FOLIA 180

Annales Universitatis Paedagogicae Cracoviensis

Studia Technica VIII (2015)

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Friction coefficient and adhesion of the PLD formed Ti-B/Ti-Si-C coatings to steel substrates

Introduction

Modern, high-performance cutting carried out with the help of ceramic tools allows high performance of machining conducted with reduced consumption of cooling lubricant liquids or without the use of lubricants of this type [1]. Dry machining is an extremely difficult working condition for cutting tools. It creates intensive wear of the tool by abrasion and heat generation in contact area, resulting in tribo-chemical reactions with working atmosphere. In order to reduce the friction in the area of contact, solid lubricants can be applied to the surface of the tool in the form of coatings [1, 2], which can perform several functions at once: to increase the hardness, wear resistance of coated tool and lower the friction coefficient. Such multifunctional coatings prolong the tool's lifetime and thus increase cutting efficiency.

Titanium diboride TiB_2 is a high-temperature material, hard and thermodynamically stable [3]. It is a good conductor of heat and electricity, which makes it an attractive material for several applications, including machining industry. Due to high melting point both the synthesis and sintering of titanium diboride are energy consuming processes, thus expensive and commercially unattractive. There are some additional problems with density and high level of intrinsic stress of produced sinters, therefore TiB_2 is used mainly as a reinforcing phase in composite materials of SiC, Al_2O_3 or steel matrix [4]. Surface engineering methods allow to obtain titanium diboride easily in the form of thin films and coatings by CVD, PVD or sol-gel methods [4, 5]. The most effective and commonly used is chemical vapour deposition, but it requires the use of substrate heating above 800°C, which precludes the use of most metal substrates. Physical vapour deposition methods allow to obtain titanium diboride on ceramic and metal substrates without heating them [5, 6]. The hardness of TiB_2 coatings obtained from the vapour phase can reach 44 – 77 GPa, depending on the method of their preparation and microstructure [6, 7]. The practical use of TiB_2 deposits is limited because of the high level of internal stresses generated during processing, which is strongly related to low fracture toughness and insufficient coating adhesion to metal substrates. Among PVD methods the PLD process is exceptional as it utilizes ablation of a target material, which is why the condition of deposition process are specific [8]. The high energy of atoms and molecules in plasma plume reaching the surface of the substrates can be particularly advantageous to phase composition, microstructure and properties of the coating [8, 9].

In this study the PLD method is used for Ti-B coating deposition on the surface of austenitic stainless steel AISI 316L with an aid of a Ti-Si-C interlayer. The aim of this work is to determine the tribological properties of coated samples and to evaluate the adhesion of Ti-B/Ti-Si-C coating to steel substrates in a scratch-test.

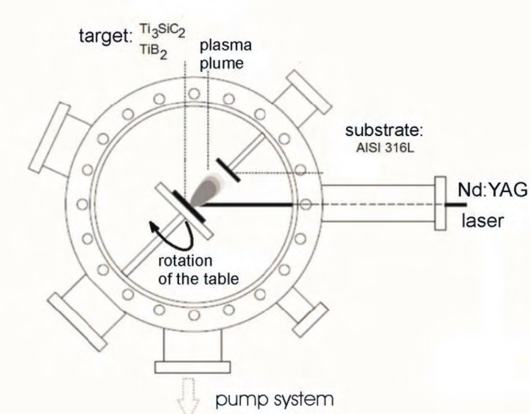
Experiment

The bilayer coatings of Ti-B/Ti-Si-C type were deposited using a PLD method on steel substrates of AISI 316L grade (X2CrNiMo17-12-2/1.4404). The chemical composition and selected properties of substrate material are presented in Table 1.

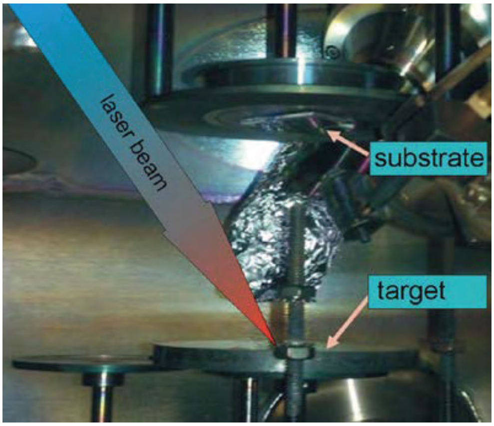
Table 1. Chemical composition [9] and selected properties of AISI 316L / X2CrNiMo17-12-2 / 1.4404 [10]

Chemical composition [% wt.]						ρ, [Mg/m³] at 20°C	E [MPa] at 20°C	R_m [MPa] supersaturated	temperature of saturation [°C]
C	Cr	Ni	Mn	Mo	other	8.0	200	530–680	1020–1120
≤0.03	17.5	11.5	≤2	2.0	N ≤0.11				

The outer layer of the coating was a Ti-B layer, which was deposited by laser ablation of TiB_2 target prepared by Goodfellow (UK) in form of a disc of 50 mm in diameter and 3 mm in thickness. The Ti-Si-C interlayer was deposited by ablation of a Ti_xSi_yC target, prepared by The Institute of Advanced Manufacturing Technology (Krakow, Poland) as a disc of a diameter of 35 mm and thickness of 4 mm. The target was prepared using Maxthal 321™ micropowder of 2.5 μm, produced by Kanthal (Sweden) and composed in 92% wt. of Ti_3SiC_2, 7% wt. $TiSi_2$ and 1% wt. of TiC_x. Substrates were prepared in the form of flat plates (10 mm x 12 mm) cut by electro-discharge from steel sheets of 2 mm in thickness. The edges of samples and one of their surfaces were grinded using a MD Primo (Struers) grinding wheel, then glued to a laboratory glass with Crystalbond™ adhesive, then mounted in a petrographic holder (Beuhler). The substrate surfaces were polished on Struers MD system polishing discs using diamond suspension Dia-duo 9 μm, 6 μm, 3 μm and 1 μm. After each step of grinding or polishing, the samples were thoroughly rinsed in a stream of distilled water, degreased in isopropyl alcohol, rinsed again in distilled water in an ultrasound bath and then dried. Pulsed laser deposition process was conducted in UST Krakow (Institute of Surface Engineering and Materials Analysis). The PLD unit consisted of a pulsed laser Nd: YAG TII LOTIS type LS-2147 and a manual vacuum system Neocera LCC with a chamber volume of 20l. As shown in Figure 1, in the PLD method the coating is deposited on the surface of the substrate from the plasma plume. Plasma is created in effect of absorption of the laser beam energy by a target material of suitably selected composition. In PLD systems the laser beam (Nd: YAG or excimer) is directed at 45° to the surface of the target. The substrate is placed parallel to a target, the distance between a target and a substrate is determined individually (usually 5–6 cm, depending on the thickness of both the target and the substrate). The PLD unit used in our experiment has a rotary table, which allows for applying up to 5 discs. It is well suited for sequential deposition of up to five different layers in the selected configuration, in one load of the chamber.



a)



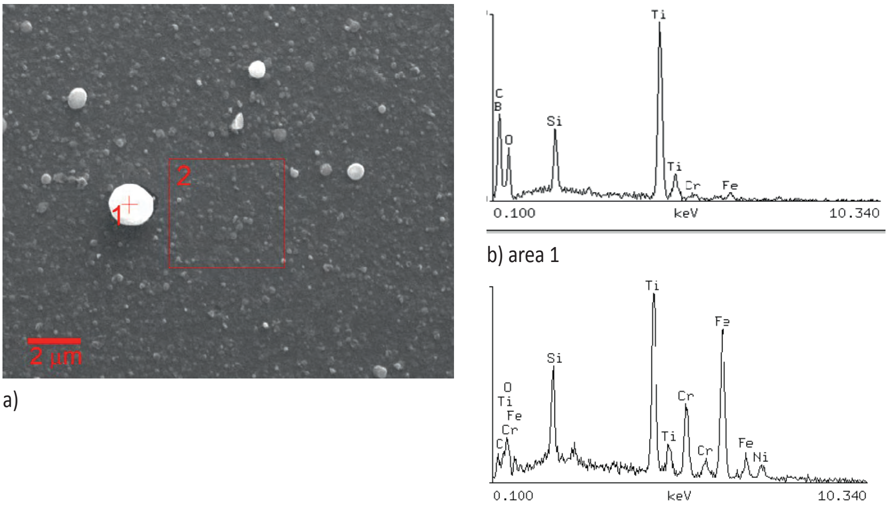
b)

Fig. 1. a) Schematic drawing of PLD chamber configuration, b) inside the chamber:
carousel tables for target's quick change and substrate position (courtesy of UST Krakow, Poland)

In the ablation process a beam of Nd: YAG laser was applied in fourth harmonic wavelength λ at 266 nm, laser pulse duration was 12 ns, the pulse repetition – 10 Hz and the pulse energy density – 10 J/cm^2. The deposition proceeded in vacuum of 10^{-2} Pa for 30 minutes for each layer. Coated samples were tested by Raman micro-spectroscopy to investigate chemical bonds. The surface morphology was examined using SEM and was accompanied by EDS analysis. The adhesion of coating to the substrate and the coefficient of friction of substrate-coating system were studied in a scratch-test. The Micro-Combi-tester (MCT) with the diamond pin of Rockwell C geometry and the radius of 200 μm was used. The scratch-test was conducted in accordance with PN-EN 1071-3. The pin was loaded in the range of 0 to 3N (linearly increased) with the load rate of 3N/min. The speed of moving of the pin was set at 4 mm/min, the length of the measuring was 4 mm.

Results and discussion

Applied parameters of PLD process allow to form continuous, flat coatings of Ti-B / Ti-Si-C type on AISI 316l steel. The thickness of coatings was less than 0.5 μm as in EDS analysis revealed predominately the presence of elements of the substrate (Fig. 2) and minor contents of titanium, silicon and oxygen in the tested samples. Oxygen was probably absorbed by the coating from the air after removing the samples from the vacuum chamber. In the case of materials containing boron, the oxidation process of the surface takes place spontaneously at room temperatures and leads to the formation of a thin and tight layer of boric acid H_3BO_3 [10]. On the top of examined coatings there were particles of a spherical shape (Fig. 2). The particles were lying on the coating surface. The shape of the particles indicates that there were liquid droplets in the plasma plume able to reach the surface of the substrate. The immediate effect of droplets presence is reduced smoothness of the coating surface but substantially it usually adversely affect the tribological properties of coating-substrate systems.



a)

b) area 1

c) area 2

Fig. 2. SEM image of the surface of the Ti-B/Ti-Si-C coating deposited on the steel by PLD with marked areas of the chemical composition analysis by EDS. EDS spectra recorded in the designated areas of the coating (corresponding to areas 1 and 2) are shown in b) and c), respectively

Raman micro-spectroscopy showed a complex structure of chemical bonds in the tested Ti-B/Ti-Si-C coatings. The experimental spectrum consisted of three very broad, asymmetric peaks. The absence of sharp peaks in recorded Raman spectra may be the result of the amorphous or nanometric microstructure of the material. The fitting of experimental spectra were assuming that each of the recorded peaks is comprised of 2 or 3 Gauss-Lorenzian peaks. Figure 3 shows the experimental and fitted spectrum matched. Items matching component peaks were compared with the referential Raman spectra, registered by other investigators for the phases of Ti-Si-C and Ti-B systems (Tab. 2). In the analyzed spectra peaks occurred at positions characteristic for silicides $TiSi_2$ (C65) and TiSi, ternary carbide Ti_3SiC_2 and titanium dioxide TiO_2 (rutile). Maximum located at 608 cm^{-1} may indicate the presence of titanium diboride TiB_2 or oxide B_2O_3 [12]. As peaks overlapping is possible in Raman spectroscopy, the presence of these two phases in the coating is not therefore excluded.

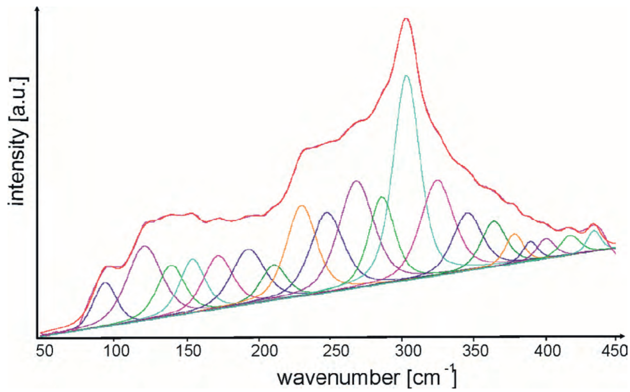


Fig. 3. Experimental (red) and fitted (violet) Raman spectra shown in the range of 50 to 450 cm^{-1}

Tab. 2. The positions of the peaks in the experimental Raman spectrum registered in the range of 150 to 680 cm^{-1} (and calculated position of maxima of the fitted spectrum) with respect to characteristic for selected phases of Ti-B [11] and Ti-Si-C [12] systems

Ti-B/Ti-Si-C coating exper (calculated)	Ti_3SiC_2	TiB_2	TiB	$TiSi_2$	Ti_5Si_3
152 (159)	**159**	–			157 168
216 (226)	**228**	–		250	215 225
270		260	**270**	**270** C54	262
278 (279)	**280**				288
(301) 311	**311**		320	**300** C54	304 326
410		409	349		402
608 (625)	631	**609**	570		
(673) 691	**678**	–			

In the scratch-test, the Ti-B/Ti-Si-C coating was easily damaged by a moving diamond pin, as evidenced by the relatively low value of critical loads and the length of L_{C1} – L_{C2} interval (Fig. 3). Under the pressure of the mandrel, the first coating material underwent deformation, the section of track cracks in this area was very short. Subsequent pin movement crashed the coating and caused its separation from the substrate (Fig. 3).

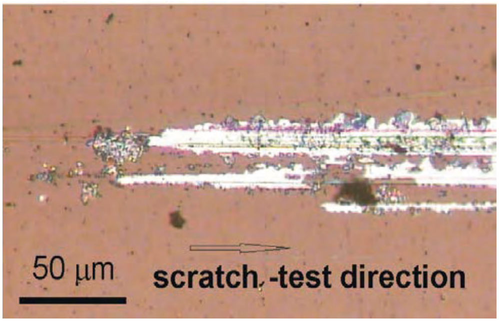


Fig. 4. Image of the surface of the coating in the area of wear (light microscopy)

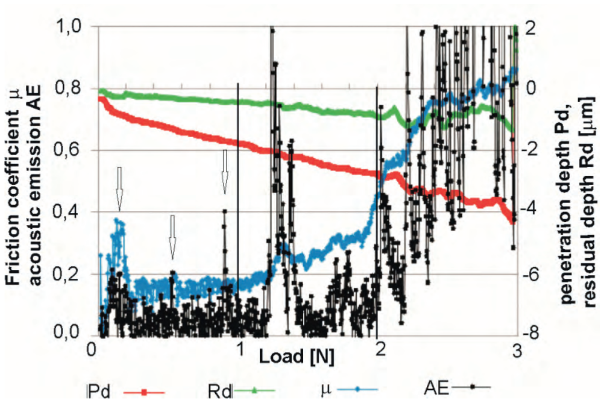


Fig. 5. Changes in the friction coefficient, acoustic emission, penetration depth Pd and the residual depth Rd, registered in the scratch-test of bilayer Ti-B/Ti-Si-C coating deposited on the surface of austenitic stainless steel AISI 316L by PLD method

The evaluation of the adhesion strength of examined coatings to steel substrates and toughness estimation is not simple and has to be done with a criticism taking into account the destructive role of hard particles which were present on the surface of the tested coating- substrate system. Particles that were in the track of the scratch acted like abrasive material. The diamond pin crushed that particles, and the resultant debris were indented into the coating. The produced tribofilm was pushed ahead by moving pin and to the edges of the track, leading even at low load (indicated by arrows in Figure 4) to a local exposing of the substrate. The values of critical loads were determined on the basis of AE signal as L_{C1} = 0.2 N and L_{C2} = 1.2 N.

The friction coefficient measured in the scratch-test does not exceed the value of 0.2 in the load range $L_{C1} - L_{C2}$, which is four times lower compared to the value of 0.8 measured in combination of diamond-steel friction. Afterwards, in the load range $L_{C2} = 1.2$ N to $L_{C3} = 1.8$ N, the coating was gradually worn, but the friction coefficient does not exceed the value of 0.33.

Conclusions

The PLD process allows to obtain a continuous and dense ceramic coatings of Ti-B/Ti-Si-C on the steel substrate without the need for additional heating of the substrate. The thickness of the coating on the deposition parameters used is small, which shows a low rate of deposition.

Coatings Ti-B/Ti-Si-C obtained by the PLD are multiphase. The lack of sharp peaks in the experimental Raman spectra indicates that the examined coatings were amorphous or nano-structured.

In the scratch-test steel substrates covered by a ceramic Ti-B/Ti-Si-C type coating showed poor resistance to scratching and toughness. In the damage process of the coatings the deleterious effect of hard and brittle particles lying on the top surface of the coating was noted.

The friction coefficient of Ti-B/Ti-Si-C coated steel with diamond counterpart is almost four times lower than the value of the friction coefficient measured for the uncoated steel.

Acknowledgements

I thank the Foundation for Polish Science for the opportunity to implement these works granted by the research project BRIDGE/13-8/13: “The mono- and multilayered, multiphase coatings based on TiB_2 for wear-resistant applications”, co-financed by the European Union under the European Regional Development Fund Program Innovative Economy.

I would like to thank Boguslaw Rajchel PhD (INP PAS Poland), Agnieszka Radziszewska PhD (UST Poland) and Sławomir Zimowski (UST Poland) for their help in the implementation of research and discussion of the results.

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Abstract

Ceramic, bilayer Ti-B/Ti-Si-C coatings produced by pulsed laser ablation of TiB_2 and Ti_xSi_yC target (containing 92% of Ti_3SiC_2 weight) on a substrate of AISI 316L (X2CrNiMo17-12-2 / 1.4404). The process for the preparation of coatings was carried out in vacuum (10^{-2} Pa) using a beam of Nd: YAG laser having a wavelength λ = 266 nm. The morphology of coated samples surface was examined using scanning electron microscopy methods accompanied by the analysis of chemical composition by EDS. Chemical bonds were studied by Raman microspectroscopy in a low and high resolution modes. Ti-B/Ti-Si-C coatings deposited on steel substrates were continuous, thin and flat. Droplets of different diameter size were present on the top. EDS analysis showed the presence of Ti, Si and oxygen in the coatings. Raman spectra indicated complex nature of chemical bonds. The peaks at positions characteristic of TiSi, $TiSi_2$, Ti_5Si_3, Ti_3SiC_2, TiB_2 and TiO_2 were present. The friction coefficient determined for coated steel substrates in a scratch-test with diamond pin as counterpart did not exceed the value of 0.23, which was almost ¼ the value of the coefficient of friction for the diamond-uncoated steel. Adhesion of coatings obtained by pulsed laser deposition method was not satisfying. Coatings were easily delaminated from steel substrates. Hard and brittle particles and droplets present in the scratch track significantly contributed to the increased wear rate of the tested coating-substrate system.

Key words: TiB_2, Ti-Si-C, coatings, PLD, scratch test, friction coefficient, adhesion

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