Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 20
ISSUES 1-2
January-February
2007

Improving adhesion and wear resistance of carbon coatings using Ti:C gradient layers

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Received 02.11.2006; accepted in revised form 15.11.2006

Manufacturing and processing

ABSTRACT

Purpose: Very interesting combination of mechanical, physical and chemical properties of carbon films results in many possibilities of their industrial applications. Unfortunately the area of their usability is restricted due to poor adhesion caused by high internal stress. This problems are being solved using many different techniques including the deposition of Me:C (metal containing) gradient layers. A new deposition system allowing for simultaneous radio frequency plasma activated chemical vapour deposition (RF PACVD) and DC magnetron sputtering is presented in this paper.
Design/methodology/approach: Ti:C gradient carbon layers were deposited on steel in a hybrid deposition chamber, employing radio frequency (13.56 MHz) plasma and DC magnetron sputtering. Layers with different thicknesses obtained by varied deposition parameters were examined. Friction coefficients and wear resistances were measured using the ball-on-disc method.
Findings: Presented hybrid deposition system makes it possible to obtain thicker and still well adherent layers. Wear resistance was also improved noticeably and became several times better then for carbon layers with the same friction parameters.
Research limitations/implications: Owed to the plasma based deposition method is the difficulty in covering complicated shapes. Use of materials other than titanium as a magnetron target, although certainly possible, is not covered in this paper.
Practical implications: Ti:C gradient layers offer better wear resistance and allow for obtaining thicker carbon layers important in many tribological applications. They can be used where low friction coefficients are required.
Originality/value: The combination of plasma deposition and magnetron sputtering in one process. This allows us to obtain varied gradients of chemical and phase composition in the deposited layers.
Keywords: Thin & thick coatings; Carbon coatings; Adhesion; Gradient

1. Introduction

For many years carbon has been the subject of studies in many research centers in the world. Among many carbon based materials in surface engineering the most popular groups are NCD (nanocrystaline diamond) and DLC (diamond-like carbon coatings). Due to their excellent combination of mechanical, physical and chemical properties, they are very interesting materials, finding use in many different industrial applications. Carbon films are known for over 25 years and since 1990 they are attracting more industrial interest every year. There are two groups of carbon coatings differentiated by the manufacturing process (PVD or PA CVD) resulting in respectively non-hydrogenated and hydrogenated amorphous carbon layers. The unique parameters of both groups strongly depend on the hydrogen content and sp^3/sp^2 bonding ratio. Due to wide range of parameters which can be controlled during the deposition process, carbon layers can have varying properties, adequate for specific applications. Mostly thanks to perfect friction, good wear resistance and chemical properties, carbon layers caused such wide research activity in mechanical and medical industry.

Currently carbon films are considered a very promising material for medical, mechanical, electrical and optical applications. Their tribological behavior and usage possibilities are presented in overviews [1 - 4].

However there are also some weaknesses. Their well known poor adhesion to steel substrates, caused by high internal stress limits their applicability. Adhesion and maximum thickness mostly depend on sample surface preparation and process parameters. Ar^+ ions sputtering of the sample surface, commonly used for adhesion improvement on transition metals, often does not give satisfactory results [5 – 6].

There are many different methods of improving adhesion of carbon layers. Among them is the incorporation of dopants like Si, F, O, N, Ti, Cr, W, Ta or Ni which affects surface energy, friction coefficient, wear resistance, anti-corrosion properties or sp^3/sp^2 bonding ratio. There are several publications discussing that kind of solution achieved by combination of two or more deposition methods [7 – 9]. Very promising results are being obtained for multi- or nanocomposite layers containing Ti, TiC, TiN, TiCN, Cr or W, deposited using many different PVD or PA CVD methods [10 – 13]. The next group of carbon based layers with better adhesion an lower residual stress are the gradient Me:C layers. There are many deposition techniques leading to that kind of layers but the most popular are based on the PVD methods [14].

Authors of this work are looking for adhesion improvement by deposition of gradient Ti:C interlayer using a combination of DC magnetron sputtering and RF PA CVD. There is one work presenting this kind of solution achieving very good results for tungsten as a magnetron target [15].

Due to high chemical affinity of titanium to carbon and very good adhesion of Ti layers to steels surfaces (much better than of carbon layers) it is possible to improve adhesion of carbon layers noticeably. Moreover it is possible to rise their wear resistance without loosing their perfect friction behavior.

2. Experimental

2.1. Material and coating procedures

Ti:C gradient layers were deposited on steel substrates (diameter 25 mm; height 6 mm), prepared from 15 HN steel assigned for carburizing and toothed gear manufacturing. Samples were mechanically grinded and polished with diamond paste. Before deposition specimens were ultrasonically cleaned in acetone and methanol for 20 min. The hybrid deposition method used in this work employs two different techniques: radio frequency plasma assisted chemical vapour deposition (RF PACVD) and DC magnetron sputtering. Chosen gradient of chemical composition of Ti and C in the manufactured layers was obtained thanks to computer controlled flow regulators and smooth changes of power on sputtered titanium target. Thickness of both Ti interlayer and Ti – C transition layer was the same for all samples and amounted to 200 nm, however for carbon layers on the top of the system it was different and amounted to 0.8 µm, as measured with a profile measurement gauge. Schematic of the reaction chamber is shown on figure below.

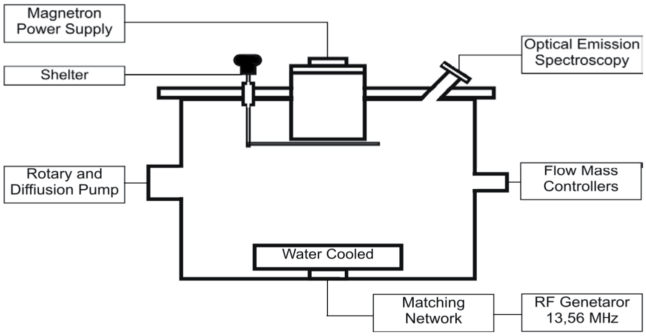

Fig. 1. Schematic of deposition system used in presented work

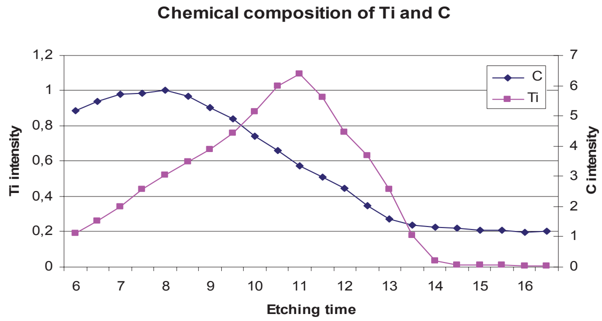

Fig. 2. Investigation of chemical composition in function of etching time, obtained in GDOES method

The main deposition parameters ranges were as follows: working vacuum of 10^{-3} – 10 Pa, rf self bias voltage of 100 – 300 V, power on Ti sputtered target equal to 40 – 80 W/cm^2.

The gradient of chemical composition of the Ti:C layer was investigated by GDOES (Glow Discharge Optical Emission Spectroscopy) and is presented on Figure 2. More precise quantitative analysis could be made after labour-intensive calibration of the apparatus for concrete components, which was left for future research.

2.2. Wear, friction and adhesion investigation

Friction coefficients and wear resistance were measured by *ball-on-disc* method in normal conditions with loads of 5 and 10 N and velocity of 0.1 m/s. ŁH15 bearing steel balls, both pure and covered by the same gradient layer as the specimen, were used as the counterface.

Adhesion researches were made by *scratch test* using two instruments with differing measurement ranges. High loads were obtained in one scratch with load increasing from 5 N to 15 N with 2.5 N steps. For low load measurements multiple 0.5 mm long scratches were used with load changing for each scratch from 1 to 3.5 N.

All researches were made on polished 15 HN steel. Gradient layers were deposited with rf self bias of 300V. Top carbon layers were deposited with rf self biases of 100, 200 and 300V. Investigation process was conducted until the layer delaminated or for 30.000 cycles, whichever came first.

3. Results

3.1. Scratch tests

Adhesion measured in scratch tests showed that only layer deposited with bias of 300 V was adherent enough to be investigated in the traditional way. As it is shown in Figure 3, its delamination started under load of about 12 N. The other situation is presented on Figure 4, where the first marks of flakes started at the beginning of the test but the layer lost its adhesion under load of about 7.5 N. The exact reason of this behavior is not certain but it may be a result of the dependency of phase composition and sp^3/sp^2 bonding ratio on self bias voltage. At lower bias voltage (200 V) the dominant phase may be graphitic or even polymer which may be the cause of decreased hardness of the layer. However, as it will be shown later, the friction parameters also change considerably.

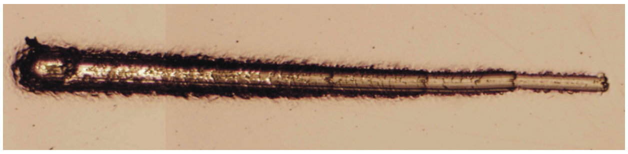

Fig. 3. Scratch test results for Ti:C layer; self bias voltage of 300 V

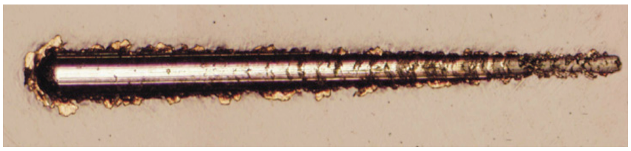

Fig. 4. Scratch test results for Ti:C layer; self bias voltage of 200 V

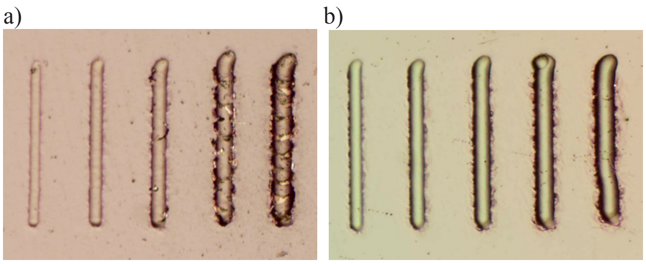

Fig. 5. Adhesion tests for Ti:C layer with load from 1 – 3.5 N; self bias voltage: a) 200 V and b) 100 V

Figure 5 presents an adhesion test with the use of 0.5 mm scratches made with loads 1 – 3.5 N. Layer deposited with self bias voltage of 100 V has better adhesion that the second one deposited at 200 V.

It's worth noticing that apart from the layer parameters the result of the tests depends on the relative hardness of the layer versus the substrate (steel in this case).

3.2. Wear and friction investigation

Friction and wear behavior tests revealed remarkable increase of wear resistance of Ti:C layers as compared with the carbon layers. Wear resistance of the latter was about 320 cycles. Friction coefficient was constantly growing up until the delamination process started (Figure 6).

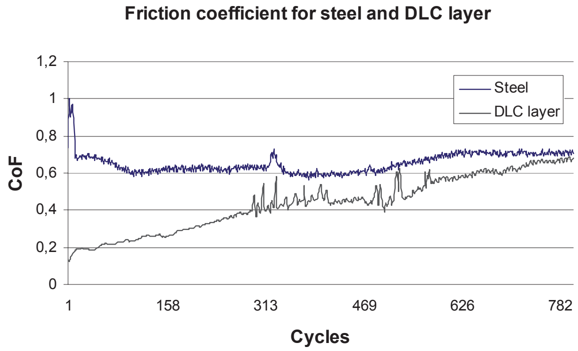

Fig. 6. Friction coefficient for steel and a DLC layer; F = 5 N, velocity = 0.1 m/s, ball – ŁH15 steel

Figure 7 presents wear resistance and friction coefficients for Ti:C gradient layers deposited with different bias voltages. Friction behavior after 30 000 cycles was almost the same for all layers but, as it is shown, best average CoF equals 0.24 and was obtained for layer deposited at 200 V bias.

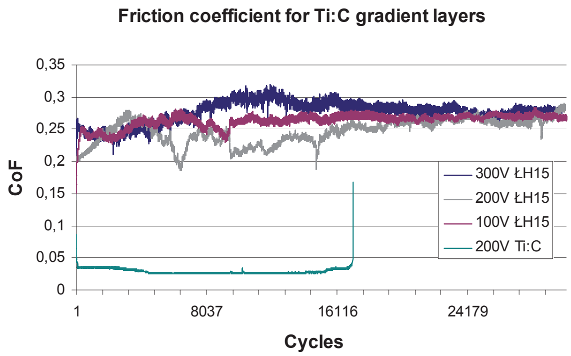

Fig. 7. Friction coefficient for Ti:C gradient layers deposited with different bias voltages; F = 5 N for pure ŁH15 ball and 10 N for Ti:C covered; velocity = 0.1 m/s

Due to that authors decided to investigate the friction behavior for its contact with the ball also coated by a Ti:C layer, in the same process as the sample. The friction coefficient decreased to a value around 0.026. Wear tests were conducted for 30 000 cycles with the exception of the last one in which both the ball and the sample were coated. After 18 000 cycles the layer on sliding ball worn out.

a) b)

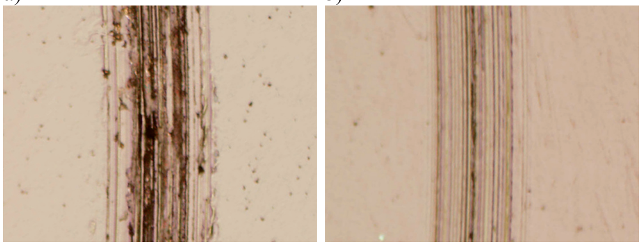

Fig. 8. Sliding character investigation for a) pure ŁH15 ball and b) Ti:C covered

The last step was sliding character investigation. Figure 8a shows the fretting character of the pure ball counterface slide. The flakes appearing on the surface are steel fragments resulting from the wear of the ball material. When the ball is covered with the same layer as the substrate the wear track is smooth as shown on Figure 8b.

4. Conclusions

Ti:C gradient layers were manufactured in a modified hybrid deposition system. Their adhesion, wear and friction behavior were investigated.

The experimental results prove that the gradient transition between titan and carbon reduces the internal stress and improves adhesion of the carbon layer.

It is also very important that the gradient transition from metal to carbon does not degrade very good friction parameters which are observed for pure carbon layers (the achieved friction coefficient is as low as 0.026).

Future work in this area should investigate the performance of these layers in tests which model realistic wear patterns occurring in mechanical applications (e.g. in toothed gears).

The promising results of Ti:C gradient layers encourage pursuing further research of other kinds of Me:C gradient interlayers.

Acknowledgements

This work has been supported by the Ministry of Scientific Research and Information Technology under grant PBZ - KBN 100/T08/2003.

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