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Mechanical properties of monolayer coatings deposited by PVD techniques

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ABSTRACT

Purpose: This research was done to investigate the mechanical properties of monolayer coatings (Ti/CrN, Ti/TiAlN, Ti/ZrN, CrN, TiAl/TiAlN, Zr/ZrN, TiN) deposited by PVD technique (reactive magnetron sputtering method) onto the substrate from the CuZn40Pb2 brass. A thin metallic layer was deposited prior to deposition of ceramic monolithic coatings to improve adhesion.
Design/methodology/approach: The microstructure of the coatings was cross section examined using scanning electron microscope. The residual stress was obtained from the parabolic deflection of the samples, after the coating deposition applying Stoney's equation. The microhardness and Young's modulus tests were made on the dynamic ultra-microhardness tester. Tests of the coatings' adhesion to the substrate material were made using the scratch test.
Findings: Obtained results show that all the coatings are in a state of compressive residual stress. The stiffness of the examined coatings is between 224 ÷ 330 mN/µm, while Young's modulus is between 258 ÷ 348 GPa. Concerning the adhesion of the coatings measured by scratch test, it has been stated that the critical load LC2 for coatings, deposited onto the brass ranges from 41 to 57 N.
Research limitations/implications: In order to evaluate with more detail the possibility of applying these coatings in products used in the building and power industries, further investigations should be concentrated on the determination of the tribological properties of the coatings.
Originality/value: The paper contributes to better understanding and recognition the structure of thin coatings deposited by PVD techniques. It should be stressed that the mechanical properties of the PVD coatings obtained in this work are very encouraging and therefore their application for products manufactured at mass scale is possible in all cases where reliable, very hard and abrasion resistant coatings, deposited onto brass substrate are needed.
Keywords: Thin&thick coatings; Mechanical properties

1. Introduction

Fast development of the PVD processes has offered the potential of the specific coatings properties on an industrial scale, not limited only to coat tool materials but also in other application domains. Analysing properties of coatings developed in the PVD processes one has to pay special attention to issues connected with their mechanical properties (adhesion, hardness, internal stresses, Young's modulus, etc.), physical properties, abrasive wear resistance, corrosion, diffusion-, and thermal protection, structure, chemical composition and thickness of the coatings [1-4]. Adhesion of the coating to the substrate features one of the key issues pertaining to coating items with the hard ceramic materials. Therefore, it is one of the most important properties of coatings deposited by PVD processes [5-7]. Should the adhesion be inappropriate, then the entire coating functionality may be lost. Employment of the thin interlayer, e.g., Ti or Cr results in improvement of the proper coating adhesion, as the soft titanium or chromium layer reduces stresses and counteracts propagation of cracks [8-10]. Internal stresses feature a serious problem connected with thin coatings deposited by PVD processes [11-13]. Mechanical properties, like hardness, adhesion, and tribological properties of the applied coatings are strongly contingent upon the values and spatial distribution of the internal stresses. These stresses develop because of the growing misfit between the coating and the substrate material, due to the temperature gradient (thermo-mechanical stresses), and because of the growth of stresses resulting from fast crystallisation and intensity of ion bombardment. The excessive tensile stresses in coatings may cause development of cracks propagating across coatings; whereas the high compression stresses may lead to delamination of coatings from the substrate surface, onto which they deposited [14-17]. Therefore, the need to determine internal stresses in coatings becomes a very important element of the quality control of the applied coatings.

The goal of this work is investigation of the adhesion of the monolayer coatings deposited by magnetron sputtering onto the brass substrate.

2. Investigation methodology

The coatings were produced by reactive dc magnetron sputtering using metallic pure targets. They were deposited on CuZn40Pb2 brass substrates. The nitride coatings were deposited when the substrates were static in front of the target in an Ar and N_2 atmosphere. The metallic layers 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 (Cr, Ti, Zr) and the 50% Ti÷50% Al alloy, featuring the substrates of phases deposited onto the charge were used to deposition the coatings. One of the thin interlayer from the pure Cr, Ti, Zr, or the TiAl alloy (about 100 nm) were applied onto the substrate to improve the coatings' adhesion. Experimental methodology was presented in [4, 15].

3. Discussion of results

Fractographic examinations of the investigated coatings' fractures, made in the electron scanning microscope, confirmed the initial statement that the coatings were correctly deposited. The columnar structure of the monolayer coatings is clearly visible (Fig. 1).

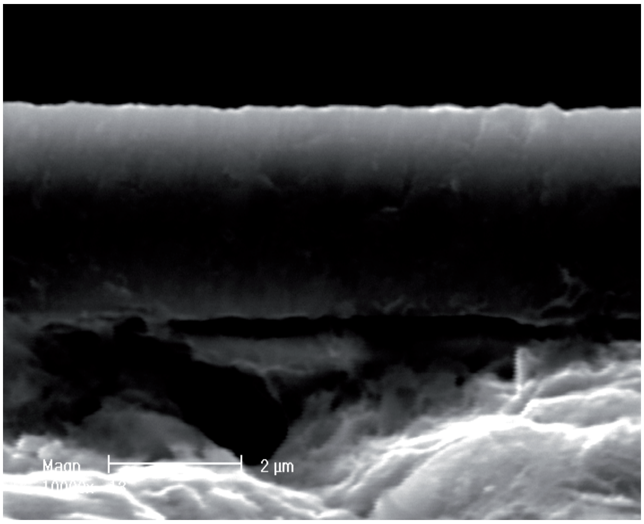

Fig. 1. Fracture of the Zr/ZrN coating deposited onto the substrate from the CuZn40Pb2 brass

The critical load L_{C2} were determined using the scratch method with the linearly increasing load („scratch test"), characterizing adhesion of the investigated coatings to the CuZn40Pb2 brass substrate, caused mostly by the adhesion and diffusion forces. The summary results are presented in Table 2.

Table 1.
Coating types and their deposition parameter: *during metallic layers deposition; ** during ceramic layers deposition

Coating type	Numbers of layers	Substrate bias voltage, V	Chamber pressure, Pa	Partial pressure, Pa		Temperature, °C
				nitrogen	argon	
Ti/CrN	1	-50	0,58	0* 0,15**	0,31	300
Ti/ZrN	1	-50	0,34	0* 0,10**	0,29	
Ti/TiAlN	1	-40	0,40	0* 0,10**	0,38	
Cr/CrN	1	-50	0,39	0* 0,15**	0,30	
Ti/TiN	1	-60	0,25	0* 0,07**	0,25	
Zr/ZrN	1	-60	0,35	0* 0,10**	0,29	
TiAl/TiAlN	1	-60	0,49	0* 0,11**	0,45	

Table 2.
Summary results of the mechanical properties

Coating type	Residual stresses, GPa	Critical load L_{C2}, N	Hardness DHV0,0025	Young`s modulus, GPa	Stiffness, mN/µm	Thickness, µm
Ti/CrN	-2.6	50	2450	258	330	5.8
Ti/ZrN	-8.9	45	3100	291	224	2.1
Ti/TiAlN	-11.9	41	2400	348	274	2.3
Cr/CrN	-10.5	48	2400	274	255	3.6
Ti/TiN	-4.2	57	2800	293	228	2.4
Zr/ZrN	-5.6	48	3100	345	252	2.0
TiAl/TiAlN	-0.3	50	2200	277	239	2.3

The critical load L_{C2} was determined as corresponding to the acoustic emission decrease, signalling a change of the friction coefficient between the diamond indenter and the coating subjected to partial spalling (Fig. 2). Employment of the additional thin (Ti, Zr, Cr, TiAl) interlayer in monolayers improves adhesion of the nitride coating to the substrate, as it counteracts propagation of cracks and reduces stresses in the coating-substrate zone.

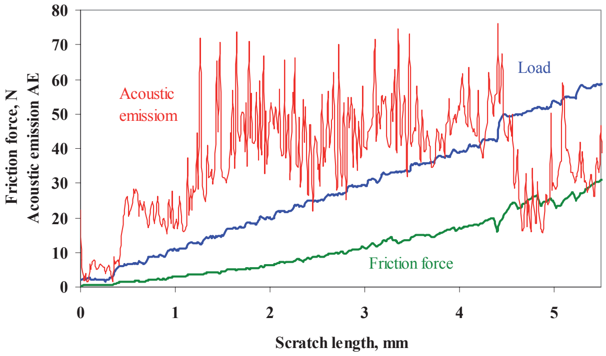

Fig. 2. Plot of the dependence of the acoustic emission and friction force from the scratch path for the TiAl/TiAlN coating deposited onto the CuZn40Pb2 substrate

The investigations made using the glow discharge optical emission spectrometer GDOS indicate that in the analysed cases, in the joint zone, concentration of elements included in the substrate grows with the simultaneous rapidly decreasing concentration of elements constituting the coatings. This may attest to the existence of the interface between the substrate material and the coating, resulting in improvement of adherence between the deposited coatings to the substrate, albeit these results cannot be interpreted unequivocally because of the inhomogeneous vaporizing of the material from the specimens' surfaces. The existence of the interface should be also connected with the increase of desorption of the substrate surface and development of defects in the substrate as well as with displacement of elements in the joint zone due to interaction of the high-energy ions. In spite of the indicated interpretation ambiguities, the obtained results are close to those published in [18, 19].

The obtained results show that the coatings are under compressive (negative) residual stress (Table 2). In this case the dominant role is played by the internal stresses, connected to the growing process itself. The external (thermal) stresses are not significant because the deposition temperatures are relatively low. The compressive stresses in the coatings, within certain limits, cause the increase of their endurance properties and especially hardness. Too big compressive stresses may, however, cause adhesion problems, as in case of Ti/TiAl and Ti/ZrN coating (Table 2), especially close to the edge.

Hardness tests of the deposited coatings were made in the ‘load-unload’ mode, in which loading of the indenter with a specified force takes place, holding it for the predetermined time, and then the indenter load force is released (Fig. 3, 4). When carrying out the test, one can observe not only plastic deformation of the material but also its elastic deformation. Microhardness determined this way is called dynamical microhardness. The precise meter circuit allows registering the depth of the created imprint while loading or unloading the indenter. The summary results are presented in Table 2.

With the use of the Hardness 4.2 software package, which is part of the ultramicrohardness tester, and the dependency between the load and the depth of the indenter into the examined coating (Fig. 3, 4), the Young’s modulus as well as the stiffness of coatings, have been determined (Table 2). The stiffness of the examined coatings is between 224÷330 mN/µm, whereas Young’s modulus is between 258÷348 GPa.

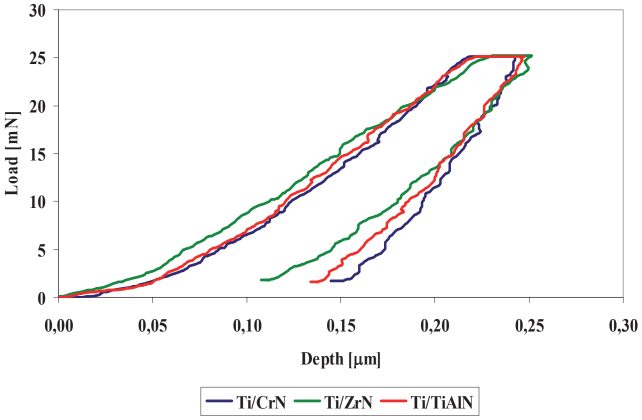

Fig. 3. Plot of the load/unload curves as a function of the depth for Ti/CrN, Ti/ZrN and Ti/TiAlN coatings

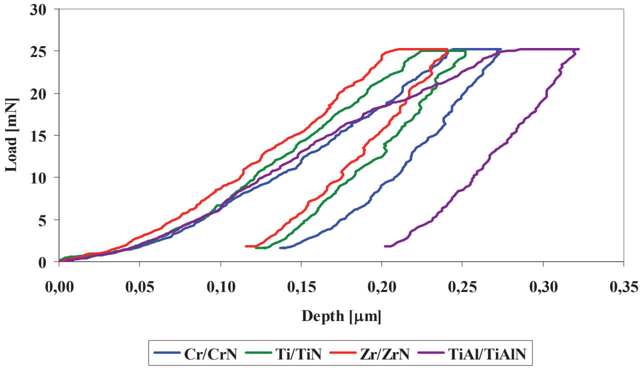

Fig. 4. Plot of the load/unload curves as a function of the depth for Cr/CrN, Ti/TiN, Zr/ZrN and Ti/TiAlN coatings

4. Conclusions

The investigated coatings demonstrate good adherence to brass substrate, which is decided not only by adhesion but also the interlayer between the coating and the substrate, developed as a result of diffusion and because of action of high energy ions causing mixing of elements in the interface zone.

On the basis of research done on the adhesion of the coatings by scratch test, it has been stated that the critical load L_{C2} for coatings deposited onto the brass ranges from 41÷57 N. The investigations made using the glow discharge optical emission spectrometer GDOS indicate to the existence of the interface between the substrate material and the coating resulting in improvement of the adhesion of the coatings deposited to the substrate. Good adhesion of the coatings deposited to the substrate should be connected with the existence of the interface.

In the investigated coatings the negative (compression) internal stresses occur, causing improvement of their tribological and mechanical properties, including their adhesion to the substrate.

The stiffness of the examined coatings is between 224÷330 mN/µm, while Young's modulus is between 258÷348 GPa.

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References

[1] L.A. Dobrzański, K. Lukaszkowicz, A. Zarychta, Properties of the monolayer ceramic coatings deposited by PVD process, Proceedings of the 12th International Scientific Conference „Achievements in Mechanical and Materials Engineering" AMME`2003, Gliwice-Zakopane, 2003, 233-236.

[2] K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, Structure, chemical and phase compositions of coatings deposited with the reactive magnetron sputtering onto the brass substrate, Journal of Materials Processing Technology, 157-158 (2004) 380-387.

[3] M. Ohring, The Materials Science of Thin Films, Academic Press, San Diego (1992).

[4] L.A. Dobrzański, K. Lukaszkowicz, A. Kriz, Properties of thr multi-layer Ti/CrN and Ti/TiAlN coatings deposited with the PVD technique onto the brass substrate, Journal of Materials Processing Technology 143-144 (2003) 832-837.

[5] D.N. Allsopp, I.M. Hutchings, Micro-scale abrasion and scratch response of PVD coatings at elevated temperature, Wear 251 (2001) 1308-1314.

[6] R. Hoy, J.D. Kamminga, G.C.A.M. Janssen, Scratch resistance of CrN coatings on nitrided steel, Surface and Coatings Technology 200 (2006) 3856-3860.

[7] R. Jacobs, J. Meneve, G. Dyson, D.G. Teer, N.M. Jennett, P. Harris, J. von Stebut, C. Comte, P. Feuchter, A. Cavaleiro, H.Ronkainen, K. Holmberg, U. Beck, G. Reiners, C.D. Ingelbrecht, A certified material for the scratch test, Surface and Coatings Technology 174-175 (2003) 1008-1013.

[8] L.A. Dobrzański, K. Lukaszkowicz, 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.

[9] F. Ashrafizadeh, Adhesion evaluated of PVD coatings to aluminium substrate, Surface and Coatings Technology 130 (2000) 186-194.

[10] B. Navinsek, P. Panjan, M. Cekada, D.T. Quinto, Interface characterization of combination hard/solid lubricant coatings by specific methods, Surface and Coatings Technology 154 (2002) 194-203.

[11] J.Y. Robic, H. Leplan, Y. Pauleau, B. Rafin, REsidual stress in silicon dioxide thin films produced by ion-assisted deposition, Thin Solid Films 290-291 (1996) 34-39.

[12] V. Teixeira, Residual stress and cracking in thin PVD coatings, Vacuum 64 (2002) 393-399.

[13] X.L. Peng, Y. Tsui, T. Clyne, Stiffness, residual stresses and interfacial fracture energy of diamond films on titanium, Diamond and Related Materials 6 (1997) 1612-1621.

[14] A.C. Vlasveld, S.G. Harris, E.D. Doyle, D.B. Lewis, W.D. Munz, Characterisation and performance of partially filtered arc TiAlN coatings, Surface and Coatings Technology 149 (2002) 217-224.

[15] K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, L. Cunha, Mechanical properties of multilayers coatings deposited by PVD techniques onto the brass substrate, Journal of Achievements in Materials and Manufacturing Engineering 15 (2006) 47-52.

[16] C. Johnson, J. Ruud, R. Bruce, D. Wortman, Relationships between residual stress, microstructure and mechanical properties of electron beam-physical vapor deposition thermal barrier coatings, Surface and Coatings Technology 108/109 (1998) 80-85.

[17] W. Wu, M. Hon, The effect of residual stress on adhesion of silicon-containing diamond-like carbon coatings, Thin Solid Films 345 (1999) 200-207.

[18] J. Musil, H. Hruby, Superhard nanocomposite $Ti_{1-x}Al_xN$ films prepared by magnetron sputtering, Thin Solid Films 365 (2000) 104-109.

[19] Z. Weiss, K. Marshall, Elemental depth profiling of coated and surface-modified materials by GD-OES: hard coatings on cutting tools, Thin Solid Films 308-309 (1997) 382-388.