a, d) X-ray energy dispersive plot the area 3 as in figure a.

Table 1.
Summary results of the electrochemical corrosion investigation

Coating type	Current density i_{cor} , $\mu\text{A}/\text{cm}^2$	Corrosion potential E_{cor} , mV	Corrosion rate, $\mu\text{m}/\text{year}$	Resistance polarization R_p , $\text{k}\Omega\text{cm}^2$	Corrosion potential $E(i_{cor}=0)$ [mV]
PVD coatings					
TiN	0,1751	52	2,04	242,1	-253
TiN+TiAlSiN+TiN	0,2325	3	2,70	201,9	-211
TiN+multiTiAlSiN+TiN	0,0802	-135	0,93	455,4	-303
TiN+TiAlSiN+AlSiTiN	0,1003	-108	1,17	272,7	-337
CVD coatings					
TiCN+Al ₂ O ₃ +TiN	0,9571	-682	11,19	53,5	-604
TiCN+TiN	0,6614	-301	7,73	58,9	-402
TiC+TiCN+Al ₂ O ₃ +TiN	0,1033	14	1,20	278,4	-307
TiN+Al ₂ O ₃	3,4229	-528	40,03	18,3	-519

4. Conclusions

Corrosion current density – corrosion rate - was determined by analysis of the potentiodynamic polarization curves. The corrosion current density for the TiN+multiTiAlSiN+TiN coatings deposited by PVD process is 0,080 $\mu\text{A}/\text{cm}^2$ and TiC+Ti(C,N)+Al₂O₃+TiN coatings deposited by CVD process is 0,103 $\mu\text{A}/\text{cm}^2$, 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 by the successively deposited coating layers. In this way, the corrosion agents' path is longer or blocked.

All PVD and CVD coatings deposited onto the oxide, nitride ceramics and tool cermets are characterized by a structure without pores and discontinuities and by tight adherence to themselves and of the entire multilayer coating to the substrate.

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References

- [1] L.A. Dobrzanski, K. Lukaszkwicz, Erosion resistance and tribological properties of coatings deposited by reactive magnetron sputtering method onto the brass substrate, *Journal of Materials Processing Technology* 157-158 (2004) 317-323.
- [2] M. Ohring, *The Materials Science of Thin Films*, Academic Press, San Diego, 1992.
- [3] K. Bobzin, E. Lugscheider, M. Maes, P.W. Gold, J. Loos, M. Kuhn, High-performance chromium aluminium nitride PVD-coatings on roller bearings, *Surface & Coatings Technology* 188-189 (2004) 649-654.
- [4] K. Holmberg, A. Matthews, *Coating Tribology*, Elsevier, Amsterdam, 1994.
- [5] L.A. Dobrzański, K. Lukaszkwicz, A. Zarychta, L. Cunha, Corrosion resistance of multilayer coatings deposited by PVD techniques onto the brass substrate, *Journal of Materials Processing Technology* 164-165 (2005) 816-821.
- [6] L.A. Dobrzański, J. Mikuła: „The structure and functional properties of PVD and CVD coated Al₂O₃+ZrO₂ oxide tool ceramics”, *Journal of Materials Processing Technology*, 167, 2005, 438-446
- [7] L.A. Dobrzański, J. Mikuła: „Structure and properties of PVD and CVD coated Al₂O₃+TiC mixed oxide tool ceramics for dry on high speed cutting processes”, *Journal of Materials Processing Technology*, 164-165, 2005, 822-831
- [8] L.A. Dobrzański, D. Pakuła, E. Hajduczek: „Structure and properties of the multi-component TiAlSiN coatings obtained in the PVD process in the nitride tool ceramics”, *Journal of Materials Processing Technology*, 157-158, 2004, 331-340
- [9] L.A. Dobrzański, D. Pakuła: “Comparison of the structure and properties of the PVD and CVD coatings deposited on nitride tool ceramics”, *Journal of Materials Processing Technology*, 164-165, 2005. 832-842.
- [10] L.A. Dobrzański, D. Pakuła, K. Lukaszkwicz: “Structure and properties of the anti-wear and corrosion resistant coatings deposited by PVD and CVD technique onto the nitride tool ceramics substrate”, *Proceedings of International Conference on Surfaces, Coatings and Nanostructured Materials - nanoSMat 2005*, University of Aveiro, Aveiro, Portugal, 218-220.