Bulgarian Chemical Communications, Volume 49, Special Edition K1, (pp. 29 – 32) 2017

Study of the mechanism of magnetron sputtering of hybrid bonded diamond as carbon film coating for the surface of cavity structures

D. Wang *, B. Hu

School of Mechanical and Electric Engineering, Soochow University, Suzhou 215131, People's Republic of China

Received, August 1, 2017; Accepted, November 21, 2017

The carbon film bonding method is an sp3 and sp2 hybrid key combination. Compared with common diamond-like carbon (DLC) films for multi-contour cavity structures, magnetron sputtering has many advantages in coating DLC films, such as high hardness, low friction coefficient, corrosion resistance, good optical transmission, etc. However, there are some problems, e.g., non-uniform film thickness and low attraction force between film and substrate. In this research paper, some strategies were developed to solve the above problems: (1) multiple rotating cylindrical magnetron sputtering targets were installed to improve the efficiency and uniformity of films; (2) gradient composite membrane structure was used to improve the poor adhesion between film and substrate and to solve the problem of easy peeling of the single film from the substrate. Based on the above strategies, a uniform DLC film of compact thickness and excellent chemical performance was coated on the complex inner cavity wall of the multi-contour cavity structured product.

Keywords: Diamond-like carbon film; Hybrid bond; Chemical stability; Multi-contour cavity; Magnetron sputtering coating.

INTRODUCTION

In recent years, diamond like-carbon (DLC) films received extensive attentions as a film material with high hardness, low coefficient of friction, corrosion resistance and good optical transmission properties. In addition, the carbon film bonding method is mainly an sp3 and sp2 hybrid key combination and its chemical stability is good. It has been widely used for surface modification and micro electromechanical systems of molds [1-3]. The internal structure of the multi outlined cavity is complex, generally composed of cavity, plane, groove, hole and so on. Compared with the ordinary cavity plane, the DLC film for the multi contour cavity structure has the following two main problems [4,5]: firstly, there is a large internal stress in the DLC film, which puts a certain limit to the ultimate film thickness - when the elastic energy in the unit volume exceeds the fracture energy of the unit volume, the film will fall off due to excessive stress; secondly, in the process of DLC film deposition by magnetron sputtering on the complex cavity wall of the multi contour cavity structure as the cathode target for planar sputtering, the latter creates a strong local inhomogeneous magnetic field component of the club and non-uniform target consumption, which leads to concave erosion and poor uniformity of the DLC film.

According to the above two problems based on the characteristics of the complex cavity structure product, this paper aimed at improving the uniformity, compactness and chemical stability of DLC films deposited by a magnetron sputtering coating process.

METHODOLOGY

Adhesion mechanism of DLC film on the substrate

Adhesion is a phenomenon in which the film is attached to the substrate by interaction between the film and the substrate surface. The film quality is an important indicator of the durability and wear resistance of the film on the substrate. Its mechanism can be divided into two kinds: 1) chemical adsorption, 2) physical adsorption [6-8].

1) Chemical adsorption is the creation of chemical bonds between the substrate and the film, including covalent bond, ionic bond, metal bond and so on, which is a kind of adsorption, generally larger than Fan De hua;

2) Physical adsorption is mainly derived from static electricity and van Edward force, mainly by dispersion force, directional force and induced force composition.

3) The film can be firmly attached to the substrate only when the substrate and the film have a chemical bond. However, this kind of chemical bond is not common, a chemical bond is only generated at the interface and forms the compound.

Growth mechanism of DLC film

The process of DLC film formation is extremely complex, and its growth mechanism is still not fully understood. The sub-implantation model presented by Lifshitz *et al*. is generally accepted in recent years [9]. Particle energy is an important condition in the physical vapor deposition of DLC films. Lifshitz proposed the sub-implantation model (shown in Fig. 1) by considering the effect of the injection on the deposition of the charged particles. The model shows

*To whom all correspondence should be sent:
E-mail: wangwangdeshan@163.com

that, with certain energy, the energetic particles, injected into the substrate beneath the surface, occupy the target location or the target becomes embedded in the interstitial atoms, causing internal pressure, resulting in the density of the film sp3 bonded components. When the energy of the charged particles is lower than a certain value, the ions cannot be injected into the surface of the substrate, and can only stay on the surface. Stress could not be formed in the film to promote the formation of graphite. When the energy of the particle exceeds a certain value, the injected atoms will escape from the original position because of the high energy, which will lower the local stress and inhibit the growth of sp3 components. When the ion energy reaches 20 keV, the local heating of the target is very serious, which makes the film complete.

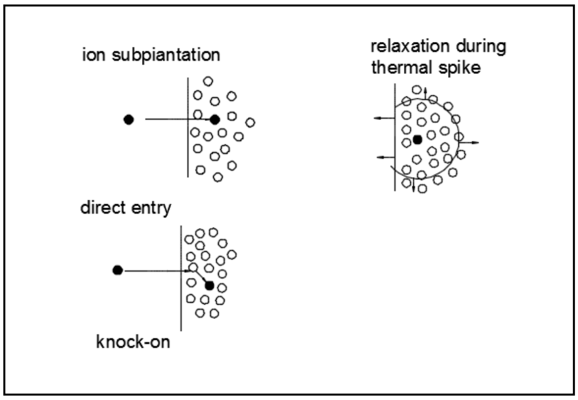

Fig. 1. Sub-implantation model [9]

Principle of DLC film deposition by magnetron sputtering

Magnetron sputtering is a common method for depositing DLC films. The method is characterized by low deposition temperature, large deposition area and high deposition rate. The basic process for manufacturing DLC films consists of: selection of high-purity graphite as the target, selection of inert gas (Ne, Ar) or carbon gas into the inert gas as working gas. Glow discharge in vacuum environment by gas ion bombardment of the target is accelerated under the action of the additional bias; the sputtered carbon ions move onto the substrate to form a thin film (shown in Fig. 2). The selection of technological parameters of magnetron sputtering has an influence on the structure and properties of DLC films: (1) sputtering power, (2) sputtering pressure, (3) sputtering bias, (4) sputtering temperature. This technology has the advantages of stable process, strong controllability, uniform thickness, high adhesion and low internal stress of the DLC thin film, and can produce films of large area [10,11].

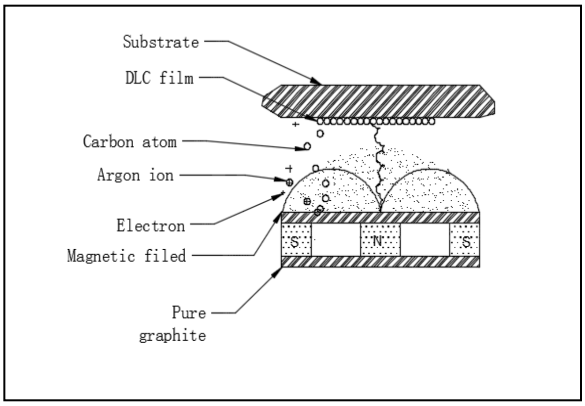

Fig. 2. Principle of DLC film formation

EXPERIMENTAL

For the multi contour cavity structure, the uniformity of the thickness of the DLC film and the quality of the adhesion will directly affect the stability and reliability of the devices. So the key technology of complex cavity structure sputtering DLC film is how to ensure uniformity and density of the DLC film and adhesion between DLC film and substrate.

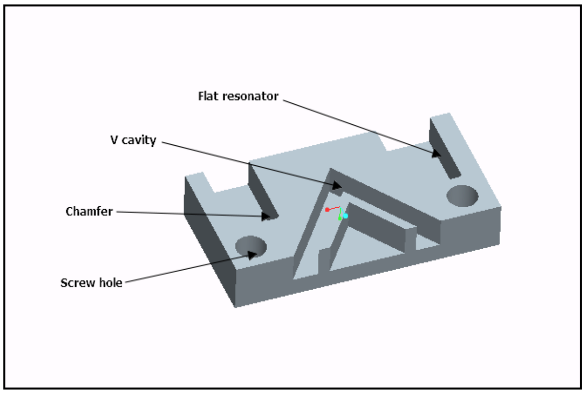

Fig. 3. The multi contour cavity structure

Setting up a number of magnetron sputtering targets and auxiliary magnetic field to improve the uniformity and density of the DLC film

The structure of the unbalanced magnetron sputtering cathode target is improved, and the plasma density of the vacuum coating chamber is enhanced by using a plurality of magnetron sputtering targets and an auxiliary magnetic field. Under the action of magnetic field, a guide pole shoe is introduced to ensure uniformity of the magnetic field intensity level, thereby improving the uniformity of the film layer and the sputtering rate. Meanwhile, by changing the distribution of the magnetic field, internal stress of the complex structure can be generated in the process of sputtering on the substrate, and the uniformity and compactness of the DLC film can be improved.

Adding metal or non-metallic elements to increase the binding force of the DLC film

By using a composite gas, composite target or co-deposition technology the binding force of DLC films substrate material is enhanced, the internal stress of the DLC film is regulated, and the thermal stability of the film is enhanced. Metals including Cr, W, Ti, Ni, etc., and non-metallic elements including Si, 0, N, P, etc., can be added.

Adopting transition layer structure to reduce the internal stress of the film layer

By adding a transition layer structure, the bonding strength between the film and the substrate, as well as the thermal stress and the internal stress between the film and the substrate can be increased. For DLC thin films, soft Ti, Cr and other metal layers can be used as transition layer to reduce the internal stress. The addition of transition metals to the DLC films enhances the bonding strength of Ti, Cr transition layer to the DLC film forming DLC thin films with gradient metal component.

Increasing the stability and adhesion strength of the DLC film

The selected appropriate process parameters, including substrate temperature, gas pressure deposition rate, etc., and the improved equipment construction effectively improved the adhesion strength between the film and the substrate interface.

RESULTS AND DISCUSSION

Laboratory equipment

The experimental equipment mainly includes: six-station magnetron sputtering equipment, Fu Liye transform infrared spectrometer, scanning electron microscope, micro hardness tester, coating adhesion automatic scratch tester, ball mill, etc. (Fig. 4).

Fig. 4. Experimental equipment

Experimental process

Table 1. Experimental process

Experimental steps	Contents	Aims
Step 1	A closed magnetic field is formed by using a plurality of magnetron sputtering targets and an auxiliary magnetic field in the coating chamber. Then, the interaction between the targets proceeds by setting the auxiliary magnetic field The plasma density increases and the bias increase to achieve the purpose of deposition for the contour cavity structure.	Making the contour cavity structure deposition coating
Step 2	Vacuum degree is 6.6 × 10^{-3} Pa, heating temperature is 300^0C. Through the argon, the vacuum degree is 8 × 10^{-1} Pa, duty cycle 80%, voltage of the bias power supply is 800V ~ 1200V, cleaning time is 10 ~ 20 min.	Forming vacuum coating environment
Step 3	Through the Ar gas, vacuum pumping to 5 × 10^{-1} Pa, bias current is set to 30A, duty cycle is 55%, voltage is 350V ~ 500V; for power supply current of 30A, voltage is 600V, time is 20 min.	Coating Ti layer
Step 4	Through the Ar, the vacuum degree is 5 × 10^{-1} Pa, the bias power supply current is 35A, the voltage is 350V ~ 500V, the duty cycle is 60%, the plating time is about 20 min.	Coating TiN (1-5) layer
Step 5	Vacuum degree is 6.67 × 10^{-3} Pa, the heating temperature reached 200^0C ~ 300^0C. Through the Ar in the coating chamber, the vacuum degree is 2Pa, the voltage of the bias power supply is 800V, duty cycle is 30%, time is about 25min.	Coating TiAlN layer
Step 6	Power supply voltage is set to 250V ~ 300V, through Ar gas, duty cycle is 30%, vacuum degree is 5 × 10^{-1} Pa, DC supply current is 20A, voltage is 400V ~ 480V, time is about 30min.	Coating Ti layer
Step 7	Through N_2, the vacuum degree is 5 × 10^{-1}Pa, duty cycle is 80%, power supply voltage is 150V ~ 250V, Ti Al target current is 20A, voltage is 450V, time is 240-350 min.	Deposition of TiAlN layer

Results: the film has good structure, compactness and smoothness, the thickness of the film is about 1 ~ 13μm, the uniformity is better than ± 5%, the hardness reaches 1800 HV, the bonding strength is high, the wear resistance and the stability are good, and the isotropic stress is small.

CONCLUSIONS

In this study, DLC films were coated on a multi-profile cavity workpiece substrate by magnetron sputtering based on the combination of sp3 and sp2 hybrid bonds. A multi-target rotating column magnetron sputtering target and a gradient composite film structure were adopted. DLC films were coated by Ti, TiN and TiAlN of different intermediate transition layers. Finally, the DLC film was coated on the inner wall of the complex contour cavity structures. The film is continuous and compact with good interface between coating and substrate, uniform and dense, with good strength, hardness, thickness, and excellent chemical stability.

***Acknowledgements**: This work is supported by Jiangsu Province basic research project (Natural Science Foundation) of China under Grant No. BK20151220. Project name: Study on the adhesion mechanism of the multi contour cavity structure in diamond-like carbon films by magnetron sputtering.*

REFERENCES

W. Huang, Z. Yu, Y. Zhang, L. Liu, T. Huang, *Chinese Journal of Materials Research*, **26**, 1 (2012).

Y.L. Guo, Y.W. Sun, S.W. Wang, X.B. Wang, Y. Chen, *Advances in Laser and Optoelectronics*, **46**, 4 (2009).

M.J. Dai, S.S. Lin, H. J. Hou, H.W. Li, *Journal of Die & Mould Manufacture*, **9**, 54 (2005).

G.H. Song, W. Du, C.L. He, Structure, Properties, Preparation and Characterization of Hard and Superhard Coatings. Beijing, Chemical Industry Press, 2007.

C.Y. Nie, C.C. Lu, B. Liao, *Journal of Functional Materials*, **40**, 2 (2009)

Y.Q. Li, H.Q. Wang, W.Y. Wang, Z.N. Yu, H.S. Liu, G. Jin, *Acta Mechanica Sinica,* **28, 5** (2012).

Y. Mabuchi, T. Higuchi. Weihnacht V, *Tribology International*, **62**, **6**(2013).

L.H. Li, L.F. Xia, H.Q. Zhang, Y.H. Zhang, Z.M. Zhou, *Journal of Tribology*, **21**, 1 (2001).

S. Miyagawa, S. Nakao, K. Saitoh, K. Baba, Y. Miyagawa, *Surf. Coat. Tech*,, **41**,**128** (2000).

Z.Z. Wu, X.B. Tian, F. Pan, K. Ricky, Y. Fu, F. Pan, *Journal of Metal Research,* **50**, 10 (2014).

Q.F. Zeng, G.N. Dong, F. Yu. G. Liu, *Journal of Vacuum Science and Technology*, **34**, **11**(2014).