Rare Metal Materials and Engineering
Volume 45, Issue 12, December 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(12): 3080-3084.

ARTICLE

Morphology and Mechanical Properties of TiN Coatings Prepared with Different PVD Methods

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Abstract: TiN coatings were prepared on the GCr15 substrate by the cathode arc deposition, medium frequency magnetron sputtering and their composite methods. The coatings were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) spectroscopy, microscratch test, friction and wear test. Moreover, the effects of different preparation methods on the structure and mechanical properties of the coatings were compared. The results show that the coating prepared by the composite method of arc and magnetron possesses a smooth surface and better comprehensive properties such as high cohesion and hardness; thus the wear rate is lower.

Key words: PVD deposition; TiN coating; wear and friction; composite deposition

TiN coatings have been widely applied in the domains of cut tools and drilling bit because of their high hardness, chemical stability, anti-oxidation and well wear resistant ability[1,2]. In the 1970 s, the TiN coating was successfully used and led to a revolution of tools. TiN coatings have been fabricated by different PVD methods, which were applied in many different fields. The PVD methods mainly include cathode arc deposition[3] and unbalance magnetron sputtering deposition[4,5]. Since it can achieve the high ionization rate, high energy and good cohesion, the cathode arc technique is much favorable. However, there are many large particles on the surface of the coating deposited by cathode arc, and the microstructure of the coating is not sufficiently dense, which seriously affects the quality of coating surface[6-8]. Another technique, medium frequency magnetron sputtering[9,10], has been also developed. Although the coating prepared by medium frequency magnetron sputtering has smooth surface and compact microstructure, the stress in the coating is large and the deposition ratio of magnetron sputtering is low. In order to overcome these disadvantages, the mid-frequency magnetron sputtering and cathode arc are composited. It is hoped that the cathode arc technique can improve the bonding strength of the coating, and the sputtering technique can improve the surface quality and microstructure characteristics of the coating. So the coatings prepared by the composite technique will possess better wear resistant property.

Many researchers have made various attempts on the composite cathode arc technique and have obtained some achievements in this field[11]. However, for the composite technique of large rectangular plane a cathode arc source is rarely reported. Our research group has developed a composite technique of medium frequency magnetron sputtering and rectangular cathode arc source. In the present paper, the TiN coatings were prepared by the composite method of cathode arc and magnetron sputtering methods. The mechanical properties of the coatings were estimated by microscratch tests and wear tests, and the coatings deposited by different PVD methods were compared to get the best one.

1 Experiment

Received date: December 25, 2015
Foundation item: National Instrumentation Grant Program (2011YQ120039)
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The reformation equipment was used in this study, as shown in Fig.1. Based on the original MEVVA source, two medium frequency sputtering sources and two cathode arc sources were added, whose dimensions were 420 mm×120 mm. The work piece holder was positioned in the center of the vacuum chamber which could rotate. In addition a pulse bias power supply was employed on the holder. There was a heating system in the vacuum chamber, which could increase the atmosphere temperature to about 450 ℃.

GCr15 bearing steel and silicon wafer were used as the substrates. The substrates were all ground, polished, ultrasonic cleaned and dried by nitrogen before put into the vacuum chamber. Then they were fixed on the specimen holder. When the air pressure in the vacuum chamber was lower than 2×10^{-3} Pa, the argon gas was introduced to adjust the pressure so as to produce a plasma discharge. A negative pulse bias voltage of 0~700 V on the sample was used for the surface etching and cleaning for 30 min, and then turn on Ti target for the deposition of Ti transition layer [2]. In this stage, −100 V DC and −500 V pulse bias voltage was applied, and the deposition time was 5 min. Then nitrogen gas was introduced for the deposition of TiN layer, and the nitrogen flow rate gradually increases from 100 mL/mim to 500 mL/mim. Other experiment parameters used were all optimized parameters when different sources were employed. The deposition parameters of different preparation methods are shown in Table 1 and the samples are denoted as S1, S2, S3, and S4.

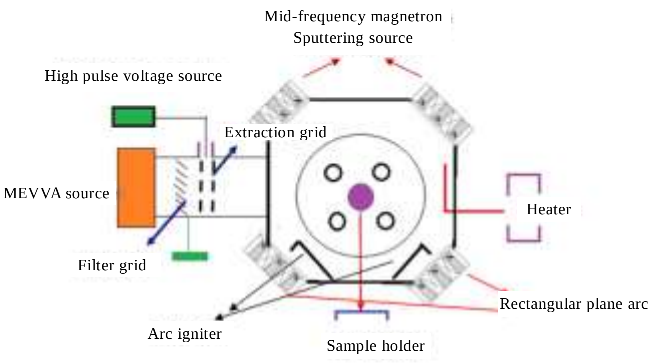

Fig.1 Structure schematic of the composite arc- magnetron sputtering equipment

Table 1 Deposition parameters and methods

Sample	Method	Deposition temperature/℃	Pulse bias /V	Deposition time/min
S1	Cathodic arc	350	160	60
S2	From arc to sputtering	350	160	60
S3	Composite	350	160	80
S4	Magnetron sputtering	350	160	100

A scanning electron microscope (SEM, USA) was used to examine the surface and fracture microstructures. A three dimensional (3D) white-light interfering surface profiler was applied to measure the surface roughness (R_a) of the films, and observe the scratched and worn surfaces. A scratch tester (WS- 2004, China) was employed to measure the adhesions between the films and substrates, expressed by critical loads. Microhardness tester (Woleprt Wilson Instruments) was applied to test the hardness, with the load of 60 N. A ball on disc tester (UMT-2) was used to evaluate the tribological properties of the samples. The ambient environment was atmosphere. A GCr15 ball of 6 mm in diameter was used as the counterpart under a normal load of 20 N. The relative sliding velocity was 5 mm/s, and the sliding time was 40 s.

2 Results and Discussions

2.1 Morphology and roughness of the coatings

The morphologies of coatings deposited by different methods are shown in Fig.2, and the roughness of the surface is got by the three dimensional (3D) white-light interfering surface profiler. In Fig.2a and 2b, we can see that many particles and small holes with the size of 1~3 μm appear in the surface. This is the intrinsic characterization of the arc deposition. The particles and holes lead to a rather rough surface. The roughness of S1 and S2 are 0.55 and 0.430 μm, respectively. For the sample of S2, due to the latter step of magnetron sputtering deposition, a part of small sized particles are buried and thus the total density of the particles decreases. However the effect of sputtering on the large grains is not obvious. The surface of the coating deposited with the composite technique, S3, is smooth. The roughness is 0.105 μm. There are only a few micro pores. Both the size and density of the particles are much smaller than those of the single cathode arc deposition. S4 is deposited with magnetron sputtering. It has the minimum roughness of 0.065 μm.

The main reasons of the high quality surface deposited with composite technique are as following. Firstly, because the sample immediately turns into magnetron sputtering mode after the cathode arc deposition, the defects and holes are filled by the tiny particles. Moreover, due to the substrate bias, large particles are sputtered into small particles, and thus a part of the particles are decomposed before stabilized on the surface of the coating. Secondly, the high density of plasma is another possible reason of the improvement of the quality of surface. Through some survey, it is found that the plasma density of the composite sources is larger than that of the single source.

2.2 Microstructure of the coatings

The cross sectional morphologies are shown in Fig.3. There are two kinds of fractures, on the silicon and on the steel, and the thicknesses are different. The coating on

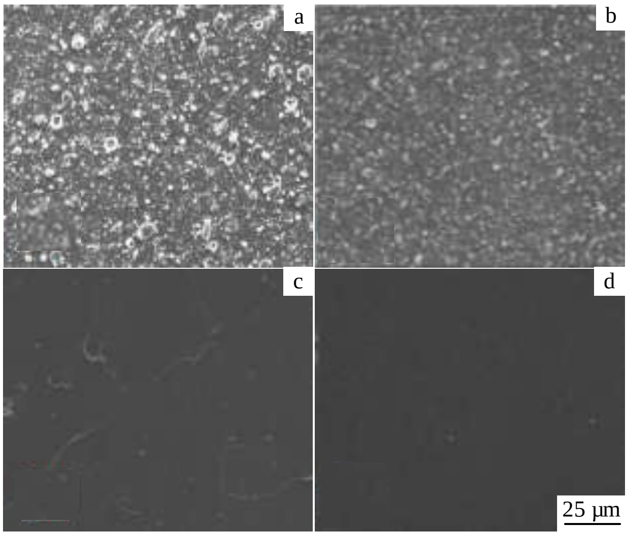

Fig.2 Surface morphologies of sample S1 (a), S2 (b), S3 (c), and S4 (d)

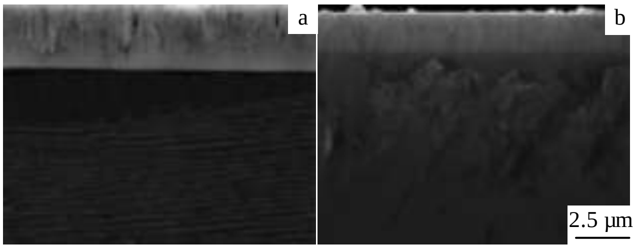

Fig.3 Cross sectional structure morphologies of S1 (a) and S3 (b) deposited on silicon substrate

silicon is thinner than that on steels due to the different electroconductibility. The micro-hardness, thickness and deposition rate of coatings prepared with different methods are shown in Table 2. The thickness and the deposition rate are obtained by evaluating the coatings on bearing steels.

From these fracture morphologies on silicon substrates, we can obtain the information of the microstructure of the coatings in micro scope. Fig.3a, the organization of S1 shows the coarse grained columnar crystalline feature, which is the typical characterization of the coatings prepared by cathode arc [12]. S3 in Fig.3b is the coating prepared by the composite method of magnetron sputtering and cathode arc deposition. Compared with S1, S3 is much thinner for the rotating of the sample holder. The microstructure of S3 is compact with clear orientations and the columnar feature is not obvious. It means the effect of composite arc-magnetron technique on the refining of coating is apparent.

2.3 XRD analysis

The XRD patterns of the samples prepared by different methods are shown in Fig.4. We can see that crystal structures in the films and the preferential orientation of the

Table 2 Microhardness, thickness and deposition rate of coatings on steel

Sample	Microhardness, HV/MPa	Thickness/ μm	Deposition rate/nm·min^{-1}
S1	11410	7.8	129.4
S2	8240	6.1	100.3
S3	9220	2.1	28.5
S4	6780	1.7	17.6

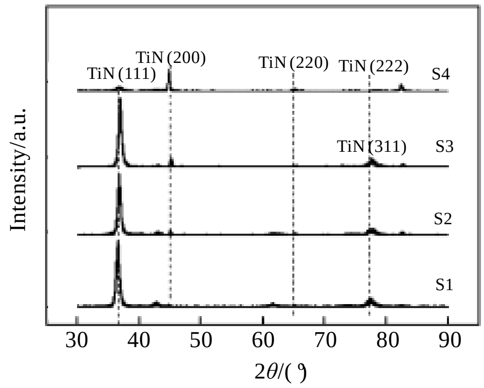

Fig.4 XRD patterns of sample S1, S2, S3, and S4

crystalline are different. For S1, S2, and S3 the preferential orientation is TiN(111) and (311), the size of the crystalline grain is similar to each other. But for S4 the main orientation is TiN(200) and (222). This is decided by the different energy produced during the preparation by different methods [3,5,8].

2.4 Microscratch

Fig.5 shows the cohesion and microscratch of coatings prepared with different methods. The cohesion of S1 is 50.3 N which is the highest. From the picture of the end of the microscratch, we can see that the indentation is uniformly pushed into the substrate. The shedding of the surrounding coating is less and there is no obvious crack. This is because the stress of coatings prepared with arc deposition is small and thus is of benefit for the film-substrate cohesion. This feature can be also used to deposit the interlayer. Both the cohesions of S2 and S3 are larger than 45 N. The morphology of microscratch shows the disintegration and fragment at the tail of the microscratch. S4 is the sample prepared with magnetron sputtering. The cohesion of S4 is 36.5 N which is the lowest, and we can to see many fragments at the tail of the scratch track. It is attributed the large stress accumulated during growth of the coating resulting in the weak cohesion of coating and substrate. From the above discussion, it can be concluded that the sample deposited by the composite method has the best cohesion of film-substrate.

2.5 Friction and wear behavior

The coefficient of fiction is shown in Fig.6. The friction

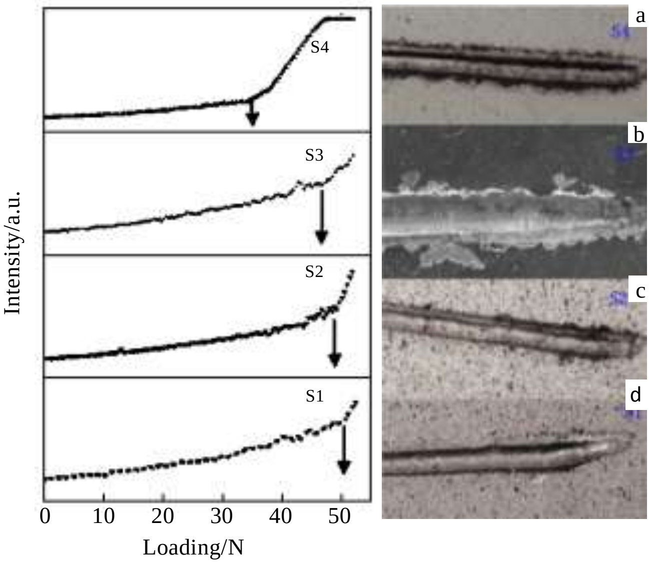

Fig.5 Cohesion and microscratch track of sample S4 (a), S3 (b), S2 (c), and S1 (d)

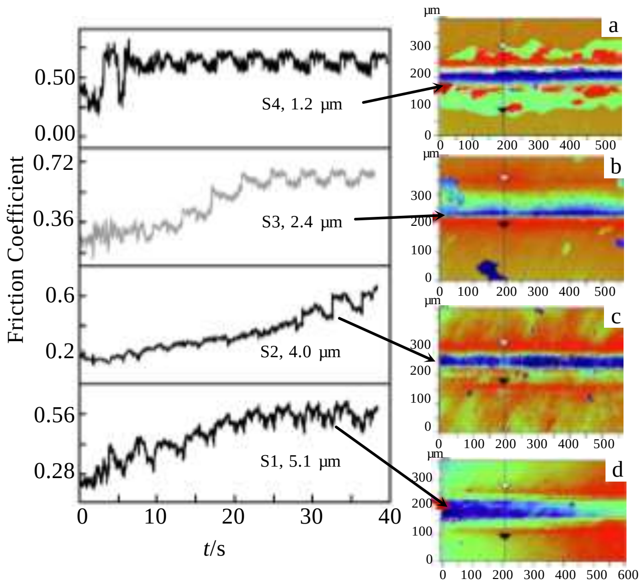

Fig. 6 Friction coefficient of sample S4 (a), S3 (b), S2 (c), and S1 (d)

coefficient is not an intrinsic feature of the material. It depends on the intrinsic factor and the testing factor. The intrinsic factors include the roughness of surface, microstructures, hardness, thickness of the coatings and film-substrate cohesion. The testing factors include the kind of the contact ball, the loading, the existence of the lubricating, temperature and so on.

According to the Archard's equation[13], the relationship of wear rate, hardness and loading is as following:

$$\frac{V}{S}=K\frac{F_N}{H} \tag{1}$$

where, S is the distance of the microscratch, F_N is the loading, H is the harness, V is wear volume, and K is the wear rate during the abrasion. Given the V, F_N, and S, K can be computed as the following:

$$K=\frac{VH}{F_N S} \tag{2}$$

Table 3 shows the abrasion volumes and abrasion ratios of the samples. In the following we will discuss the wear property of different samples based on the curve of fiction coefficient and scratch morphology.

There is a variation in the contact mechanism and wear process in sliding contacts between titanium nitride and steel. However, it is possible to identify 4 stages in the wear process including initial wear, rising, steady-state wear, and coating failure[14].

In the wear test, the contact ball used is the same to the substrate, GCr15. For the friction coefficient between the steels is also ranged from 0.5 to 0.6, the fourth stage cannot be seen, and even the coating is destroyed (as the sample of S4).

For S1 and S2, the variation pattern is basically the same, which can be divided into three stages, however the little difference is that the second stage of S2 is much longer and it creases more steadily, because S2 is relatively soft (HV= 8240 MPa), thus having a much smaller inner stress and better toughness; therefore the ground particles are smaller and less during the second stage. From the auxiliary photo in Fig.6, we can also see that S2 has the lowest wear scars. The surface roughness of S1 is larger (0.5 μm). It is harder and much brittle, so the ground particles are larger during the wear process. After a few cycles of fluctuation, the friction rises to the third stable stage quickly, and the wear rate of S2 is slightly lower than that of S1.

Sample S3 is much thinner than S1 and S2. However, due to the special preparation technique, the composite method of magnetron sputtering and cathode arc, its surface roughness is much smaller than that of S1 and S2, the micro structure is more compact, and the cohesion between the coating and the substrate is fine, so there are few wear particles in the initial stage. As a result, it possesses a

Table 3 Abrasion volumes and abrasion ratios of the samples

Sample	Wear depth/ $\times10^{-3}$mm	Wear width/ mm	R_a/ μm	Wear rate/$\times10^{-6}$ $mm^3(N\cdot m)^{-1}$
S4	4.3349	0.2205854	0.065	1195.31
S3	0.4466	0.1647334	0.105	91.95
S2	0.3315	0.133227	0.43	55.2
S1	0.3368	0.187	0.55	109.6

longer platform of the first stage compared to S1 and S2. Then some wear particles gradually emerge, the friction coefficient rises to the second stage mildly, and no crack or coating spalling phenomenon can be observed. When an oxide protective film is formed on the surface of the steel ball, the friction coefficient enters into the stable stage, namely the third stage. The coatings are not worn as confirmed by the photo taken by the optical microscope (as shown in the auxiliary picture in Fig.6). It is also due to advantages of the composite method. The wear rate of S3 is close to that of S1, and S2, which are much thicker than S3.

For the cohesion of S4 is poor, it is damaged immediately when loading is applied, so the first stage is very short. Then the film fractures and produces large ground particles, as a result the friction rises to the second stage suddenly. For the failure of the coating, there are no feature of the third stage in the curve. At the fourth stage, the friction fluctuates regularly, which is also owing to that oxide layer is formed on the ball surface. Based on the above analysis, we can see that the coating prepared by the composite method of magnetron sputtering and cathode arc has satisfactory surface quality, compact microstructures, good adhesion, and excellent anti-wear properties.

3 Conclusions

1) We have prepared TiN coatings with the cathode arc, magnetron sputtering and the composite methods.

2) The coating hardness, adhesion and thickness, as well as the microstructure and surface quality of the coating have an important influence on the friction performance.

3) The coating prepared by the composite technique (S3, 2.1 μm) has a smooth surface and a compact structure, due to the alternate deposition of different technique. So it has better mechanical properties, such as the cohesion larger than 45 N, the microhardness HV 9220 MPa, which is higher than that of S1 (7.8 μm). Besides, the friction and wear rate of S3 are lower.

4) The thick coatings prepared by the composite method will have more advantages in wear resistant properties when used under high loading conditions.

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不同 PVD 技术沉积 TiN 涂层的形貌和力学性能研究

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摘　要：采用阴极弧沉积、中频磁控溅射及二者的复合技术在GCr15基底上制备了TiN涂层。通过扫描电镜、XRD谱、微米划痕测试、硬度测试以及摩擦磨损测试对涂层的组织结构和力学性能进行了表征及对比。结果表明，采用复合磁控阴极弧技术制备的TiN涂层具有较好的综合性能，如较光滑的表面、较高的结合力和硬度，故磨损率较低。

关键词：物理气相沉积；TiN 涂层；摩擦磨损；复合沉积

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