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A cathodic arc enhanced middle-frequency magnetron sputter system for deposition of hard protective coatings

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Abstract A new cathode arc enhanced magnetron sputter system for deposition of hard protective coatings is reported in this article. This system consists of eight targets: four outer targets are mounted on the wall of the chamber and four inner targets are placed around the center of the chamber. The outer and inner targets form four pair targets and are powered by four middle frequency power supplies. One of the outer targets can run either in the cathode arc mode or in the magnetron sputter mode. The Ti-containing diamond-like carbon nanocomposite coatings were deposited by using this system. The prepared coating exhibits high hardness (~20 GPa), good adhesion (critical load is 50 N), very low friction coefficient (~0.07), and excellent tribological performance with a wear rate of 1.4×10^{-16} $m^3\cdot N^{-1}\cdot m^{-1}$.

Key words Cathodic arc, Middle frequency magnetron sputtering, Diamond-like carbon.

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1 Introduction

Hard coating is a type of coating that includes metallic nitrides, metallic carbides, diamond, diamond-like carbon (DLC), and ceramic. These coatings can effectively reduce friction coefficients and wear rates of the workpieces and increase surface hardness, toughness, and resistance to chemical corrosion; hence, they are widely used as protective coatings on cutting tools and on wear-exposed components. [1-3] Plasma chemical vapor deposition (PCVD), magnetron sputtering, and cathode arc deposition are the three most popular methods for preparation of hard coatings. Among them, PCVD is a high-temperature process and is not appropriate for most metal substrates. Cathode arc deposition is one of the most reliable technologies for the production of hard coatings. The plasma of the cathodic arc delivers high degrees of ionization (up to 50%) at relatively low pressures (<1 Pa); hence, arc deposition is a high-rate process and arc deposited coatings exhibit good adhesion. During the process of arc deposition, the electric current at the cathode is concentrated on small, mobile "hot spots", which results in the production of not only fully ionized metal plasma but also tiny droplets of $0.1-10$ μm size at these cathode spots. The morphology of such coatings prepared by the cathode arc method is rough. Macroparticle filters are used to separate the macroparticles from the plasma, but this significantly reduces the deposition rate. [4, 5]

Magnetron sputtering is a technique that has good reproducibility and controllability with technological advantages such as high deposition rates, coverage of large areas, and low deposition temperature despite low utilization ratio of the target materials. An unbalanced field has been introduced to effectively improve

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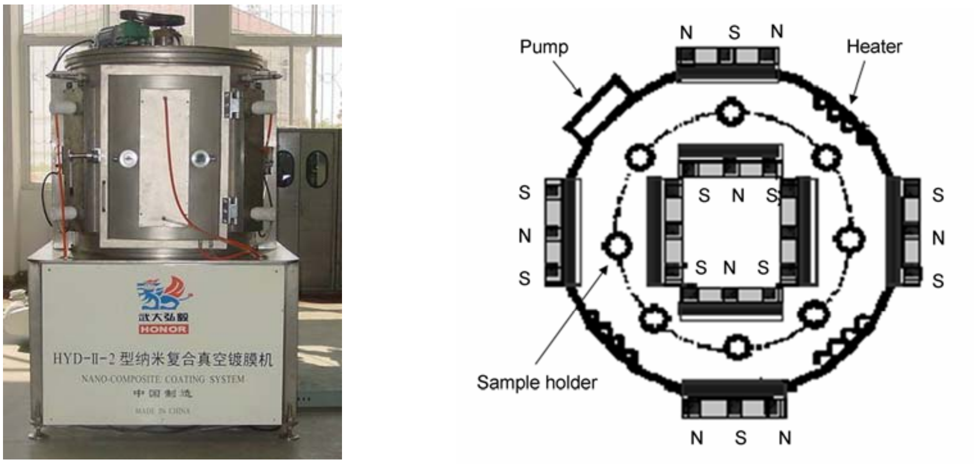
the adhesion and quality of the coating owing to the enhancement of the plasma density near the substrate in the magnetron sputter deposition.[6] Neighboring magnetrons are of opposite magnetic polarities and are arranged to form a closed field in the multimagnetron system. This arrangement confines to the plasma region and prevents losses of ionizing electrons, thereby resulting in significant enhancement of the plasma density.[7, 8]

There are three types of magnetron sputter deposition. The process of direct current (DC) sputtering is used for metallic coating, but it is unstable and has a lower plasma density. Radio frequency (RF) sputtering is used for insulating coatings. It produces finer particles and results in the film having higher density, but it has a lower deposition rate and may be harmful to health. Middle frequency (MF) sputtering technology offers a high deposition rate and is a stable process. It can be used for insulating coatings with low surface roughness and high mass densities due to effective elimination of arc discharge at the target surface.[9]

In hard coating deposition, the stability and reproducibility of the processing, the deposition rate, and the adhesion and thickness uniformity of the coatings are of great importance, all of which are influenced by the density and distribution of the plasma. A cathode arc enhanced middle frequency closed field unbalanced magnetron sputter system has been designed considering the above-mentioned parameters, and Ti-containing DLC noncomposite coatings were prepared in this machine.[10, 11]

2 Equipment

Fig. 1 shows a photograph and a schematic cross-section view of the arc-enhanced MF magnetron deposition system. The vacuum chamber is ϕ1000 mm $\times$1000 mm in size and is equipped vertically with 4 pair magnetrons, which are rectangular and 150 mm $\times$ 800 mm$\times$20 mm in size. Of the eight targets, four targets, i.e., the outer targets, are placed on the sidewall of the deposition chamber and the other four targets, i.e., the inner targets, are placed around the center of the chamber. Cool water is maintained at 15°C using a refrigerator to increase the ultimate power density of the target source and to prevent the production of macroparticles by restraining thermal evaporation. A background pressure of 7×10^{-4} Pa is attained using a diffusion pump with a Roots pump and two mechanical pumps as backing. The electric heaters mounted on the sidewalls of the chamber raise the substrate temperature and eliminate the adsorbed gases on the substrates and the coatings. The carrier gas and the reactive gas are leaked into the chamber through mass flow meters controlled by piezoelectric valves. The substrates are placed vertically on a rotating sample holder arranged between the inner and outer targets. The power supply consists of four bipolar 40 kHz MF power supplies, a 20 kW cathode arc supply, and a DC-pulsed bias voltage supply that can be varied between 0 and 2000 V.



(a) (b)

Fig.1 Photograph (a) and schematic cross-section view (b) of the cathode arc enhanced closed-field twin unbalanced magnetron sputter system.

An opposed magnetic field configuration is arranged between the pair targets producing an unbalanced magnetic field for each target with an optimum arrangement of NdFeB magnets. This arrangement can force the plasma to flow toward the substrates, thus allowing some secondary electrons produced during sputtering to follow the field lines and cause additional ionizing collisions. The unbalanced field results in the increased ionization levels near the substrate. A closed field is formed within the area of four outer targets, four inner targets, and the twin targets, which leads to an increase in the collision probability and hence increases the incident current density.

Intensive research has proved that the bombardment of the substrate surface with metal ions before the deposition can result in a mixed layer of substrate material and metal that is several nanometers thick and remarkably improves the adhesion of the deposited coating. For example, in Cr-based coating deposition, a bias voltage of 1.2 kV could incorporate Cr^+ into the surface, leading to a high critical load, e.g., 50 N, in hard coatings.[12] To improve the adhesion, a dual-purpose cathode is designed, which either runs in the cathode arc mode or in the magnetron sputtering mode. In the process of glow cleaning, this target works in the cathode arc mode, and the work-piece surface is etched by inert gas and metal ions produced by the cathode arc. In the deposition process, this target works together with its counterpart inner target in the MF magnetron mode. To ensure uniform thickness of the coatings, the work-piece experiences three kinds of rotation modes: the carrier holder rotation mode around the center of the chamber, the holder spinning mode, and the work-piece spinning mode.

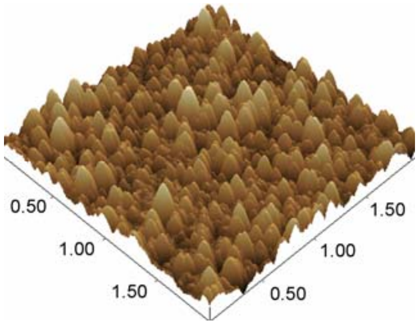
3 Applications

Ti-DLC nanocomposite coatings were prepared using the above system. Three pairs of graphite targets (99.99%) and one pair of Ti targets (99.99%) were used in this experiment. The outer Ti target was in the dual mode. The base pressure before coating deposition was 7×10^{-4} Pa. The pulsed substrate bias was 100 V with an 80% duty factor. The output power of the Ti pair targets was fixed at 2.2 kW and that of the C pair targets at 12 kW. All depositions were performed in a pure Ar glow discharge. The Ar gas flow rate was kept constant at 80 sccm throughout the deposition process. The substrates were not heated, and the chamber ambient temperature was lower than 100°C during deposition. The coating process consisted of a 15 min deposition of the pure Ti layer and a 120 min deposition of the Ti-DLC compound layer. A polished stainless steel sheet, 650 mm in length and 100 mm in width, was used as the substrate to check the uniformity of the coating. After the coating was completed, the sheet was cut at four corners and in the middle position, and the thickness of these pieces was measured by using a Talysurf FormS4C-3D Profiler. The results show that the thickness of the coating at different positions of the sheet was within (1 ± 0.05) μm. The coatings had a root mean square roughness of 2.65 nm and an arithmetic mean roughness of 3.30 nm based on a SHIMADZU SPM-9500J3 atomic force microscope, as shown in Fig.2(a).

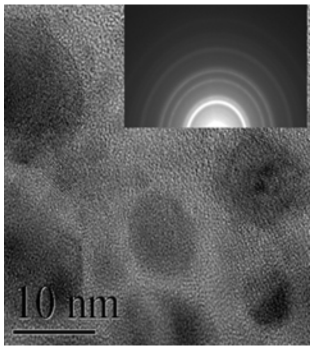
Cemented carbide substrates were coated to investigate the mechanical and tribological properties of the coatings. The coatings exhibit good adhesion, with a critical load of 50 N measured by the scratch test and a hardness of 19.7 GPa and an elastic modulus of 350 GPa measured with a fully calibrated MTS Nano Indenter XP.

The high-resolution transmission electron microscopic image (Fig.2(b)) showed nanocrystals embedded in the amorphous carbon matrix with fine interface between the grains, and no obvious defects were observed. The average grain size of the nanocrystals is about 10 nm. The inset of Fig.2(b) shows the selected-area diffraction pattern, and Table 1 shows the corresponding diffraction indices. These data indicate that the nanocrytals are of Ti.

The friction and wear measurement of the Ti-DLC nanocomposite coatings were measured by an MS-T3000 ball-on-disc tester in ambient air at 23°C and a relative humidity (RH) of 60 %, with a WC-Co ball used as the mating material. The friction coefficients were continuously recorded during the test at a load of 5 N and a sliding speed of $0.02\ m\cdot s^{-1}$ for a fixed time of 100 min. The wear rate is defined as the volume of material removed per unit applied load per unit sliding distance. To calculate the volume of the coating removed, the groove dimensions were measured using the Talysurf Profiler. At optimum conditions, Ti-DLC coatings were obtained that had a friction coefficient as low as 0.07 and a wear rate of $1.4\times10^{-16}\ m^3\cdot N^{-1}\cdot m^{-1}$, which is approximately an order of magnitude smaller than that of the metal containing DLC coatings deposited by conventional DC magnetron sputtering. The detailed parameters of coatings are listed in Table 2.



(a)



(b)

Fig.2 Typical three-dimensional AFM image (a) and high-resolution TEM micrograph (b) of the Ti-DLC nanocomposite coatings. The inset shows the selected-area diffraction pattern of the nanocrystals.

Table 1 Diffraction indices of the Ti-DLC coating prepared by the cathode arc enhanced magnetron sputtering

Diffraction ring	Crystalline plane	Ti	Graphite
R1	2.3520	(002)	
R2	2.0260		(101)
R3	1.4260	(110)	
R4	1.2290	(202)	

Table 2 Properties of the Ti-DLC nanocomposite coatings prepared by the eight-target cathode arc enhanced magnetron sputtering

Parameters	Values
Coating thickness (μm)	~1
Root mean-square roughness (nm)	2.65
Critical load (N)	>50
Hardness (GPa)	19.7
Elastic modulus (GPa)	350
Friction coefficient	0.07
Wear rate ($m^3\cdot N^{-1}\cdot m^{-1}$)	1.4×10^{-16}

4 Conclusions

To summarize, an eight-target cathode arc enhanced closed field twin unbalanced magnetron sputtering system was designed, which worked stably at a high deposition rate. Ti-DLC nanocomposite coatings were deposited by using this system at a substrate temperature lower than 100°C. The coatings were of Ti nanocrystal embedded in an amorphous carbon matrix. At optimum conditions, Ti-DLC coatings were obtained with good adhesion, high hardness (~20 GPa), very low friction coefficient (0.07), and wear rate of $1.4\times10^{-16}\ m^3\cdot N^{-1}\cdot m^{-1}$.

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