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Effect of Low-Energy Nitrogen Ion Implantation on Friction and Wear Properties of Ion-Plated TiC Coating

Zhongyu Dou ^{1,*}, Yinglu Guo ¹, Faguang Zhang ² and Dianxi Zhang ¹

¹ College of Physics and Electronic Science, Anshun University, Anshun 561000, China; gyl15772325021@163.com (Y.G.); xiwa_315@163.com (D.Z.)

² Refabrication, Guizhou Electromechanical Research and Design Institute, Guiyang 550025, China; zhangfg89@163.com

* Correspondence: 2012620@asu.edu.com

Abstract: To further improve the performance of the coated tools, we investigated the effects of low-energy nitrogen ion implantation on surface structure and wear resistance for TiC coatings deposited by ion plating. In this experiment, an implantation energy of 40 keV and a dose of 2×10^{17} to 1×10^{18} (ions/cm²) were used to implant N ions into the TiC coatings. The results indicate that the surface roughness of the coating increases first and then decreases with the increase of ion implantation dose. After ion implantation, the surface of the coating will soften and reduce the hardness, and the production of TiN phase will gradually increase the hardness. Nitrogen ion implantation can reduce the friction coefficient of the TiC coating and improve the friction performance. In terms of wear resistance, the coating with an implant dose of 1×10^{18} ions/cm² has the greatest improvement in wear resistance. Tribological analysis shows that the improvement in the performance of TiC coatings implanted with N ions is mainly due to the effect of the lubricating implanted layer. The implanted layer mainly exists in the form of amorphous TiC, TiN phase, and sp²C–C phase.

Keywords: N ion implantation; TiC coating; microstructure; friction coefficient; wear

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1. Introduction

Hard alloy material is widely used in cutting tools, deep processing, and other fields because of its good hardness, strength, and elastic modulus. However, the requirements of some application environments can be demanding, which necessitates further improvement of the friction and wear performance of the tool surface. The use of tool coating treatments is an important method for improvement of comprehensive performance. Its pivotal role is to combine the features of the metal substrate and the hard coating, thereby maintaining the toughness of the metal substrate while adding hardness and other characteristics of the coating [1]. Many studies have reported coating preparations on tool surfaces because a coating with excellent performance can fully protect the tool and significantly reduce the wear degree of the tool [2–6]. At present, coatings prepared by the PVD (Physical Vapor Deposition) or CVD (Chemical Vapor Deposition) method are not enough for the use requirements, and the composite treatment of coatings are a good choice. Iram et al. improved the wear resistance of AlCrN coating by adding Mo or V elements [7]. Zhang et al. reported that laser substrate pretreatment improved the antiadhesive wear resistance of TiAlN coating on WC/CO substrate surface [8]. Li et al. reported inserting Ti layers to enhance the performance of TiAlSiN coated carbide tools [9]. Additionally, posttreatment of the coating surface is an effective method to further improve the performance of the tool. There are several ways to perform posttreatment of a coating surface, including nitriding [10], carburizing [11], heat treatment [12], and ion implantation [13]. Among these technical solutions, ion implantation has become one of the most preferred surface treatment methods. Research achievements in the regulation of alloys or nano films include the use of nitrogen or carbon atoms for modification by ion implantation technology

as the nitrides or carbides formed have excellent wear and corrosion resistance [14–17]. Sharkeev et al. revealed the effect of N saturation and reported that high-dose N ion implantation significantly improved the wear resistance of TiN films deposited by physical vapor deposition [18]. Yang et al. reported that the improvement of friction and wear properties of TiN films implanted with N and Ti ions was due to the formation of nano-scale TiN grains in the thick amorphous layer [19]. Shum et al. reported that TiAlN coating after C ion implantation can greatly improve the wear resistance [20]. TiC film has high hardness, medium elastic modulus, and good oxidation resistance, and has been widely used in tool steels and coated tools. Some studies have shown that TiC films have lower friction coefficients and surface roughness than TiN and TiCN films, as well as higher oxidation resistance [21,22]. For coated tools used in high-speed cutting or dry machining, we need to further improve the surface properties of TiC films to maintain a low friction coefficient while improving its wear resistance. Revati et al. reported that the TiC film of DC (direct-current) magnetron sputtering with 600 keV·C ion implantation improved the wear resistance, and the improvement of the properties was related to the amorphicity of the TiC phase [23]. Typically, the implanted ions diffuse from their Gaussian-type distribution into the surface to provide a relatively smooth gradient between the un-implanted and implanted regions. In addition to the shallow implanted zone near the surface, there are additional beneficial work-hardening effects in the deeper regions extending to depths of the order of a micrometer [24].

It is believed that injecting nitrogen (N) or carbon (C) into the TiC coating can improve the friction and wear properties of the TiC coating. However, the surface modification of coatings by nitrogen ion and ion implantation is not simple, largely due to complexities of the ion dose and energy. At present, there is no report on the effect of low-energy N ion implantation on TiC coatings. In this work, TiC coatings were prepared on the surface of the cemented carbide material by vacuum ion-plated technology, and the effect of different doses of low-energy nitrogen ion implantation on the microstructure, mechanical properties and friction and wear properties of TiC coatings were studied. The correlation of friction and wear was established by the changes in the microstructure and mechanical properties of TiC coatings implanted with N ions. The surface structure was studied using an X-ray diffractometer and atomic force microscope, and the mechanical properties were tested by nanoindentation.

2. Materials and Methods

The experimental substrate materials were 16 mm × 16 mm × 4.8 mm YG8 cemented carbide tools, purchased from Hunan Zhuzhou Diamond Alloy Tool Co., Ltd. (Zhuzhou, China). Initially, the tool surface was mechanically polished and ultrasonically cleaned with anhydrous ethanol. After drying, it was held in a vacuum chamber for preparation. For coating, the substrate was cleaned with Ar ion (99.999%) to remove the surface oxides and other pollutants. The chamber was evacuated to 5×10^{-3} Pa, and the deposition temperature was 350 °C. High purity Ti (99.999%) and C₂H₂ were used for TiC coating, with a target current of 60 A, a substrate negative bias of −400 V, and a deposition time of 150 min. Implantation equipment was used for nitrogen ion implantation treatment for the coated specimens by a Kaufman gas ion source (Southwestern Institute of Physics, Chengdu, China). The N ion implantation, with an implantation dose range of 2×10^{17} to 1×10^{18} (ions/cm²), was carried out with the cavity evacuated to 2×10^{-3} Pa and an implantation energy of 40 keV, as presented in Table 1.

Table 1. The parameters of the ion implantation process.

Sample	Dose (ions/cm ²)	Implant Energy (keV)	Implanted Ion
S1	0	40	Nitrogen
S2	2×10^{17}	40	Nitrogen
S3	5×10^{17}	40	Nitrogen
S4	1×10^{18}	40	Nitrogen

SRIM/TRIM (The stopping and range of ions in matter) software (2013) was used to simulate the ion concentration distribution of N ions with an energy of 40 keV in the TiC coating [25]. An X-ray diffractometer (PANalytical X'Pert PRO, Almelo, Holland) was used to analyze the crystal structure of the coatings with a detection angle of 20° – 80° , a scanning speed of $10^\circ/\text{min}$, and a step size of $0.013^\circ/\text{s}$. The 3-dimensional morphology and surface roughness of the TiC coating were measured with an atomic force microscope (Bruker Dimension Icon AFM, Karlsruhe, Germany). A Nanoindenter (CSM UNHT, Shanghai, China) and friction and wear tester (Bruker UMT-2, Karlsruhe, Germany) were used to study the surface mechanical properties and friction and wear properties of the TiC coatings, and a laser 3-dimensional microscopic imaging system (OLYMPUS, Tokyo, Japan) was used to measure the wear cross-sectional area to judge the amount of wear. The friction method used a circular motion of 300 rpm/min for 30 min, with a load of 5 N and a wear scar radius of 12 mm. Dry friction was carried out with an 10 mm Al_2O_3 ball (HRC95) at room temperature, and the surface of the wear scar was observed with a scanning electron microscope (ZIESS SUPRA40, Jena, Germany).

3. Results

3.1. Ions Penetration Data

Figure 1 shows the impurity profile simulated using TRIM software for nitrogen ions having an energy of 40 keV, where the red dots show the ion track. Ion bombardment causes the ejection of atoms or cluster, which then diffuse to the surface due to motion [26]. SRIM is commonly used for the calculation of overall stopping power and ion range. In this case, however, dynamic simulation (TRIM) was used for calculating the ion ranges of all ions employed in the simulation [25]. Figure 1a shows that, when the 40 keV energy ion beam struck the TiC film surface, it followed different trajectories. Finally, most of the nitrogen ions diffused into the film surface at the depth of about ~ 75 nm, while a few of the N ions may have also reflected from the surface of the TiC film at some angles. Figure 1b shows the pattern of nitrogen ion distribution after implantation, from 170 nm in depth to the surface area of the TiC film. It was found that the implanted N ions exhibited a nearly Gaussian distribution and had a peak concentration at a depth of about 83 nm below the surface. The depth of the implanted zone (IZ) will increase with the implantation dose.

Figure 1. TRIM simulation for the (a) ion beam pattern, (b) ion distribution profile.

3.2. The Structure and Surface Morphology of the Coatings

Researchers often use scanning electron microscope (SEM) to observe the microstructure of coating. The surface and cross section morphology of TiC coating in the deposition state are shown in Figure 2. The SEM pictures indicate that the coating had a homogeneous distribution of small grains and was free from crystal defects such as cracks. From Figure 2b, it can be seen that the thickness of the coating sample was about 6.5 μm .

Figure 2. SEM micrograph showing the morphology of the as-deposited TiC thin film: (a) Surface (b) cross-section.

The X-ray Diffraction (XRD) results of N ion-implanted TiC coating with different implant doses are shown in Figure 3. We clearly see that, when the dose of N ion implantation was increased, the TiC diffraction peak shifted to a higher 2θ angle. A similar effect was observed by Singh et al., and they attributed it to the development of compressive stress on the surface of the nitride layer [26]. Another reason for this kind of shift may be due to the presence of light impurities, such as carbon and oxygen, in the sample [27]. The XRD analysis results of the implanted and un-implanted samples differed little when the dose was 2×10^{17} ions/ cm^2 . There was no significant shifting in the peak position (2θ) of diffraction peaks in the pattern, but variation in the peak intensity was clearly visible. When the implantation dose reached 5×10^{17} ions/ cm^2 , the TiN diffraction peak appeared. As the implantation dose further increased, the diffraction peak intensity also increased. From the perspective of the constant characteristics of ion implantation, this result was due to the increase of N ions and the TiN phase [28]. In addition, we noticed the existence of C element in the coating, which was considered to be due to the existence of sp^2 hybrid rich carbon in the TiC coating prepared by vacuum ion plating [29,30].

Figure 3. XRD patterns of TiC coatings implanted with different doses of N ion.

Ion implantation has been reported to be able to modify the surface morphologies and roughness of samples [31]. Surface roughness of the samples is subject to change by

bombardment, which was observed by AFM (Figure 4). The changes of the average and root mean square (RMS) roughness of each sample with ion dose are presented in Table 2. As the ion implantation dose increased, the surface morphology of the coating changed significantly, with a notable growth in surface roughness. Ion implantation induced roughening of the crystalline surface that was mechanistically related to implantation-induced mass transfer, the generation of dangling-bonds, radiation-enhanced segregation, and diffusion. Nuclear energy loss in the ion implantation led to surface erosion by elastic collisions. Since the ion interaction is a stochastic process and sputtering events are spatially distributed in variable magnitudes, the surface is generally roughened during ion bombardment [23]. However, when the even larger dose of 1×10^{18} ions/cm² was applied, the RMS roughness dropped. The roughness decrease at the largest dose might be attributed to the sputtering, etching, and diffusion processes occurring at that high concentration.

Figure 4. Three-dimensional AFM images of the samples: (a) Un-implanted; (b) implanted, dose 2×10^{17} ions/cm²; (c) implanted, dose 5×10^{17} ions/cm²; (d) implanted, dose 1×10^{18} ions/cm².

Table 2. Roughness information.

Sample (#)	Pristine	2×10^{17} (ion/cm ²)	5×10^{17} (ion/cm ²)	1×10^{18} (ion/cm ²)
RMS roughness (nm)	12.8	27.6	38.4	12.3
Average roughness (nm)	9.59	21.6	26.9	9.96

3.3. Hardness Measurement

An ultra-micro hardness test was carried out to observe the influence of N ion implantation on the mechanical properties of the implanted zone (IZ). The nanoindentation test used a maximum load of 1 mN and a loading and unloading rate of 0.3 mN/min. The Oliver and Pharr continuous stiffness method was used to analyze the indentation size. Based on these measurements, the hardness value was calculated. Different samples of results obtained by depth-sensing indentation test are shown in Figure 5. We found that the maximum indentation depth was higher for the ion-implanted films than for virgin TiC films, which suggests softening of all the coatings after the treatment. Many scholars have reported similar phenomena [23,32–34]. It is believed that this is due to defects and possible amorphization caused by ion bombardment. The implantation-affected zone (IAZ) contains the volume of material affected by ion bombardment and is located between the substrate and the implanted (nitrogen-rich) layer. The characteristics of this zone signifi-

cantly affect the mechanical properties of the implanted layer and the amorphization of the top layers of similar PVD, TiC, or TiN coatings when implanted by light elements in this range of energy. Table 3 shows the average hardness and Young's modulus of each sample. The average values of hardness and Young's modulus in pristine TiC coating were found to be 20.586 and 231.9 GPa. As the ion implantation dose increased, the hardness and Young's modulus increased. It is well known that elastic modulus scales with its crystalline fraction, so the increase in surface elastic modulus after irradiation can be related to the change in crystallinity [35]. Initially, the increase in surface microhardness is attributable to the formation of additional TiN phases in nitrogen ion-irradiated TiC coatings. This increasing trend in surface hardness value continued at higher fluences ranging from 5×10^{17} to 1×10^{18} ions/cm². The increase in surface hardness at higher fluences is mainly attributed to the formation of ion induced points defects [36]. The concentration of point defects increased by increasing ion fluence and, correspondingly, an increase in surface hardness was observed. The decrease in crystallite size at higher fluence may also be considered as the possible factors responsible for the increase in microhardness at higher fluences [37].

Figure 5. Depth-sensing indentation test results of different samples.

Table 3. Hardness and Young's modulus information.

Sample (#)	Pristine	2×10^{17} (ion/cm ²)	5×10^{17} (ion/cm ²)	1×10^{18} (ion/cm ²)
Average hardness (GPa)	20.586	4.332	6.758	7.265
Young's modulus (GPa)	231.9	130.8	163.3	280.9

3.4. Friction and Wear Performance

The friction coefficient and the amount of wear are important indicators for friction and wear performance. Figure 6 shows the friction coefficient curve of the samples under different implantation doses. The average friction coefficient of the surface coatings of all samples with differing implantation doses reached about 0.6 after different sliding distances. The period from the onset of friction to the sharp rise of the friction coefficient was the effective period of the sample surface modification layer. The friction coefficient of the unimplanted sample coating increased sharply after sliding for 30 m and tended to stabilize with a final friction coefficient of about 0.6. In the sample with a dose of 2×10^{17} ions/cm², the friction coefficient began to increase after the sliding distance increased to 55 m and stabilized at about 0.6 after sliding for 90 m. In the sample with a dose of 5×10^{17} ions/cm², the sliding distance reached 110 m before the coefficient increased to about 0.6. In the sample with the highest injection dose of 1×10^{18} ions/cm², the friction coefficient of the coating remained stable within a sliding distance of 260 m, with an average friction coefficient of 0.235. In this study, the posttreatment of N ion implantation process on the

TiC coatings trended toward a decrease of the friction coefficient, which may have been due to the soft surface layer formed on the surface. This softening reduced the shear stress at the contact point, thereby reducing the friction coefficient, making the IZ layer act as a solid lubricant [38]. However, solid lubricants cannot heal themselves and will gradually disappear with wear [39]. Under the condition of high-dose N ion implantation, the surface modification layer forms a composite structure mainly composed of TiN/TiC phase and mixes with oxides, which acts as self-lubricating during the friction process. This has a positive effect on the performance of the friction coefficient.

Figure 6. Variation curve of friction coefficient of different samples.

The wear resistance of the coating can be measured by the sliding distance or the amount of wear under dry friction, and the reduction of wear directly indicates wear resistance or improvement in the anti-wear ability of the sample. Figure 7 shows the cross-sectional areas of the coating wear scars for different implant doses after 30 min of the friction and wear test. The wear amount of the sample coatings implanted with N ions was lower than that of the un-implanted TiC coatings. When the N ion implantation dose increased to 1×10^{18} ions/cm², the alloy had the greatest increase in wear resistance, with the best anti-wear effect among all samples, consistent with the friction coefficient results. The wear morphology of each sample observed by SEM and three-dimensional micrographs is shown in Figure 8. The TiC coatings with a high dose of N implantation generally showed smoother and more uniform wear, with a decrease in the width of wear scar. In addition, the observed phenomena, such as peeling pits, particle fragments, and slight plastic deformation, indicate that abrasive wear was the main form of wear after coating failure.

The softening of the IZ layer and production of the TiN phase can explain the decrease in friction coefficient at different doses. The wear behavior can be explained by the model of the grain-mixed thin, soft layer, which describes the friction coefficient μ as the ratio of the surface shear strength (S) to the hardness, thereby explaining the variation of the friction coefficient with the ion implantation dose [33,39]. When the implantation dose was 1×10^{18} ions/cm², the IZ layer increased with the increase of the dose. The μ decreased with the increase of the dose, while the implantation effect was optimal at this time, so a very low friction area was observed within 260 m. The wear trajectory in Figure 7 shows that, after the implantation layer fell off, the wear debris was deposited in the wear scar or the edge of the wear scar. During the friction process, the debris deposited in the wear scar was deformed and debonded, and the debonded particles were transferred and redeposited in the wear track. When deposited in the form of a continuous layer, it can also act as a barrier between the friction ball and the surface of the sample, thereby reducing the wear rate. Perhaps due to this effect, the coating with a dose of 1×10^{18} ions/cm² had the

most wear resistance. In addition, the presence of amorphous carbon in the TiC coating prepared by ion plating is also an important factor affecting performance. The sp^2C-C phase with graphite structure can have an excellent lubricating effect during the friction process, which has been confirmed [24,40]. In conclusion, the improvement of friction and wear performance of TiC coating by N ion implantation is due to the comprehensive effect of many effects.

Figure 7. Cross-sectional area of coating wear scars with different implant doses.

Figure 8. Cont.

Figure 8. SEM and 3-dimensional micrographs show the wear morphology of the samples. (a) sample 1, Pristine (b) sample 2, 2×10^{17} (c) sample 3, 5×10^{17} (d) sample 4, 1×10^{18} .

4. Conclusions

The friction and wear properties of TiC coating post-treated with low-energy N ion implantation were studied. The results showed that the friction coefficient and wear rate of the TiC coating modified by N ion implantation were improved. Under 1×10^{18} ions/cm² implantation dose, the improvement of the wear resistance of the coating was the greatest. In the first stage of wear, the friction coefficient was 0.235, and it remained stable within 260 m. XRD, AFM, and nano-hardness tests showed that the surface roughness of the coating increased first and then decreased with the increase of ion flux. The hardness of the modified surface coating decreased, but further increases of ion fluences from 5×10^{17} to 1×10^{18} ions/cm² improved the hardness of the modified layer, which is mainly attributed to the formation of point defects and TiN phase. From the worn surface morphology, it can be concluded that abrasive wear is the main form of wear after N ion implantation. The mechanical and tribological properties of TiC coating can be controlled by the dose of N ion implantation, which is of great significance to the industrial application of TiC coating.

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