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INCREASE OF ADHESION FORCE OF SUPERHARD BORON NITRIDE COATINGS TO CEMENTED NANOCARBIDES USING INTERFACIAL LAYERS[1]

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Abstract

.In the article the selected investigations of the adhesion force of thin, superhard coatings to the cutting edges made of cemented nanocarbides are presented. For identification of the adhesion force of coatings to substrate an automatic scratch tester constructed at Poznan University of Technology was applied. The estimation of the adhesion force (value of critical load measured during scratch test) was carried out on the base of the vibration signal. Results of investigations are pointed at the influence of a surface preparation (degreasing, etching, low and high-temperature sputtering) on a critical load values. It was found that the most effective method for surface preparation is low temperature sputtering. The influence of the TiC+TiN interfacial layer on increase of the adhesion force of BN coating to cemented carbides substrate was observed.

Key words: Cubic boron nitride; Physical vapour deposition; Adhesion; Cutting tools.

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1 INTRODUCTION

It can be found on the base of literature data,[1-7] that except of hard coatings (for example nitrides and carbides of transient metals), increasing interest in superhard materials like boron nitride and diamond for wear-resistant coatings deposited on cutting tool edges is still growing.

Diamond having a great affinity to iron reacts easily with Fe. It is a serious limitation when using diamond for steel machining. For this reason tools with diamond coating are used for machining non-ferrous alloys. Diamond is thermodynamically metastable and transforms easily into graphite or oxidizes in air at high temperatures.[2,6,7]

Boron nitrides are not found in natural state. Depending on parameters of a synthesis (pressure, temperature) BN exhibits allotropy. Three forms of BN have their structural equivalent in carbon forms. Regular form c-BN of covalent bonds is equivalent to diamond, wurtzite-like form w-BN of covalent-ionic bonds is equivalent to hexagonal diamond (lonsdaleite), hexagonal BN (h-BN) of covalent and van der Waals bonds is equivalent to graphite. The fourth form of BN: E-BN (BN shock-wave compressed) has not an equivalent among the carbon forms. Allotropic forms of BN differ essentially in physical and mechanical properties.[2-5] Superhard boron nitride coatings are formed among other things in low-temperature PVD processes. Its lower affinity to iron enables using BN coatings for steel machining. In practice, a tool covered by BN are used for cutting hardened steels, cast irons and Ni/Co-based superalloys at a high cutting speed.[2,3] Moreover, BN coatings are effective oxidation barriers.

It was found that the basic condition necessary for coatings usefulness, besides structure and hardness, was their good adhesion to substrate.[8-23]

The purpose of this study was an increase of the adhesion of complex BN coatings (c-BN+h-BN) deposited on cutting edges in order to improve its durability during machining.

In these investigations for the purpose of additional increase of an adhesion of BN coating to cutting edges an interfacial layers were applied. By this means it is possible decrease of a shearing stresses in an interface by gradually change of hardness:[10,23 24]

- from “soft” substrate made of cemented carbides (1550 HV);
- through hard interfacial layer (2400-2600 HV); and
- to superhard boron nitride coating (3650-4050 HV).

2 MATERIALS AND METHODS

2.1 Materials

Boron nitride coatings (c-BN+h-BN) were deposited by the pulse-plasma method[3-5,23,28] on a surface of the cutting insert edges made of the S30S cemented carbides . Boron nitride coatings were obtained by pulse-plasma method using 6.0 kV discharge voltage.[23] The coatings produced by this method had fine-grained structure. The microscopic observations of hard coating structure were carried out on a scanning electron microscope VEGA – TS 5135. Observations were accomplished on the base of both SE and AE fracture images using magnification of 25 000 times.

During an adhesion investigations a cutting insert edges made of:

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- S30S (P15-P25 according to ISO) cemented carbides coated with boron nitride (c-BN+h-BN),
- S30S cemented carbides with interfacial layer (TiC+TiN) and additionally coated with boron nitride (c-BN+h-BN)

were applied.

The interfacial layers (TiC+TiN) were deposited on cutting edges by CVD method. In Figure 1 the fracture of TiC+TiN interfacial layer deposited on cutting edge made of S30S cemented carbides is shown.

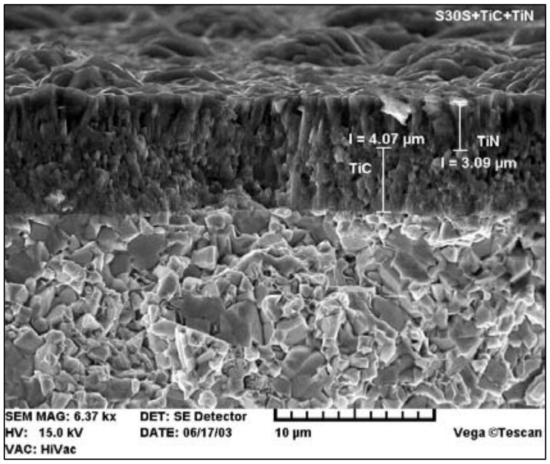

Figure 1. Fracture of TiC+TiN interfacial layer deposited on cutting edge made of cemented carbides.

The surfaces of the cutting edges made of cemented carbides and coated with interfacial layers were prepared by the following procedures:

- degreasing in acetone with subsequent ultrasonic cleaning;
- chemical etching in the 1:1 mixture of 20% aqueous solution of KOH and 20% aqueous solution of $K_3Fe(CN)_6$ (duration of etching: 20 s) or 3g $FeCl_3$ + 10 ml HCl + 90 ml C_2H_5OH;
- low-temperature sputtering of substrate surface; and
- high-temperature sputtering of substrate surface.

In these investigations for the purpose of additional increase of an adhesion of BN coating to cutting edges an interfacial layers were applied.

2.2 The Scratch Adhesion Test

The scratch test has particular application for checking the adhesion (critical load) of hard layers. It is a simple, non-destructive, mechanical method for direct application on tools. The adhesion is measured by putting a normal force on the system: coating-substrate. This coating is removed when the load has exceeded the critical value L_c. The scheme of the scratch adhesion test is presented in Figure 2. In this Figure the principle as well as relation between applied load and adhesion are shown.[2,9,10] The scratch test was introduced by Heavens.[9] The mechanics of the scratch test were first presented by Benjamin and Weaver[8] using plasticity theory developed for fully plastic indentation and scratching. This analysis gave a value of the critical shearing force for coating removal as a function of substrate properties, frictional force on the stylus and the scratch geometry.

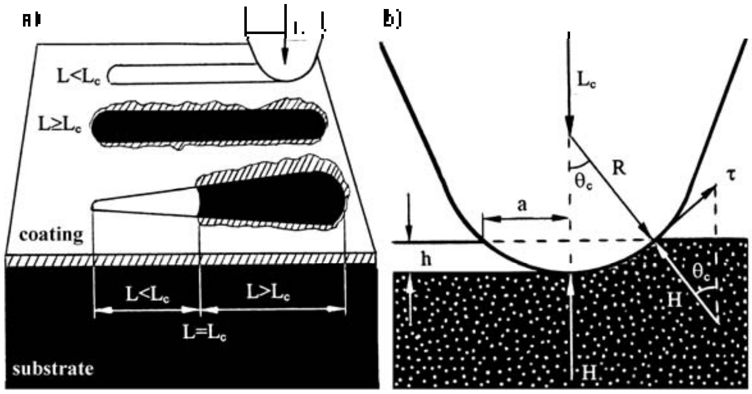

Figure 2. The scheme of scratch adhesion test: a) principle, b) relation between applied load and adhesion $A = \tau_A = H \, tg\theta_c$, $H = L_c/\pi a^2$, $\tau_A=[L_cH/(\pi R^2)]^{1/2}$ [2, 9, 10] where: A – adhesion force, H – substrate hardness; L_c – critical load; R – the stylus radius (Rockwell diamond tip with angle of 120^0); a – the half-width of the scratch channel.

In the work[11] Butler, Stoddart and Stuart, investigating the reliability of the scratch test by scanning electron microscope, concluded that the scratch process was more complex then the description by Weaver and Benjamin indicated. They showed that mechanism varied with each system and it was not possible to deduce absolute values of adhesion forces from a simple general theoretical model. Similar result was reported by Oh, Cailler and Roptin.[12] These investigations concerned the scratch shapes in the case of ductile coatings. Weaver later showed also that the assumption of fully plastic behaviour of the substrate was inappropriate in a case of metal coatings on glass and silica substrates. He applied an elastic-plastic indentation description of the substrate deformation.[25] Lately, Laugier[13] introduces a dynamical model of the test in which the friction has played the central role. He suggested that, if the coating and substrate are hard materials (e.g. nitrides of transient metals deposited on cemented carbides), the adhesion loss mechanism be modelled in terms of the strain energy released during the removal of the coating.

Recently, Bull, Rickerby, Matthews, Leyland, Pace and Valli[10,14,17,26] gave a critical estimation of the previously published models and Burnet and Rickerby[16] presented analysis based largely upon elastic-plastic indentation theory.

In spite of these complications, the scratch test has been widely used to characterise quantitatively the adhesion strength of well-adhering, hard coatings on substrates by means of the critical load.

In the supplement it can be stated that an acustic emission detection technique for adhesion failure was developed by Hintermann, Perry, Steinmann, Hammer and Laeng[17-20] in order to investigate the adhesion of coatings deposited on steel substrates by PVD and CVD techniques. But Valli, Makela, Matthews and Murawa[26] found that in the case of very thin films (less then 1 μm) friction force method of adhesion failure was more sensitive then the acoustic emission. In some cases there is a large dissipation in the critical load values due to local heterogenous.[20] In such cases, it is possible to obtain reliable information about the mean critical load using a statistical method based on the Weibull analysis. In our investigations it is not necessary because hard coatings deposited on cutting tools have more then 1μm thickness.

Sometimes strong inner stresses may act in the coating, for example as the results of different values of thermal expansion coefficient of the coating and substrate. In extreme cases, very strong inner stresses can lead to coating delamination or substrate decohesion. Such situation appears particularly in the case of some borides, carbides, and silicides of transient metals on HSS substrate. For nitrides of Ti, Nb, V, Zr the difference in values of thermal expansion coefficient is small and strong inner stresses are not present in thin coatings.[2,10,21]

2.3 Conditions of Investigations

Measurements of adhesion were carried out on the scratch test device computer-aided made in Institute of Mechanical Technology, Poznan University of Technology[2,10,22,23,27] (Figure 3).

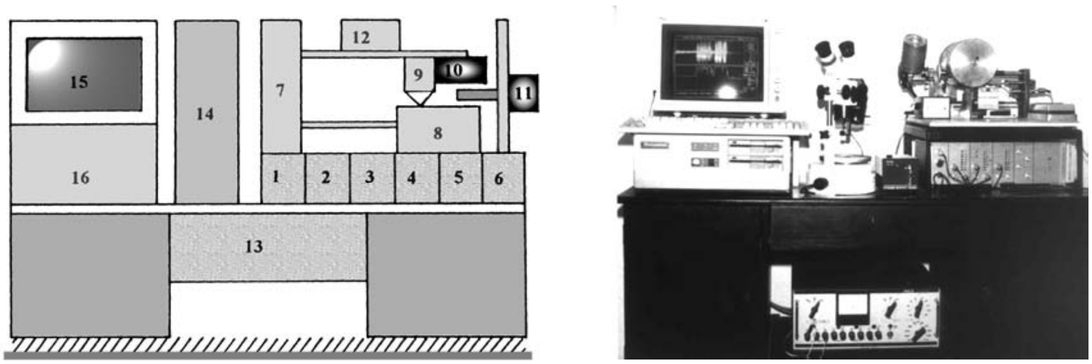

Figure 3. The scheme and general view of the station to critical load measurement by the scratch method on the base of vibration signal estimation: 1) first preamplifier, 2) second preamplifier, 3) filters system, 4) amplifier, 5) AC input, 6) power supply, 7) power transmission system, 8) sample holder, 9) diamond stylus, 10) piezoelectric accelerometer, 11) sound lever meter, 12) loading system, 13) power supply of feed system, 14) stereoscopic microscope, 15) computer, 16) data processing system.[10]

Critical load was evaluated taking into account the actual value of A_{acc} (amplitude of vibration accelerations signal), intensity of vibration signal and its absolute value. Exemplary printout of amplitude of vibration accelerations signal obtained during scratch test for boron nitride coating deposited on cemented carbides is presented in Figure 4. In Figure 4 is visible sudden increase of vibration accelerations signal value follows after exceeded the critical load value.

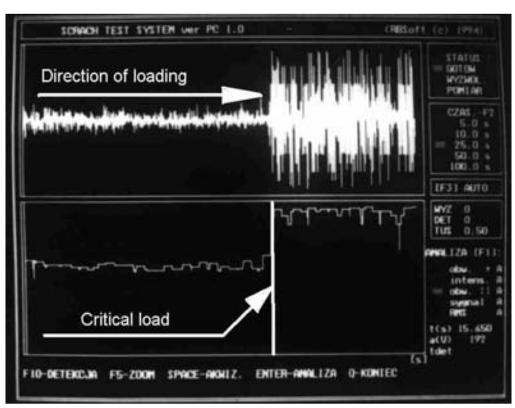

Figure. 4. Printout of vibration signal (actual value and positive envelope).

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The description of the self-constructed an automatic scratch tester was presented in the works.[2,8,27] The following parameters can be applied using this station – load: L = 0 - 200 N; scratching speed: dx/dt = 3.0-10.0 mm min^{-1}, loading rate: dL/dt = 0-300 N min^{-1}, ratio: dL/dx = 0-80 N mm^{-1}, length of the scratch: l = 2.5-7 mm and the radius of diamond indenter tip was 0.20 mm. The standard values of parameters of the scratch test for hard coatings, applied during this investigations, were defined by Kupczyk on the base of investigations[2,10] (dx/dt = 7.5 mm min^{-}1, L = 0 - 200 N; dL/dt = 300 N min^{-1}, dL/dx = 40 N mm^{-1}, R = 0.20 mm). The presented above standard parameters have been defined taking into account duration of one scratch, average deviation s of measurements, critical load variation coefficient ξ ($\xi = s/L_c$) and lower value of the slope of the straight line describing the relation $L_c = f(dx/dt)$. During measurements the indenter was loaded in the direction normal to the substrate surface applying continuously increasing load. The results of the critical load have been obtained by averaging the data for three different scratches.

Additionally, precise observations of the scratch topography were realised using scanning electron microscope equipped with WDS type spectrometers and on the base of the images obtained by using profile measurement gauge (PERTHOMETER S8) Perthen-Mahr production.[23]

3 RESULTS OF ADHESION MEASUREMENTS

Table 1 contains results of mean critical load of boron nitride coatings deposited directly on S30S cemented carbides and on S30S cemented carbides with TiC+TiN interfacial layer for different surface preparation of substrates (degreasing, etching, low-temperature sputtering, high-temperature sputtering). In Table 1 are shown adhesion results for boron nitride coatings obtained by using discharge voltage amounts 6 kV.

Table 1. Results of measurements of critical load values for boron nitride coatings deposited on S30S and S30S+(TiC+TiN) substrates

No	Surface substrate preparation	Critical load L_c [N]	Mean square deviation ΔL_c [N]	Confidence interval $\pm\Delta$ [N]
without interfacial layer				
1a	Degreasing	20.3	4.13	±5.16
2a	Chemical etching	26.2	5.04	±6.30
3a	Low-temperature sputtering	28.7	4.30	±5.37
4a	High-temperature sputtering	19.0	5.98	±7.47
with TiC+TiN interfacial layer				
1b	Degreasing	47.3	6.34	±7.92
2b	Chemical etching	50.1	6.64	±8.30
3b	Low-temperature sputtering	63.7	8.09	±10.11
4b	High-temperature sputtering	44.3	9.93	±12.41

Figure 5 presents AE image of the scratch of boron nitride coating deposited on S30S cemented carbides with TiC+TiN interfacial layer.

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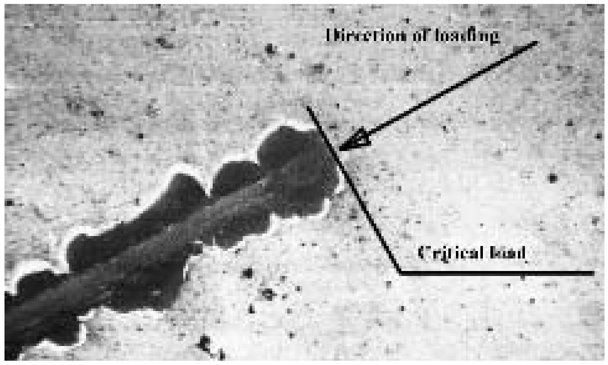

Figure 5. AE image of the scratch of boron nitride coating deposited on cemented carbides substrate with TiC+TiN interfacial layer.

Figure 6 contains the graphically interpretation of the results of mean critical load of boron nitride coatings deposited directly on S30S cemented carbides and on S30S cemented carbides with TiC+TiN interfacial layer.

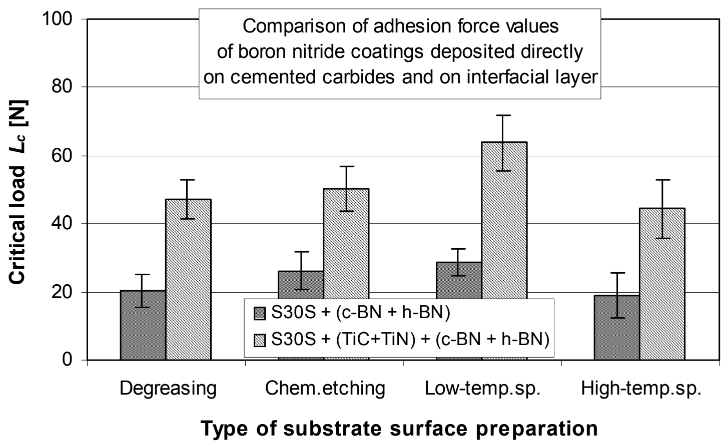

Figure 6. Comparison of critical load values for boron nitride coatings deposited directly on S20S cemented carbides and on TiC+TiN interfacial layer.

Statistical analysis of adhesion results for 5 measurements (significance level: α = 0.05, critical value of Student' t-test: t_{cr} = 2.776) shows on essential difference between mean values of critical load for boron nitride coatings deposited directly on cemented carbides substrate and on interfacial layer after degreasing, chemical etching, low-temperature sputtering and high-temperature sputtering.

4 CONCLUSIONS

Investigations presented in this work of an adhesion of boron nitride coatings obtained by the pulse-plasma method to cutting edges made of cemented carbides were confirmed usefulness of the scratch test for measurement of adhesion force of superhard coatings on the base of vibration signal. Therefore the scratch test can be used for measurement of superhard coatings adhesion both in laboratory and industry practice due to its simplicity and repeatability.

Investigations results are pointed at the influence of a surface preparation (degreasing, etching, low and high-temperature sputtering) and interfacial layers on a critical load values. It was found that TiC+TiN interfacial layer has profitable influence on increase of the adhesion force (critical load) of boron nitride coating to cemented carbides substrate. The most effective method for surface preparation is low-temperature sputtering.

Confirmation of the critical load results received during scratch test by observations of scratches using scanning electron microscope and profilograms images was obtained during investigations.[23]

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