Study on Properties of TiSi/C, TiSiN/C and TiSiO/C Multilayer Thin Films Prepared by High-Power Pulsed Magnetron Sputtering

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Abstract. This paper studies the effect of nitrogen or oxygen on the properties of TiSi/C hard films. Three sets of nano-multilayer composite hard films TiSi/C, TiSiN/C and TiSiO/C were prepared on tungsten carbide, 304 stainless steel and Si wafer substrates by high-power pulsed magnetron sputtering and DC magnetron sputtering. Meanwhile, X-ray diffraction (XRD), field emission-scanning electron microscope (SEM), Vickers hardness tester, tungsten carbide ball friction test, Raman spectra and electrochemical corrosion tests were performed to investigate the effects of nitrogen or oxygen on the microstructure, mechanical properties, tribology and corrosion resistance of TiSi/C films. The results show that the hardness of TiSiN/C film is 27.7% higher than that of TiSi/C film, and the hardness of TiSiO/C film is 67% higher than that of TiSi/C film. Besides, the hardness of the TiSiO/C film reaches 3771 HV, the friction coefficient is only 0.25, and the corrosion resistance is also the most excellent.

1. Introduction

Tools and molds are widely used in the industrial field. It is hoped that the tools and molds used will last longer and the quality will be better to produce more precise products. Therefore, there is an increasing demand for improving the coating performance of tools and molds. TiSiN is a very popular coating material, and there are many related research [1, 2]. The hardening mechanism is as follows: In TiSiN nanocrystalline composite structural film, nanocrystalline TiN is encapsulated by amorphous Si_3N_4. Since the grain size of nanocrystalline TiN is small, dislocations are hardly generated, and the thickness of the amorphous Si_3N_4 interfacial phase is very small, making it difficult to spread the cracks on the crystal surface, thereby giving the film a superhard effect [3]. In recent years, more and more researches have been conducted on the improvement and application of TiSiC hard films. It is found that TiSiC films have excellent oxidation resistance, abrasion resistance, corrosion resistance and high hardness [4-6]. At the same time, some studies have pointed out that the sliding of TiN nanocrystals along grain boundaries is an important factor in the deformation of TiSiN hard films. However, the amorphous SiCN interface phase in TiSiCN hard film can limit the slip of TiN

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nano-grain, so TiSiCN nano-composite hard film is expected to further improve the hardness of TiSiN nano-composite hard film [7]. Due to the excellent mechanical properties of nano-multilayer films, it is considered to be an excellent protective layer for processing applications, and more and more hard films have been made into nano-multilayer composite structure films [8-9].

Therefore, we attempt to prepare a TiSi/C nano-multilayer composite structure hard film, and then dope the TiSi/C multilayer hard film with nitrogen, which may form an amorphous SiCN interface phase to limit the slip of the TiN nano-grain along the grain boundary. Thus, it is possible to obtain a film having an extremely high hardness and a low coefficient of friction.

Nowadays, few studies have used magnetron sputtering technology to add oxygen to TiSi/C multilayer hard films. However, studies have shown that TiO_x and SiO_x oxide films have self-lubricating effects that reduce friction coefficient and wear rate [10]. Therefore, the addition of oxygen to TiSi/C film may form oxides such as TiO_x and SiO_x, which may have important significance for obtaining a film with high hardness and low friction coefficient.

High-power pulsed magnetron sputtering deposition is one of the most popular PVD techniques for producing hard-coated tools [11-13]. Based on this technique, high-power pulsed magnetron sputtering deposition technology can generate more average energy ions than conventional DC magnetron sputtering techniques [13]. Besides, the films obtained by magnetron sputtering have high purity, good compactness, and good uniformity of film formation, and can obtain a film with a uniform thickness on a large area of the substrate [14, 15]. Based on the above studies, in order to find more excellent films, we tried to use the above processes and methods to prepare three groups of nano-multilayer composite structure hard film, including TiSi/C, TiSiN/C, and TiSiO/C, by adding nitrogen or oxygen to TiSi/C multilayer hard films. Then, compared with TiSi/C nano-multilayer hard film, it may be due to the addition of nitrogen or oxygen to TiSi/C nano-multilayer hard film to improve the hardness, abrasion resistance, corrosion resistance and other properties. Therefore, it is of great significance to find a new film material and film synthesis process.

2. Experiment

In this paper, three sets of nano-multilayer composite films TiSi/C, TiSiN/C and TiSiO/C were deposited on the test piece by high-power pulsed magnetron sputtering and DC magnetron sputtering. The test piece were tungsten carbide, 304 stainless steel and Si wafers. The coating system was a dual target magnetron sputtering system. Before the coating, the surface of the test piece was cleaned and dried. The TiSi target (Ti: 80%, Si: 20%) was then subjected to DC magnetron sputtering with a set power of 1 kW. The C target used high-power pulsed magnetron sputtering technology with a set power of 1.5 kW and a pulse current duty cycle of 3%. After making the TiSi and TiSiN interlayers for the three sets of test pieces, the test piece was rotated at 2 rpm, a certain amount of Ar gas was introduced into the first set of test pieces, the second set of test pieces was fed with 10% N_2 mixed gas and the third sets of test pieces were passed through a 10% O_2 mixed gas. The total coating time was 70 min, and finally three groups multilayer of TiSi/C, TiSiN/C and TiSiO/C hard films were obtained.

The crystal structure of the film was analyzed by an X-ray diffractometer (Model: PHILIPS PANalytica X'Per PRO MRD) with a grazing incidence angle of 1° and CuKα radiation (λ = 1.54060 Å). The surface, side topography and film thickness measurement of the film were carried out by a scanning electron microscope (FE-SEM, model: JOEL JSM-5600). Semi-quantitative analysis of the composition of the three groups of films was carried out by an X-ray energy dispersive analyzer (EDS). The hardness of the film was measured by a Vickers indentation device with a load of 25 g. Three groups of films were subjected to an abrasion test by a disk friction test using a tungsten carbide ball, and the friction coefficients of the three groups of films were measured. Raman spectroscopy was used to determine the fine structure of the film. Electrochemical corrosion experiments were used to test the corrosion resistance of the film. Finally, the roughness of the three sets of films was also measured.

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3. Results and Discussion

3.1 Microstructure, morphology, composition and hardness of the film

Table 1 presents the basic properties of the TiSi/C, TiSiN/C and TiSiO/C three groups multilayer hard films, including the composition, thickness, hardness and roughness of the film. The hardness of the film was measured by a Vickers indentation device with a load of 25 g. The hardness of the TiSi/C, TiSiN/C and TiSiO/C films on the tungsten carbide substrate is shown in Table 1. It can be seen from Table 1 that the hardness of TiSi/C is 2256 HV, the hardness of TiSiN/C film is increased to 2882 HV, which is increased by 27.7%, and the hardness of TiSiO/C film is increased to 3771 HV, which is increased by 67%. Here, it is particularly mentioned that the TiSiO/C film has the highest hardness. The crystal structures of TiSi/C, TiSiN/C and TiSiO/C films were analyzed by X-ray diffractometry as shown in Fig. 1. Since the film thickness of the three groups of films taken in the SEM of Fig. 2 is less than 1 μm, the position where the diffraction peak signal is more frequently is the diffraction peak signal from the 304 stainless steel substrate. In addition, the three groups of films do not have strong characteristic peaks, so the three groups of films may be mainly amorphous structures. Among them, TiSiN/C film may be mainly coated with amorphous film on TiN nanocrystals to produce dispersion strengthening phenomenon, which improves the hardness [7]. Moreover, the content of N in TiSiN/C film is only about 3.77%.It is expected that the more content of N, the more likely the hardness will be improved.The TiSiO/C film may be mainly coated with amorphous film on TiO_2 and SiO_2 nanocrystals, which occurs a dispersion strengthening phenomenon occurs, thereby the hardness is also improved. The reason why the hardness of TiSiO/C film is higher than that of TiSiN/C film may be that EDS shows that the content of nitrogen in TiSiN/C film is small, while the content of oxygen in TiSiO/C film is more. Therefore, there are more nanocrystals in the TiSiO/C film, which makes the effect of dispersion strengthening and hardness enhancement more obvious.

The film thickness and side morphology of the TiSi/C, TiSiN/C and TiSiO/C films is observed by scanning electron microscopy. It can be seen from Fig. 2 that the three sets of films are layered, and the TiSi/C film and the TiSiO/C film produce distinct columnar crystals, while the TiSiN/C film has no columnar crystals.

The EDS analysis of the film is shown in Table 1， the content of nitrogen in the TiSiN/C film is small, and the content of oxygen in the TiSiO/C film is obviously more. This may be because the reactivity of nitrogen is worse than that of oxygen, so that under the same experimental conditions, oxygen accounts for about 15.8% of TiSiO/C film, while nitrogen accounts for only about 3.77% of TiSiN/C film.

Table 1. Basic properties of TiSi/C, TiSiN/C and TiSiO/C films

Test piece	Elemental composition (at.%)					Film thickness (μm)	Hardness (HV0.025)	Roughnes s (Ra, μm)
	Ti	Si	C	N	O			
TiSi/C	42.94	17.09	39.97	—	—	0.93	2256	0.0243
TiSiN/C	38.96	18.1	39.18	3.77	—	0.84	2882	0.0227
TiSiO/C	30.49	17.23	36.48	—	15.8	0.92	3771	0.0213

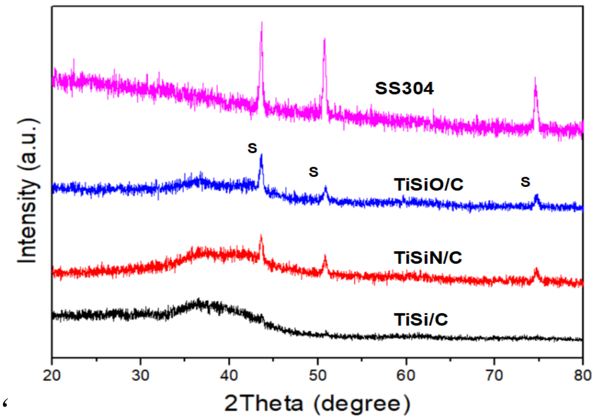

Figure 1. X-ray diffraction analysis of TiSi/C, TiSiN/C and TiSiO/C films

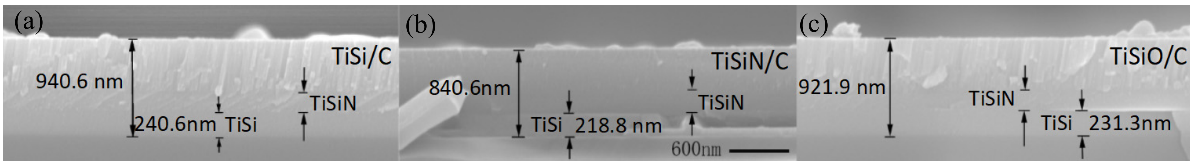

Figure 2. Side profile of the film (a) TiSi/C, (b) TiSiN/C, and (c) TiSiO/C

The surface morphology of TiSi/C, TiSiN/C and TiSiO/C films is observed by scanning electron microscopy, as shown in Fig. 3. The results show that the surface morphology of the three films is flat and almost no large particles appeared. It can be seen from Table 1 that the roughness of the three groups of films is very low, wherein the roughness of the TiSi/C film is 0.0243 μm, the roughness of the TiSiN/C film is 0.0227 μm, and the roughness of the TiSiO/C film is 0.0213 μm. Therefore, it can be seen that the film obtained by magnetron sputtering has high purity, good compactness and good film formation uniformity, and a film having a uniform thickness can be obtained on a large-area substrate [14, 15].

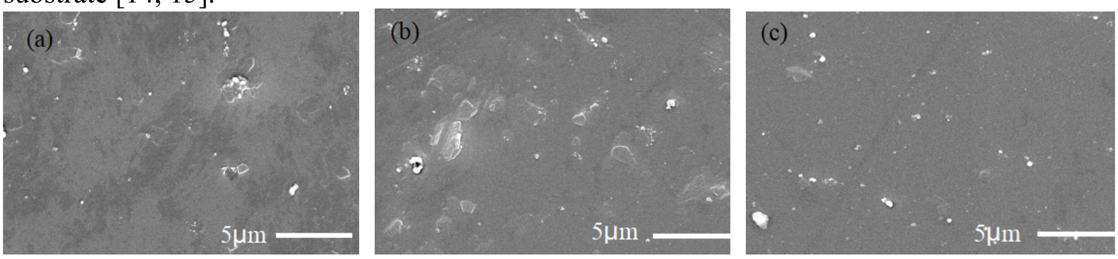

Figure 3. Surface morphology of the film (a) TiSi/C, (b) TiSiN/C, and (c) TiSiO/C

3.2. Disk friction test of films on tungsten carbide balls

Figure 4 is the result of a disc friction test of TiSi/C, TiSiN/C and TiSiO/C films on tungsten carbide balls. The TiSiO/C film has a low coefficient of friction of about 0.25, and the TiSi/C and TiSiN/C films have a high coefficient of friction of about 0.7-0.8. Compared with TiSi/C and TiSiN/C films, the TiSiO/C film has a much lower friction coefficient and a more stable sliding curve, which may because the surface of TiSiO/C film forms oxides such as SiO_x and TiO_x. The oxide has a self-lubricating effect of reducing the friction coefficient and the wear rate [9], and the hardness of the TiSiO/C film is higher, reaching 3771 HV, which also makes the TiSiO/C film have a lower friction coefficient [4].

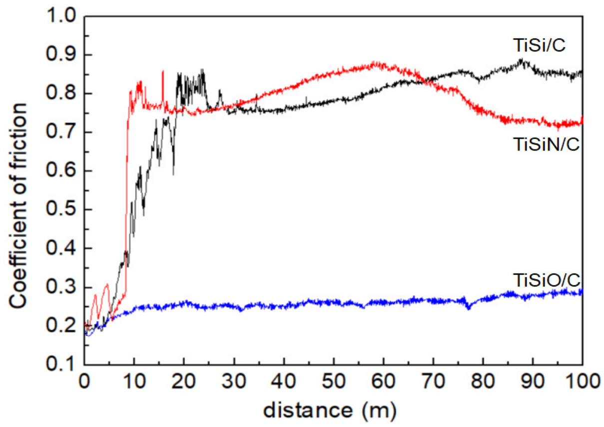

Figure 4. The comparison of friction coefficients of TiSi/C, TiSiN/C and TiSiO/C films on tungsten carbide balls

3.3. Raman spectroscopy of thin films

The Raman spectra and Gaussian fitting results of TiSi/C, TiSiN/C and TiSiO/C films are shown in Table 2. The D peak of TiSi/C and TiSiN/C is around 1405 cm^{-1} and the peak of G peak is around 1566 cm^{-1}. The ratio of Id/Ig is also about 1.6, which is the cause of this phenomenon. From Table 1, it is found that the content of nitrogen in the TiSiN/C film is small, about 3.77%, and only a small amount of nitrogen formed a bond with the components in the TiSi/C film. Therefore, the ratio of TiSiN/C to TiSi/C film Id/Ig does not differ much. However, the peak position of the D peak of the TiSiO/C film is shifted to 1394 cm^{-1}, the peak of the G peak is shifted to 1564 cm^{-1}, and the ratio of Id/Ig is increased to 4.22. Since the ratio of Id/Ig is larger, the content of sp^3 in the film is smaller, and the more defects are formed [11], Thus, this indicates that the content of sp^3 in TiSiO/C film is lower than that of in the TiSi/C film, and the defects are increased.According to Table 1, the results of EDS show that the proportion of oxygen in the TiSiO/C film is relatively large, accounting for 15.8%. This maybe the film generates a large amount of oxides, so that the ratio of Id/Ig becomes large, the defects become large, and the content of sp^3 becomes low.

Table 2. Raman spectra and Gaussian fitting results for TiSi/C, TiSiN/C, and TiSiO/C films

		D peak			G peak		
Test piece	Peak position /cm^{-1}	Half width /cm^{-1}	Integral area	Peak position /cm^{-1}	Half width/cm^{-1}	Integral area	Id/Ig
TiSi/C	1405.24	171.12	2902.64	1566.24	96.96	1812.88	1.60
TiSiN/C	1405.24	171.11	2902.53	1566.24	96.96	1812.95	1.60
TiSiO/C	1394.21	251.57	9395.78	1564.39	86.02	2228.98	4.22

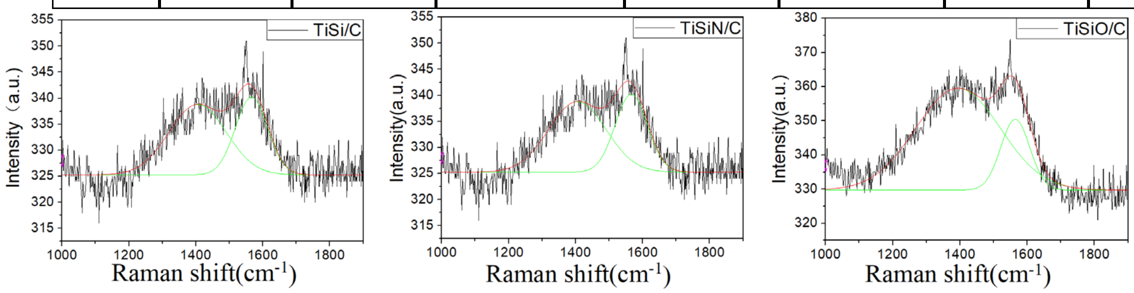

Figure 5. Raman and Gaussian fitting curves of TiSi/C, TiSiN/C and TiSiO/C films

3.4. Electrochemical corrosion testing of thin films

In the electrochemical corrosion experiment, the closer the corrosion potential is to positive electricity, the smaller the corrosion current density, and the better the corrosion resistance of the film [16]. The anodic polarization curves of TiSi/C, TiSiN/C and TiSiO/C films on 304 stainless steel substrates are shown in Fig. 6. When the three groups of films begin to corrode, the corrosion current density and corrosion potential are almost the same. However, after the first corrosion of TiSiN/C and TiSiO/C films, the second segment of corrosion occurs, which makes the corrosion current density smaller and the corrosion potential closer to positive. The reason for this phenomenon may be that during the corrosion process, a new protective layer is created to suppress corrosion. Therefore, due to this phenomenon, we can speculate that TiSiN/C and TiSiO/C has better corrosion resistance than TiSi/C film. Moreover, in the last stage of corrosion, TiSiN/C and TiSiO/C have similar corrosion current densities, while the corrosion potential of TiSiN/C is -0.25 V, and the corrosion potential of TiSiO/C is -0.02 V, which indicates TiSiO/ C has more excellent corrosion resistance.

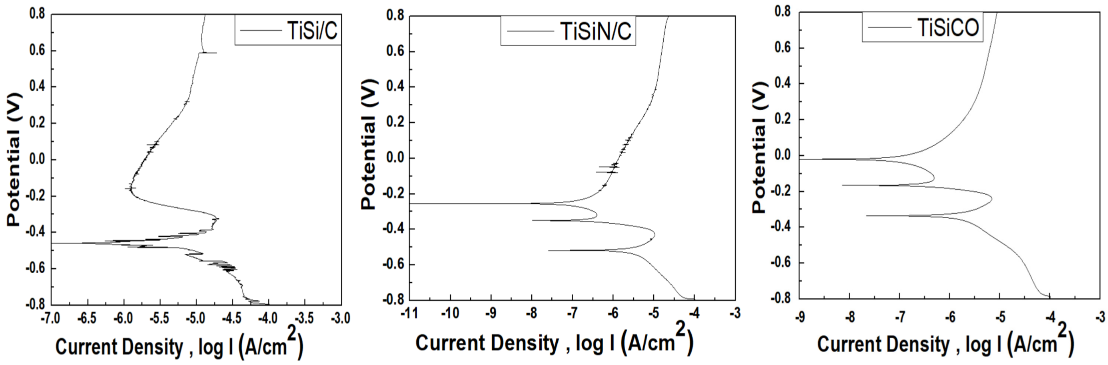

Figure 6. Anodic polarization curves of TiSi/C, TiSiN/C and TiSiO/C films on 304 stainless steel substrates

4. Conclusion

In this paper, three groups of nano-multilayer hard films TiSi/C, TiSiN/C and TiSiO/C are successfully prepared on tungsten carbide, 304 stainless steel and Si wafers by high-power pulsed magnetron sputtering (C target) and DC magnetron sputtering (TiSi target) technology. The Vickers hardness test shows that the hardness of TiSi/C is 2256.4 HV, the hardness of TiSi/C film after nitrogen addition is increased by 27.7%, and the hardness of TiSi/C film after oxygen addition is increased by 67%. The disc friction test of the tungsten carbide ball shows that the friction coefficient of the TiSi/C and TiSiN/C films is about 0.7-0.8, and the friction coefficient of TiSiO/C is only 0.25. It can be inferred by electrochemical corrosion test that the corrosion resistance of TiSi/C film after nitrogen or oxygen addition is improved, and the TiSiO/C film has more excellent corrosion resistance. After this experiment, the oxygen-added TiSi/C film has better performance and the film hardness reaches 3771 HV. At the same time, the coefficient of friction decreased from approximately 0.7-0.8 to 0.25, and the corrosion resistance performance is also more excellent.

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