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Microstructure and Tribological Properties of Pulsed Laser Deposited WS_x/a-C Composite Films

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Abstract: WS_x/a-C composite films with various carbon contents were prepared on monocrystalline silicon substrate by ablating a set of graphite/WS_2 combined targets with pulsed excimer laser. The composition, morphology, microstructure and chemical state of the films were characterized by energy disperse spectroscopy (EDS), scanning electron microscopy (SEM), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS). The hardness, adhesion to substrate and tribological properties in air (RH=50%~55%) of the films were evaluated by nano-indentation, scratch tester and ball-on-disk tribometer. The results show that the S/W ratio maintains a constant value about 2.0 and a WS_2 phase with (002) preferred orientation is formed in the films. With increasing carbon content, the hardness peaks at 36.1%C, the adhesion increases and a maximum value is reached at 52.4%C, the friction coefficient decreases first and then increases and a minimum value 0.144 is reached at 41.2%C. The wear rate varies in the range of (0.91~1.61) $\times10^{-15}$ m^3 (N m)$^{-1}$ and the film with 36.1%C shows the best wear resistance.

Key words: WS_2; a-C; composite film; mechanical properties; pulsed laser deposition

WS_2 has been widely used to improve the lifetime and performance of bearings, gyro and aerospace due to its attractive lubricating properties[1-3]. Nevertheless, owing to its easy degradation in the presence of oxygen or moisture, many researches[4-8] have been conducted to improve the lubrication performance of WS_2. In humid air, the tribological performance of MoS_2/WS_2 multilayer film[9] deposited by magnetron sputtering was significantly improved compared to the single-layer MoS_2 or WS_2 film, with a low friction coefficient about 0.05. The W-S-C film's hardness[10] reached a maximum of 10 GPa at C content of 40%, higher than single WS_2 film and the wear life has been greatly improved.

Ref. [11,12] reported that WS_2 film with different S/W ratios (atomic percentage ratio of S to W) could be prepared by pulsed laser deposition (PLD). Owing to the integrated properties of low friction coefficient, high hardness, chemical inertness of amorphous carbon (a-C) [13], easy synthesis and the promising performance of WS_2 film near stoichiometric ratio[14], in this research, the WS_x/a-C composite films with S/W ratio about 2.0 were prepared by PLD technique. The effects of C content on chemical composition, morphology, crystallinity, mechanical properties and tribological properties of the films in atmosphere were discussed.

1 Experiment

WS_x/a-C composite films with different C contents were prepared by pulsed laser deposition with a set of graphite/WS_2 combined targets. The combined target [15] was assembled with twelve sectorial portions whose sector angles were determined by the area ratio of graphite to WS_2 (abbreviation G/WS_2). Prior to deposition, the polished Si substrate was cleaned ultrasonically in acetone and absolute alcohol for 30 min separately, the base pressure of vacuum chamber was pumped to 2.0×10^{-3} Pa and Argon gas was used as working gas. The detailed deposition parameters are as following: laser wavelength 248 nm, laser flux 5 J/cm^2, repetition rate 5 Hz, target-to-substrate distance 45 mm, deposition pressure 2 Pa, substrate temperature 180 °C, deposition duration 2 h. The film's thickness is about 0.8~1.2 μm.

The morphology, composition, microstructure and chemical state of the films were characterized by scanning electron microscopy (ZEISS ΣIGMA), energy dispersive spectroscopy (accessory device of ZEISS SEM), X-ray diffractometry (Thermo X'TRA) and X-ray photoelectron spectroscopy (Kratos AXIS Ultra DLD). The nano-indentation hardness and the adhesion to substrate were examined by nano-hardness tester (Agilent G200) and conventional scratch tester (WS-2005). The wear tests were performed by ball-on-disk tribometer (WTM-1E) at normal load of 0.98 N and sliding

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speed of 0.106 m/s for 15 min in air (RH=50%~55%). The film served as the disk and GCr15 ball (62 HRC in hardness) acted as the coupled part. The average values of the instantaneous friction coefficient were used and the wear rates were calculated from measuring the abrasion volume by a profilometry (Dektak3).

2 Result and Discussion

2.1 Composition and microstructure of the films

Chemical composition of the films measured by EDS is listed in Table 1. The contents of S, W and O element decrease with increasing the G/WS_2 ratio of target. We believe that the decrease of O content can be attributed to the increased reducibility of the ablation plume with higher C content. In addition, the S/W ratio remains very close to stoichiometric ratio and hardly depends on C content. It's suggested that WS_2 phase with hexagonal lamellar structure can be easily formed, resulting in a better tribological property.

Table 1 Chemical composition and S/W ratio of the films

G/WS_2 in target	S/at%	W/at%	O/at%	C/at%	S/W ratio
0 (single WS_x)	58.85	31.3	9.85	-	1.88
1:12	49.13	24.32	8.63	17.92	2.02
1:6	39.56	19.93	8.41	36.10	1.99
1:4	34.92	16.74	7.12	41.22	2.09
1:2	29.67	14.48	6.20	49.65	2.05
1:1	27.73	13.98	5.86	52.43	1.98

SEM morphologies of the films are shown in Fig.1. The surface particles on single WS_x film are larger with a size of 50~300 nm. With increasing C content, the decrease in average particle size and amount of surface voids (marked with white dashed circles) is confirmed for the composite films, indicating an improved density of the film. Based on its cross-sectional morphology (not shown), the film's thickness also decreases owing to a significantly higher deposition rate of WS_x than a-C. The homogeneous and non-feature morphology indicates that the composite films without the characteristics of multi-layered structure can be obtained with combined target.

Fig.2 shows the XRD patterns of the films. Single WS_x film shows obvious diffraction peaks of (002) and (101) corresponding to two theta angle of 14° and 33°, respectively. For the composite films, with increasing C content, peak (101) disappears, while peak (002) always exists with larger diffraction width, indicating the preferred orientation growth and the decrease in content and grain size of WS_2 crystals. A weak peak of WC rather than WO_3 is detected at C content of 41.22% and the presence of WC is conducive to improving the film's hardness.

Fig.3 shows the detailed W 4f and C 1s XPS patterns of the film with C content of 41.22%. The W 4f spectrum can be deconvoluted into six peaks[16], in which the binding energies centered at (32.0±0.1) eV and (34.1±0.1) eV are attributed to WC, (32.9±0.1) eV and (35.0±0.1) eV to WS_xO_y, and (35.7±0.1) eV and (37.9±0.2) eV to WO_3. The C 1s spectrum

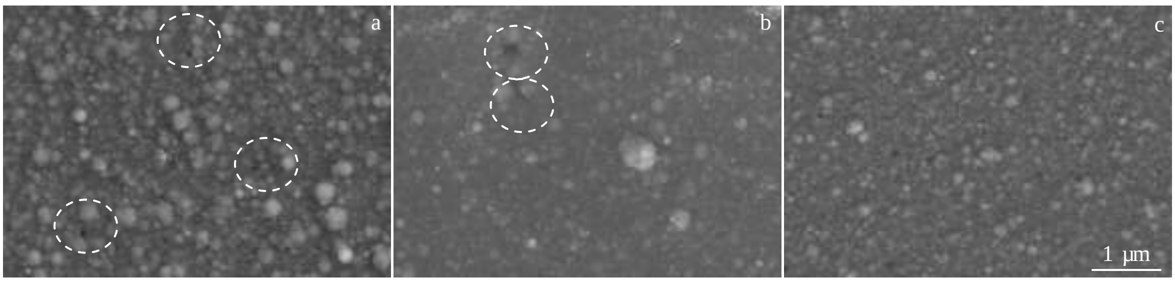

Fig.1 SEM surface morphologies of the films with different C contents: (a) single WS_x; (b) WS_x/a-C, 19.72%C; (c) WS_x/a-C, 49.65%C

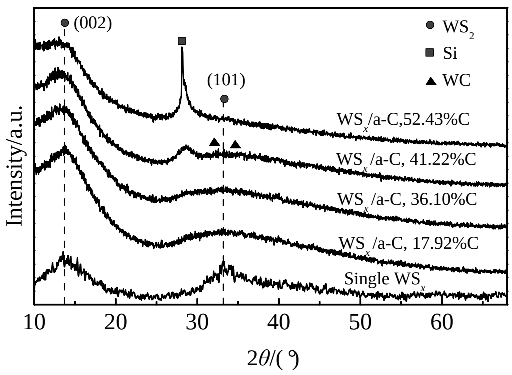

Fig.2 XRD patterns of the films

can be deconvoluted into four peaks[17] centered at the binding energy of (283.3±0.1) eV, (284.5±0.1) eV, (285.2±0.1) eV and (286.2±0.1) eV, corresponding to the W-C, sp^2C-C, sp^3C-C and C-O bonds, respectively. Based on the above results, we can conclude that the WC phase is formed in the present film.

2.2 Tribological properties of the films

In Fig.4, relatively high adhesion is found in the composite films and it gradually increases to a maximum of 31.7 N at C content of 52.43%, which illustrates that the addition of a-C can greatly improve the film's adhesion. The increase of adhesion can be attributed to significantly improved densification caused by staggered coverage between WS_x and a-C clusters. Compared to single WS_x film, the composite film

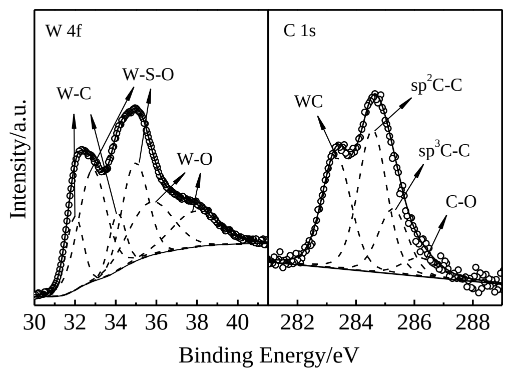

Fig.3 W 4f and C 1s XPS patterns of the composite film with 41.22%C

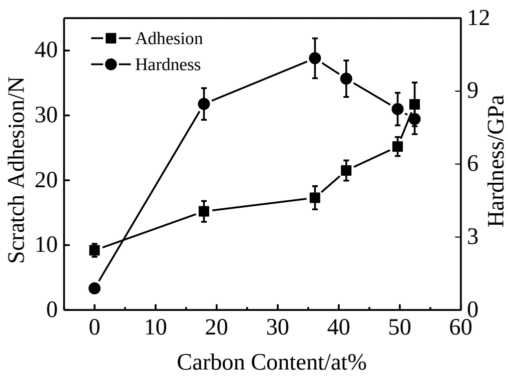

Fig.4 Effect of C content on adhesion and hardness of the films

shows a marked increase of hardness. With increasing C content, the hardness increases first and then decreases slightly. A maximum of 10.4 GPa occurs at C content of 36.10%, but much lower than that of single a-C film (~27.3 GPa). The interface strengthening effect[18] and the rule of mixture can explain the increase of hardness well. The very low hardness of single WS_x film should be related to the columnar and loose morphology.

SEM morphologies of the wear scars of the films are shown in Fig.5. Single WS_x film has been worn out (Fig.5a), while the composite films (Fig.5c and Fig.5e) are in contrast with the former, indicating that the addition of a-C improves the film's wear resistance. However, small cracks presented in the partial enlarged images of the film with 36.10%C (Fig.5d) are subjected to its high hardness and relatively poor adhesion. Owing to good adhesion to substrate, relatively wide grooves except cracks appear on the wear scar of the film with 49.65%C (Fig.5f). The chemical components within the white boxes are listed in Table 2. The content of oxygen and silicon of single WS_x film is remarkably higher than that of the composite films, confirming a damaged surface. Low oxygen content and similar S/W ratio to the as-deposited film in the composite films suggests that no oxidation occurs during wear test. The trace amount of Fe and Cr shows the less abrasion loss of the counterpart ball.

In Fig.6, the friction coefficient of the composite films decreases sharply to a minimum of 0.144 and increases again with increasing C content, though the friction coefficient of the film with 17.92%C is very close to that of single WS_x film. The trend can be explained by the synergistic effect of the

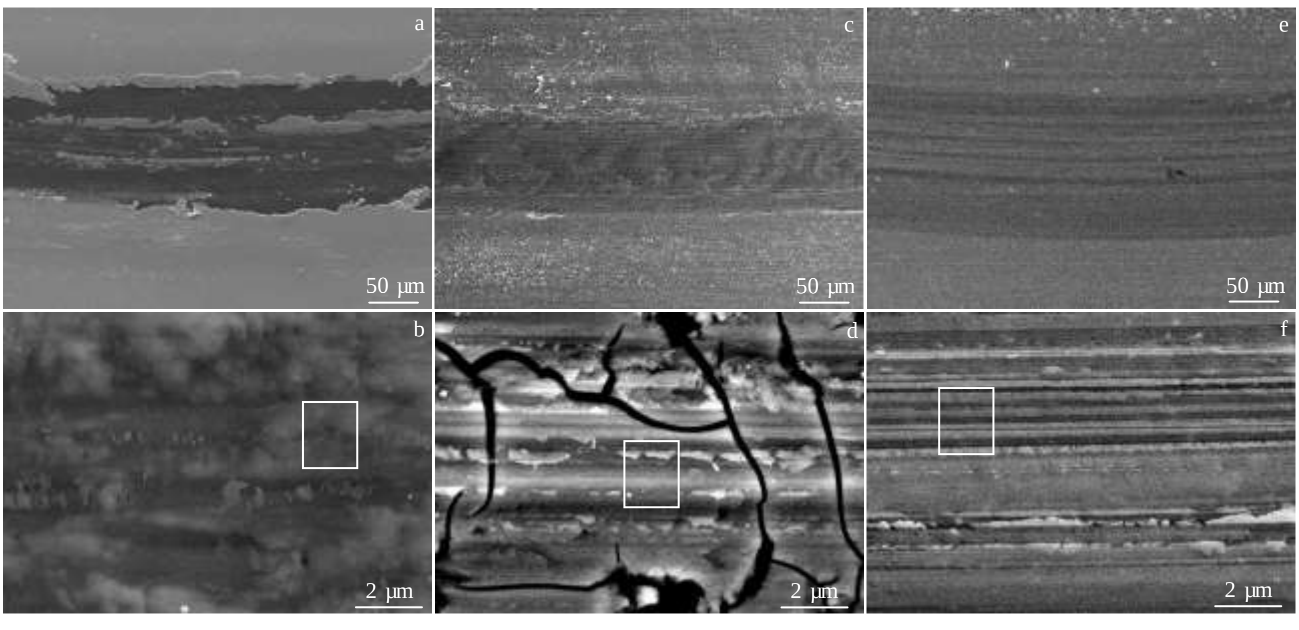

Fig.5 SEM morphologies of wear scars (a, c, e) and its local magnification (b, d, f): (a, b) single WS_x, (c, d) WS_x/a-C, 36.10%C, and (e, f) WS_x/a-C, 49.65%C

Table 2 Chemical composition of wear scars (at%)

Sample	S	W	O	C	Fe	Cr	Si	S/W
Single WS_x	6.76	5.81	15.68	1.31	1.46	0.35	68.63	1.16
36.10% C	27.99	14.24	3.60	53.70	0.07	0.02	0.38	1.97
49.65% C	20.87	10.48	3.41	64.55	0.10	0.03	0.57	1.99

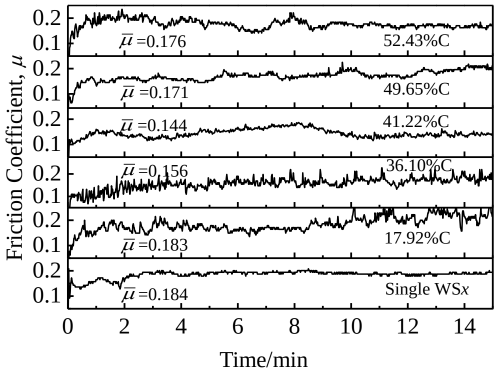

Fig.6 Instantaneous friction coefficient of the films with test time

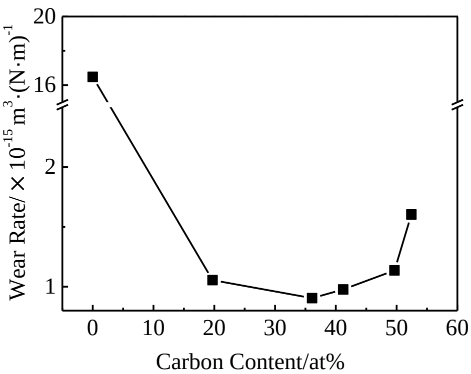

Fig.7 Variation of wear rate of the films with C content

tribological characteristics of WS_2 and a-C: in the air, a-C presents low friction coefficient by absorbing water vapor and small molecules and WS_2 exhibits excellent lubrication before oxidation and absorption of moisture. The friction coefficient of the composite film with 36.10%C or 17.92%C fluctuates obviously due to more cracks in wear scar, while the friction coefficient of single WS_x film is more stable than the former's.

The wear rate of the films is shown in Fig.7. Single WS_x film has a higher wear rate of 1.65×10^{-14} m^3 $(N·m)^{-1}$ and exhibits poor wear resistance owing to its loose structure and low hardness. With increasing C content, the wear rate of the composite films decreases first and then increases slightly, the least value of 9.1×10^{-16} m^3 $(N·m)^{-1}$ is present at 36.10%C, which indicates the film has the best wear resistance.

3 Conclusions

1) The WS_2 phase in the pulsed laser deposited WS_x/a-C composite films exhibits a (002) preferred orientation.

2) The S/W ratio of the films is hardly dependent on the graphite/WS_2 ratio of target.

3) The adhesion to substrate increases with the film's C content and the maximum value of 31.7 N is obtained at 52.43%C.

4) The friction coefficient and wear resistance of the films are significantly improved with the addition of a-C and the film with 36.10%C shows the best wear resistance.

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脉冲激光沉积 WS_x/a-C 复合薄膜的结构与摩擦学性能

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摘　要：采用脉冲激光烧蚀石墨/WS_2组合靶，在硅基片上沉积不同碳质量分数的 WS_x/a-C 复合膜。用能谱仪、扫描电子显微镜和 X 射线衍射仪对薄膜的成分、形貌和微观组织进行了表征。采用纳米压痕仪、涂层附着力划痕仪和球-盘式摩擦磨损试验机对薄膜的硬度、结合力和大气中(相对湿度 50%~55%)的摩擦学性能进行了测试。结果表明，薄膜的 S/W 比稳定在 2.0 左右且形成了(002)择优取向的 WS_2 相。随着薄膜中碳质量分数的增加，薄膜的硬度在 36.1%C 时出现最高值，结合力随之增大且在 52.4%C 时达到最高值，摩擦因数先降低后增加，在 41.2%C 时有最小值 0.144。薄膜磨损率在(0.91~1.61)×10^{-15} m^3 (N·m)$^{-1}$ 范围内变化，36.1%C 的 WS_x/a-C 复合膜具有最佳耐磨性能。

关键词：WS_2；a-C；复合膜；机械性能；脉冲激光沉积

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