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Influence of Si content on structure and mechanical properties of TiAlSiN coatings deposited by multi-plasma immersion ion implantation and deposition

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Abstract: TiAlSiN nanocomposite coatings were prepared by multi-plasma immersion ion implantation and deposition (MPIIID). The chemical composition, microstructure and mechanical properties of these coatings were investigated by energy dispersive X-ray (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nano-indentation and scratch tests. XRD patterns reveal that the main reflection in the as-deposited coating corresponds to a strong TiN (200) preferred orientation. XPS results show that AlN, Si_3N_4, Al_2O_3 and Ti_2O_3 are also formed in the coating. Comparing with the TiN coating, when the Si content in the coating is 0.9%, the film shows an increased hardness of 32 GPa, while its fracture toughness and adhesion strength are weak. When the Si content is increased to 6.0%, the coating exhibits a super hardness of 57 GPa as well as excellent fracture toughness and adhesion strength.

Key words: TiAlSiN; ion implantation; deposition; structure; nanohardness

1 Introduction

Hard coatings，such as TiN deposited on machining tools, have been widely used to increase the lifetime and performance of cutting tools [1−2]. However, TiN begins to oxidize in air at 500 °C, which limits its industrial applications in high speed cutting process. Some researchers incorporated another element, such as Al, Si, Cr or B into TiN to prepare nanocomposite coatings [3−6], which can remarkably improve the oxidation resistance and the hardness of the coating. At present, Si is the most frequently added element because of its hardness and thermal stability [7−9]. The content of Si has significant influence on the structure and hardness of the composite coatings. Several theories have been developed to explain the mechanism of hardness enhancement, such as solid solution hardening [10] and grain boundary hardening by spindle phase segregation [11].

Up to now, various approaches have been used to prepare TiAlSiN coatings, such as plasma-enhanced chemical vapor deposition (PECVD) [12−13], sputtering [14−15], cathodic arc plasma evaporation [16−17], ion beam deposition [18]. However，the PECVD process usually needs a relatively high substrate temperature, which limits its application in precision component. In addition, the coating synthesized by reactive magnetron sputtering usually shows poor adhesion strength. Meanwhile, large amounts of macro-particles in ion plating degrade the surface quality and mechanical properties of the as-deposited coating. Comparing with these methods, plasma immersion ion implantation and deposition (PIIID) works at a low substrate temperature (t<200 °C), and can obtain a high adhesion strength through ion implantation [19]. In this study, a PIIID facility equipped with a multi-cathodes vacuum arc plasma source was used to fabricate TiAlSiN coatings. In addition, the effects of the Si content on the structural and mechanical properties of these coatings were studied.

2 Experimental

In this experiment, Si (100) wafer and polished M2 tool steel were used as substrates. Fabrications of the TiAlSiN coating were carried out in a multi-purpose plasma immersion ion implantation and deposition facility [20]. The multi-cathodes plasma source in the facility, as shown in Fig. 1, equipped with four individual cathodes, can synchronously produce composite plasma with different ions. The composite plasma was guided

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into the processing chamber through a duct. Pure Ti (99.9%) and Si-Al alloy cathodes (70%:30%, mass fraction) were used for this study. During the experiment, the vacuum chamber was evaluated to a base pressure of 5.0 mPa. Prior to deposition, the substrates were cleaned by Ar^+ sputtering at a bias voltage of 6 kV for 30 min to remove residual pollution and the native oxide. To form the TiAlSiN coating, nitrogen (N_2) was introduced into the chamber when the composite plasma was formed. In addition, through turning the discharge duration time of different cathodes, the composition of the composite plasma can be controlled. The TiAlSiN coatings were synthesized using the following parameters: A working pressure of 0.3 Pa, a pulsed bias voltage of 20 kV, a pulse repetition frequency of 50 Hz, a pulse bias voltage duration time of 60 μs. Further details of the experimental details are given in Table 1.

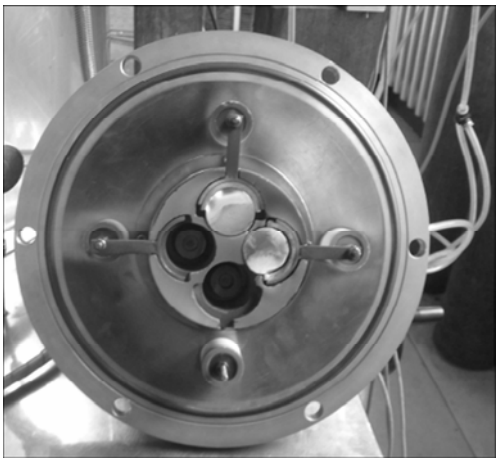

Fig. 1 Schematic of multi-cathodes plasma source

Table 1 Experimental parameters of TiAlSiN coatings

Sample	Pulse duration time for Ti cathode/ms	pulse duration time for Si/Al cathode/ms	Deposition time/h
S0	3	−	3
S1	3	0.5	3
S2	2	2	2.5
S3	1	3	3.5

The composition of the as-deposited TiAlSiN coatings was determined by energy dispersive X-ray spectroscopy (EDX). A high-resolution field emission SEM (FEI-Quanta-200) was used to study cross sectional structure of the coatings. The crystalline phase of the films was determined by X-ray diffraction (XRD, Philips-X'pert) with Cu K_α radiation, and the diffraction angles scanned from 20° to 90°. In addition, an X-ray photoelectron spectroscopy (XPS, Thermo, K-Alpha) was employed to detect the chemical composition of the elements in the coating. A MTS XP nano-indenter equipped with a Berkovich diamond tip was used to measure the hardness of the coatings in a mode of continuous stiffness measurement, and six indentations were conducted in each sample. In order to measure the adhesion strength, scratch test was employed for each sample. The parameters of the scratch test are shown as follows: a scratching speed of 1 mm/min, a loading rate of 20 N/min and a maximum load of 80 N.

3 Results and discussion

3.1 Composition and microstructure

Table 2 shows the composition of the TiAlSiN films determined by EDX. Through changing the arc duration of different cathodes, the Si contents can be varied from about 0.9% to 15.7%, the Al contents can be varied from 0.4% to 5.6%.

Table 2 Compositions of TiAlSiN coatings determined by EDX

Sample	*x*(Ti)/%	*x*(Si)/%	*x*(Al)/%	*x*(N)/%
S0	45.1	−	−	54.9
S1	46.1	0.9	0.4	52.6
S2	40.2	6.0	2.7	51.1
S3	35.5	15.7	5.6	43.2

Figure 2 displays the XRD patterns of different TiAlSiN coatings. TiN (200) and TiN (311) peaks can be found in all patterns, and the intensity of TiN (200) peak is higher than that of TiN (311) peak. In addition, with an increase of Si and Al contents, the intensity of TiN (200) and TiN (311) peaks reduce obviously, which hints that the TiAlSiN coating tends to become a nanocrystal or amorphous structure when the content of Al or Si is increased. Some studies [21−22] showed that the maximum solubility of Al in cubic TiN systems was

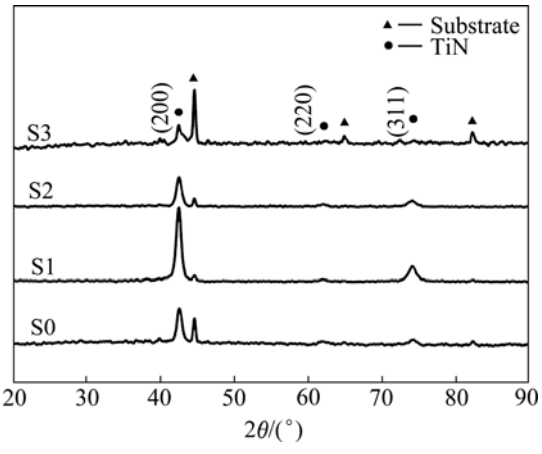

Fig. 2 X-ray diffraction patterns of TiAlSiN coatings

between 60% and 70%. Since the content of Al is less than this value, Al should be dissolved in TiN structure and a solid solution of TiAlN phase should be formed.

The chemical shifts of Ti, Al, Si and N in the TiAlSiN coating determined by XPS are displayed in Fig. 3. According to Fig. 3(a), Ti is presented as TiN (455.2 eV), Ti_2O_3 (457.4 eV) and TiO_2 (458.7 eV). Figure. 3(b) reveals that AlN (74.3 eV) and Al_2O_3 (75.2 eV) are formed. Figure. 3(c) shows that Si is presented as Si_3N_4 (101.9 eV), and SiO_2 (103 eV), and Fig. 3(d) indicates that TiN, AlN and Si_3N_4 are formed.

Figure 4 presents the SEM cross-sections of TiN and TiAlSiN coatings on Si wafer. It can be seen that both the TiN and TiAlSiN coatings have a columnar morphology.

3.2 Mechanical properties

Figure 5 shows the hardness of all samples. The hardness of the TiN film is approximately 19 GPa. As the Si content is 0.9%, the hardness is increased to 32 GPa. Further increasing of the Si content from 0.9% to 6.0%, a rapid increase in hardness from 32 GPa to 57 GPa takes place. When the Si content is increased to 15.7%, the hardness decreases to 28 GPa. The hardness difference of the TiAlSiN coatings with different Si contents may result from different hardening mechanisms. For sample S1 (Si 0.9%), the Si and Al atoms dissolving in the TiN will bring a lattice distortion due to different atom radius. The hardness enhancement can result from a solid solution hardening effect [8]. For sample S2 (Si 6.0%), the hardness enhancement may be based on a stable nanostructure by self-organization duo to the spindle phase segregation [7, 10−12]. The amorphous Si_3N_4 is thin and envelops TiN grain, and the interfaces between different phases can hinder dislocation formation or movement, which will lead to a super hard effect. However, it does not mean that a large volume of Si is benefit for hardness improvement. For sample S6 (Si 15.7%), the hardness reduces to about 27 GPa. Because of an increase in the amount of amorphous Si_3N_4 matrix, the percent of interface area exceeds a certain optimum value, the phase grain separation and the blocking effect of grain boundaries are limited [11].

Figure 6 shows the optical micrographs of the Rockwell indentation of samples S1 and S2. In Fig. 6(a), a large amount of peelings and spalls of the coating (S1) can be found around the indentation margin, which indicates that the adhesion strength of the coating on sample S1 is small. However, for sample S2, except some slight cracks around the indentation margin, few

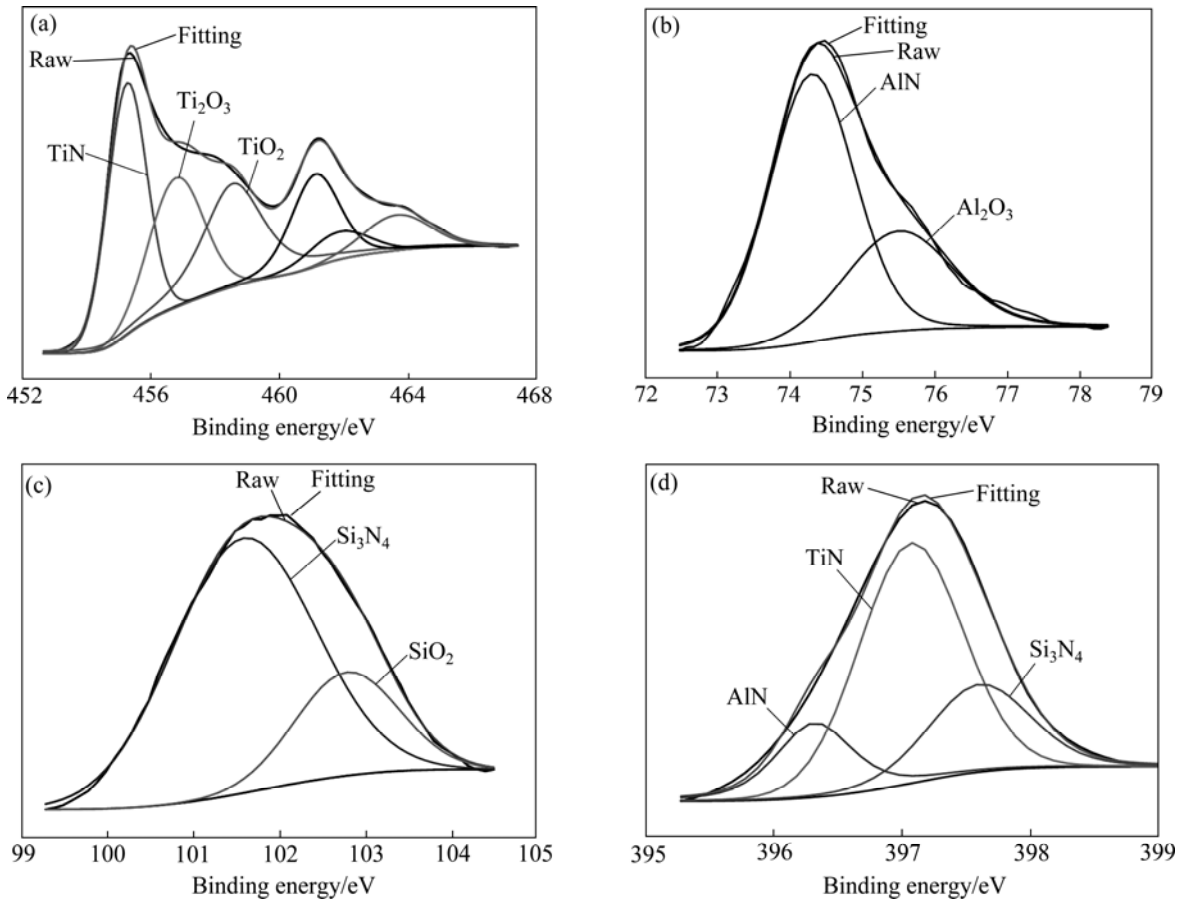

Fig. 3 XPS results of TiAlSiN coating (S2): (a) Ti 2p; (b) Al 2p; (c) Si 2p; (d) N 1s

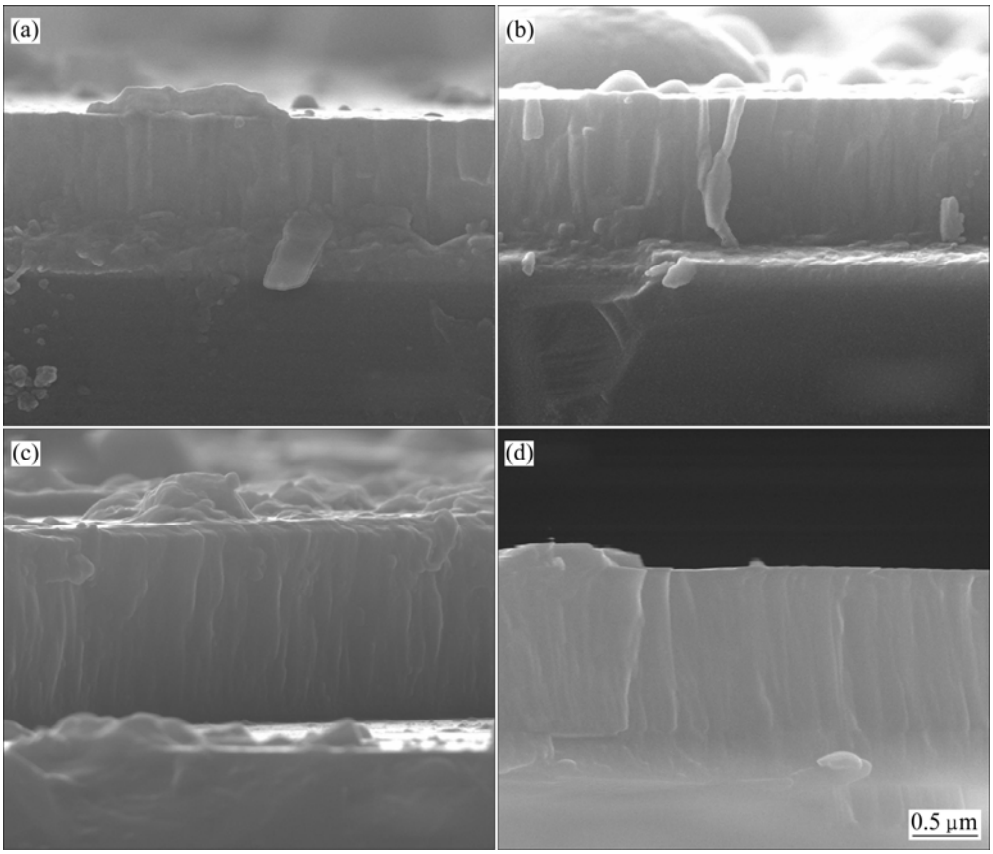

Fig. 4 SEM cross-sections of TiAlSiN coatings deposited on Si substrate: (a) S0; (b) S1; (c) S2; (d) S3

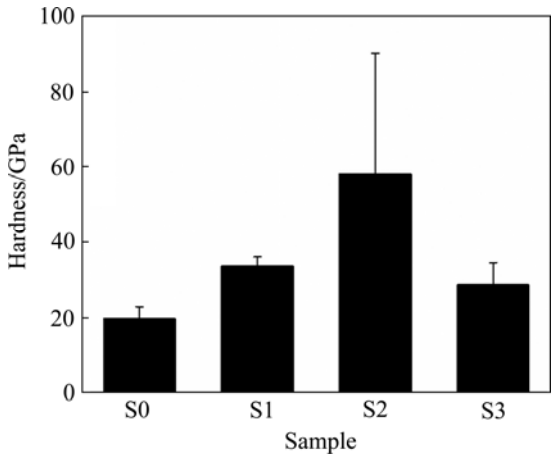

Fig. 5 Hardness of TiAlSiN coatings on M2 tool steel

peelings or spalls can be found, which shows that the TiAlSiN coating in sample S2 has a larger adhesion strength.

Figure 7 compares the acoustic signals of all samples during scratch tests. For sample S0, the intensity of acoustic signal is small. However, for sample S1, strong acoustic signal increases rapidly when the load exceeds 30 N, which means that the cracking or delaminating in the scratch test after 30 N is serious. For samples S2 and S3, the acoustic signal keeps at a small value during the test, which hints that the delaminating in the scratch track is negligible.

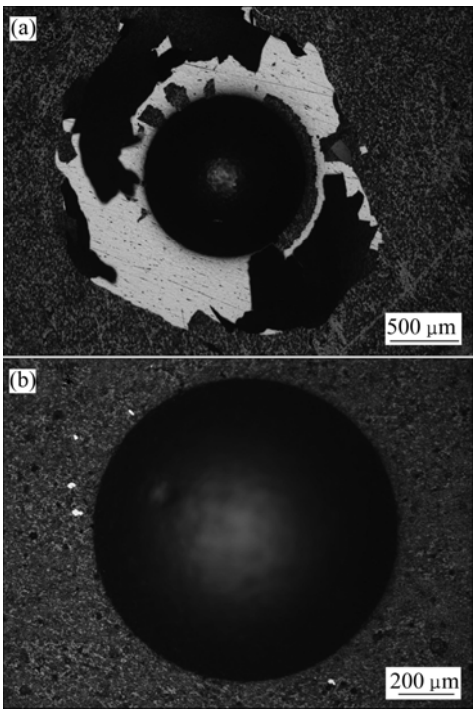

Fig. 6 Optical micrographs of indentation: (a) S1; (b) S2

Figure 8 shows the optical micrographs of scratch tracks for different samples. For sample S0, as shown in

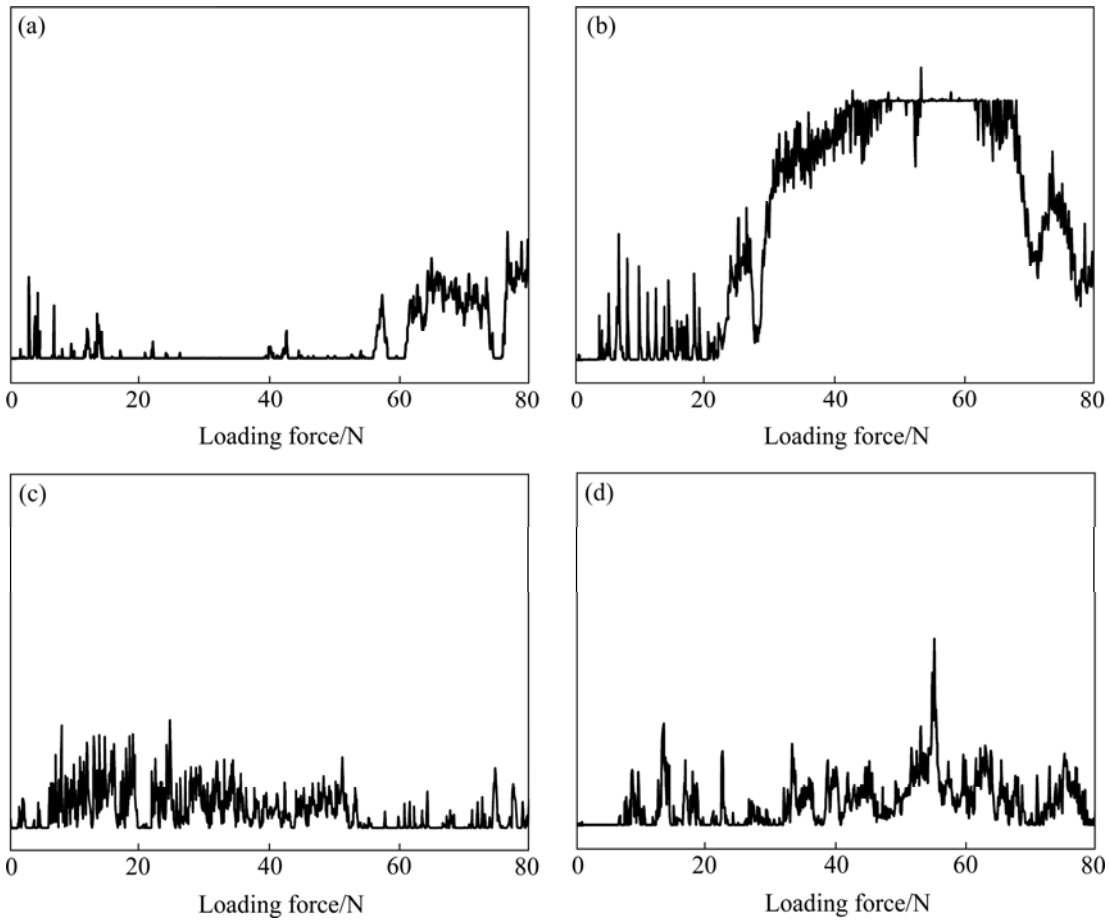

Fig. 7 Acoustic signal intensity curves in scratch test: (a) S0; (b) S1; (c) S2; (d) S3

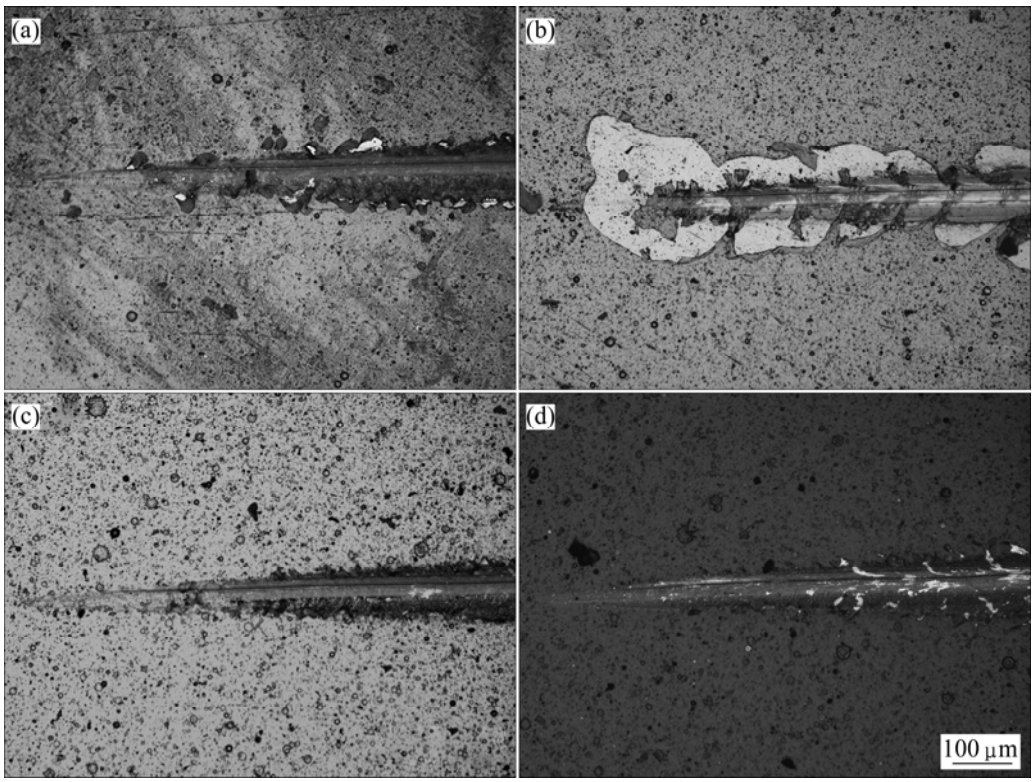

Fig. 8 Scratch traces of different TiAlSiN coatings: (a) S0; (b) S1; (c) S2; (d) S3

Fig. 8(a), only slight peeling can be found in the scratch track, demonstrating that the TiN coating has a high adhesion strength with the substrate. However, obvious delamination is formed in the scratch track of sample S1, which proves that the TiAlSiN coating on sample S1 has a poor adhesion strength. For samples S2 and S3, as shown in Fig. 8(c) and Fig. 8(d), only a small flaking can be found, which shows that these coatings process an excellent toughness and adhesion strength.

4 Conclusions

1) Through adjusting the arc duration of different working cathodes, the TiAlSiN coatings with different Si and Al compositions can be synthesized by multi-plasma immersion ion implantation and deposition.

2) The TiAlSiN coating shows a well-defined polycrystalline cubic structure and exhibits a strong orientation of TiN (200).

3) The TiAlSiN coated with the Si content of 6.0% (mole fraction) has the largest hardness, excellent fracture toughness and adhesion strength.

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Si 含量对多元等离子体浸没离子注入与沉积技术制备 TiAlSiN 涂层微结构和机械性能的影响

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摘 要：采用多元等离子体浸没离子注入与沉积制备 TiAlSiN 纳米复合涂层，利用 EDX，XRD，SEM，XPS，纳米探针和划痕试验对涂层成分组成、微结构和机械性能进行测试分析。XRD 测试表明，TiAlSiN 涂层具有较强的 TiN(200)择优取向。XPS 测试表明，TiAlSiN 涂层中也含有 AlN、Si_3N_4、Al_2O_3 和 Ti_2O_3。与制备的 TiN 涂层相比，当涂层中的 Si 含量为 0.9%时，TiAlSiN 涂层表现出较高的硬度，达 32 GPa，但涂层的断裂韧性和结合强度较低；当涂层中的 Si 含量增加至 6.0%时，TiAlSiN 涂层具有超高的硬度 57 GPa，并表现出较好的断裂韧性和结合强度。

关键词：TiAlSiN；离子注入；沉积；结构；纳米硬度

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