Microstructure and Properties of Cr-Doped Graphite Carbon Films Prepared by Unbalanced Magnetron Sputtering

Yongmei Wang[1*], Sihua Zhou[1], Xiaodong Zhou[2], Songfeng Zhang[2]
[1]School of Physics and Telecommunication Engineering, Zhoukou Normal University, Zhoukou, Henan, China
[2]School of Mechanical and Electrical Engineering, Zhoukou Normal University, Zhoukou, Henan, China
**Corresponding Author*

Abstract: Preparation of graphite-like (GLC) films using unbalanced magnetron sputtering technology. The investigation of their microstructure properties, mechanical properties, and tribological properties were studied. The introduction of a small amount of chromium into the graphite-like (Gr-GLC) films not only maintains their high hardness, low friction coefficient, low wear rate, and high load-bearing capacity but also results in a decrease in the friction coefficient as the load increases. Additionally, metallic chromium in the coating enhances toughness and anti-oxidation properties, significantly improving the comprehensive performance of the coating.

Keywords: Magnetron Sputtering; GLC Films; Doped with Cr; Mechanical Properties

1. Introduction

Graphite-like carbon (GLC, similar to carbon) films are a type of amorphous carbonaceous film primarily structured with sp^2 bonds. They exhibit high environmental adaptability and demonstrate excellent tribological performance in various environments such as air and water, making them one of the most promising lubricating protective coatings [1-4]. However, due to differences in lattice structure and physical properties (hardness, elastic modulus, thermal expansion coefficient, etc.) between the film and substrate, issues such as increased internal stress and poor film-substrate adhesion arise. Typically, depositing a metallic transition layer on the substrate can effectively alleviate this problem while simultaneously enhancing the film's load-bearing capacity, improving interfacial bonding strength and mechanical tribological performance. Moreover, the structure and properties of amorphous carbon-based films can be adjusted by doping heterogeneous elements [5-10]. Whereas, Cr exhibits excellent wear resistance, strong oxidation resistance, and good bonding performance with steel substrates. Based on this background, this experiment employed Cr as a gradient transition layer between the film and substrate to optimize the GLC film. Furthermore, the study investigated the effects of Cr doping on the structure and multi-environmental tribological properties of GLC films under the premise of using Cr as the gradient transition layer [11-12].

In this paper, pure GLC film and Cr doped GLC films were successfully constructed by magnetron sputtering technology, and the influence of metal doping on the structure of GLC membrane and mechanical properties were systematically studied. The results demonstrate that metal doping plays a significant role in optimizing GLC film properties, providing crucial theoretical and experimental foundations for developing high-performance thin-film materials in the future.

2. Experimental Details

Using medium frequency non-equilibrium magnetron sputtering target of non-equilibrium magnetic field is not only by changing the size and strength of the internal and external magnet, but also produced by two groups of electromagnetic coils or electromagnetic coils and permanent magnet mixed structure, and add additional solenoid between the cathode and matrix to change the magnetic field between the cathode and substrate, and with it to control the proportion of ions and atoms in the deposition process. By combining theory and studying plasma diagnosis, an arc discharge power supply is suitable for magnetron construction environment.

On the basis of conventional sputtering target change the magnetic field distribution, appropriate increase the edge N pole magnetic field or weaken the S pole magnetic field, ensure that the target surface form transverse magnetic field effectively constraint sputtered secondary electrons, maintain a stable magnetron sputtering discharge, while the other part of the electron toward the strong longitudinal magnetic field from the target surface, fly to the coating area, enhance the coating area plasma concentration. High purity argon was used as the working gas, and the samples were cleaned with deionized water, acetone and absolute ethanol for 20 minutes before depositing the film, and then the sample was heated in the chamber to 100℃, vacuuming to 10-3Pa, followed by bombarded the surface of the sample with argon plasma for 20 minutes at 600V bias and 1.6Pa pressure to remove the surface oxide layer.

The main sputtering deposition process includes the following three steps:

(1) Pure Cr layer with a thickness of about 400nm is deposited on the substrate.

(2) Gradually reduce the titanium target current and increase the three-block graphite target sputtering current deposition thickness of about 200nm GLC composite layer.

(3) In the composite Cr-GLC layer of upper deposition with about 1 um thick. The main parameters of carbon film deposition are: working pressure 0.3 Pa; pulse bias 125 V; sputtering current 6A (twin AC to target) and 3A (DC target); deposition time 3h; bias pulse duty cycle is 20%, 30%, 40% and 50% respectively.

3. Results and Discussion

3.1 Microstructure of the GLC Thin Films

As can be seen from the currently prepared carbon film AFM image (**Figure 1**) of the film, the surface of the currently prepared film is composed of a large number of particles of different sizes, and the rough surface of the film has no obvious defects. The surface roughness and composition of thin films prepared under different pulse duty cycle are different. Its surface square root mean roughness (30 nm), the current preparation of graphite film its roughness is larger than sp3 content higher diamond carbon film, this is because of film deposition formed in the process of sp2 clusters, these clusters in the film surface diffusion accumulation to form a larger size particles, causing the rough film surface. As the pulse ratio increases, the sp3 content in the film increases, and then more sp3-bonded carbon connects the surrounding carbon ring cluster bridge, which enhances the connectivity of the whole film structure, improves the rigidity of the carbon network structure, and improves the hardness of the film. When the pulse proportion is further increased, the hardness and connectivity begin to decrease as the sp3-bonded carbon content in the film structure decreases due to substrate heating.

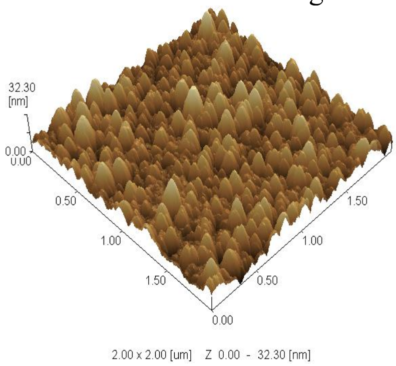

Figure 1. AFM Image of the Nanocomposite GLC Films

To further reveal the internal microstructure of the nanocomposite graphite-like coating, the cross-sectional SEM characterization was performed on the samples, as shown in **Figure 2**. It can be easily seen from Figure 2 that the thin film adheres tightly to the substrate without any gaps, and the fracture interface is not flat but has wrinkles, indicating good toughness of the film. There is a white line between the thin film and the substrate, which is the Ti transition layer, mainly used to enhance the bonding performance between the GLC film and the substrate. Above the Gr transition layer is the Gr/GLC buffer layer, and above the buffer layer is the nanocomposite graphite-like (Gr-GLC) film.

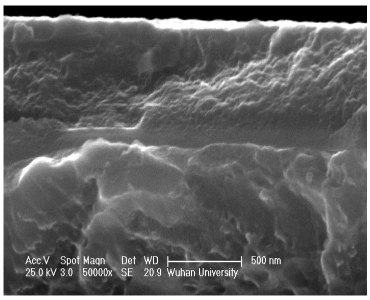

Figure 2. Cross-Sectional SEM Image of Nanocomposite GLC Films

Figure 3 shows the typical graphite-like Raman spectra. For graphite-like membranes, the Raman spectra are significantly different from graphite or diamond, with 2 wide peaks appearing. The spectrum has a broad peak in the 1580 cm-1 range, which conforms with the characteristic peak of the spectrum of the graphite crystal, corresponding to the G peak, indicating the Sp2 hybrid phase in the carbon film, and a broad peak in the 1350 cm-1 interval, called the D peak, which coincides with diamond, and shows the Sp3 hybrid bond. The hybridized carbon of sp2, sp3, chromium carbide and metallic chromium are present in the chromium-doped carbon membrane. At the same time, the content of carbon and chromium atoms with different valence bond structures in the film is a function of the chromium target current. When the chromium target current is below 0.3A, the content of sp3 hybrid carbon atoms in the film is kept at a high level and with the increase of chromium content in the film, its maximum value appears around 0.1A. When the chromium target current is greater than 0.3A, the beginning of sp3 hybrid carbon atoms in the film decreases rapidly with the increase of chromium content in the film. However, the content of sp3 hybrid carbon atoms in the film decreases with the chromium content of the film. On the contrary, the content of metal chromium and carbon chromium compounds constantly increases as the content of chromium increases. This shows that the doping of chromium has a significant impact on the valence bond structure of carbon itself in a graphite-like film.

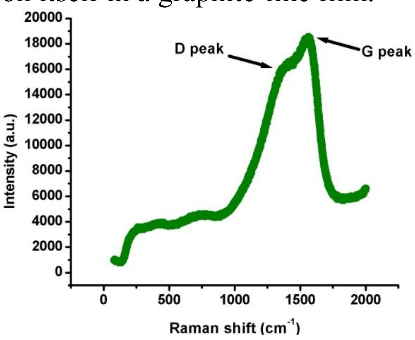

Figure 3. Raman Spectrum of Nanocomposite GLC Films

3.2 Fricbological Properties of the GLC Thin Films

Figure 4 shows the friction curve of metal doping during the dry friction of GLC films in the atmosphere, and it can be seen that different metal doping has different effects on the dry friction properties of GLC membranes. As shown in **Figure 4**, the friction coefficient of pure GLC film is approximately 0.05, indicating excellent solid lubrication properties. The addition of Cr significantly reduces the dry friction coefficient of the GLC film, primarily due to the promotion of graphitization in the film. Graphite-like carbon films prepared under different pulse duty cycles exhibit a low friction coefficient (approximately 0.055) and a low wear rate (approximately 10^-11 cm3/N-1.m-1). This suggests that the currently prepared thin films have excellent ferroelectric properties. Additionally, it is noteworthy that the graphite-like carbon films have a high load-bearing capacity. In humid conditions, the maximum contact stress can reach up to 2.5 GPa, significantly higher than that of diamond-like carbon films. Previous studies have shown that high hardness is a key factor in the excellent tribological performance of diamond-like carbon films, which typically exhibit outstanding wear resistance. However, despite having a maximum hardness below 15 GPa, the graphite-like carbon films still exhibit excellent tribological performance.

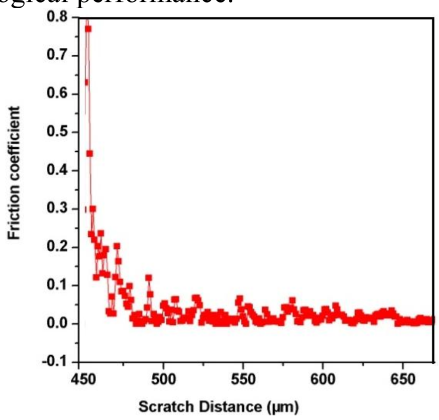

Figure 4. Friction Coefficient of Nanocomposite GLC Films

3.3 Load-Bearing Capacity of The GLC Thin Films

As shown in **Figure 5**, the loading-unloading curve indicates that the coating has a hardness of approximately 10 GPa and an elastic modulus of around 300 GPa. This suggests that while the coating's hardness is relatively low, it has a good ability to resist deformation. When subjected to external forces, although the coating's hardness is insufficient to completely prevent scratches and wear, its high elastic modulus allows it to effectively return to its original shape, maintaining a smooth surface.

Additionally, the coating's low hardness also means that it may offer better adhesion and toughness in certain applications, making it suitable for scenarios requiring flexibility and impact resistance.

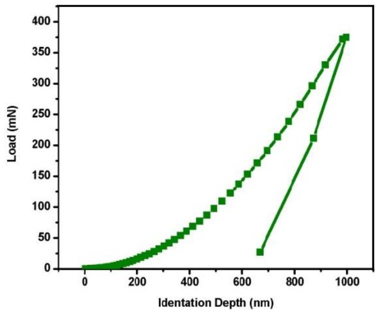

Figure 5. Load-Unload Curve of Nanocomposite GLC Films

3.4 Effect of Chromium on Stress and Hardness in Graphite-Like Film

The hybridized carbon of sp2, sp3, chromium carbide and metallic chromium are present in the chromium-doped carbon membrane. At the same time, the content of carbon and chromium atoms with different valence bond structures in the film is a function of the chromium target current. When the chromium target current is below 0.3A, the content of sp3 hybrid carbon atoms in the film is kept at a high level and with the increase of chromium content in the film, its maximum value appears around 0.1A. When the chromium target current is greater than 0.3A, the beginning of sp3 hybrid carbon atoms in the film decreases rapidly with the increase of chromium content in the film. However, the content of sp3 hybrid carbon atoms in the film decreases with the chromium content of the film. On the contrary, the content of metal chromium and carbon chromium compounds constantly increases as the content of chromium increases. This shows that the doping of chromium has a significant impact on the valence bond structure of carbon itself in a graphite-like film [9,10].

In general, the internal stress and hardness of the amorphous carbon film are mainly based on the ratio of sp2 carbon and sp3 carbon in the film. The higher the content of sp3 carbon, the greater the internal stress of the film, and the higher the hardness. The addition of chromium significantly changed the relative content of the original sp2 and sp3 hybrid carbon in the pure carbon membrane. The reason why the stress in the carbon film gradually decreases is that the sp3 carbon content in the thin film gradually decreases with the increase of the chromium content. The higher internal stress in the amorphous carbon film is directly related to the formation of the sp3 structure in the carbon film, and the high hardness of the amorphous carbon film is also quite attributed to its own high internal stress. In addition, adding a small amount of chromium to the film also significantly increased the content of sp3 carbon in the carbon film. This shows that chromium suppresses the formation of sp3 structure and also promotes the formation of sp2 structure, and then significantly reduces the ratio of sp2 carbon and sp3 carbon in the thin film. This is the main reason why the hardness of the carbon film can be sharply reduced by adding a small amount of chromium [12]. When more chromium is mixed, the presence of more and more metal chrome particles in the film also significantly changes the composition and structure of the carbon film, which must make the hardness of the chromium-mixed carbon film gradually close to the hardness of the metal chromium.

4. Conclusions

Both the mechanical and tribological properties of chromium-mixed graphite films are strongly affected by the chromium content of the films. Chrome incorporation in graphite-like films has obvious softening and destress effects. Adding an appropriate amount of chromium can not only reduce the surface roughness and improve the density of the amorphous carbon film, but also improve its tribological properties. When the chromium content increases, the hardness and internal stress of the chromium-doped graphite film gradually decrease with the decrease of the sp3 hybrid carbon atoms in the film. The friction coefficient and specific wear rate decrease and increase almost synchronously with the decrease of sp2 carbon atoms in the film. The smallest friction coefficient corresponding to the highest sp2 hybrid carbon content in the film structure shows a significant correlation between the mechanical and tribological properties of chromium-mixed graphite films with the increasing chromium content and the evolution of the valence bond structure of carbon in the films.

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