Wear-corrosion performance of Si-DLC coatings on Ti-6Al-4V substrate

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Abstract: Si-incorporated diamond-like carbon (Si-DLC) coatings ranging from 0 to 2 at % Si were deposited on Ti-alloy substrate by means of radio frequency plasma-assisted chemical vapor deposition (r.f. PACVD) technique, using a mixture of benzene (C_6H_6) and silane (SiH_4) as the reaction gas. The synergy in wear and corrosion of Si-DLC coatings was investigated by tribological and electrochemical techniques. The electrolyte used in this test to simulate the corrosive environment of body fluid was a 0.89 wt % NaCl solution of pH 7.4 at 37°C. This study provides quantitative data for the assessment of the effect of Si incorporation on the synergistic effect between wear and corrosion in the simulated body fluid environment. In conclusion, tribological and electrochemical measurements showed that the Si-DLC films could improve wear-corrosion resistance in the simulated body fluid environment owing to the lower friction coefficient, corrosion rate, delamination area, and water uptake. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res 86A: 41–47, 2008

Key words: wear; corrosion; DLC; biomaterial; Ti

INTRODUCTION

Wear and corrosion are defined as the electrochemical and mechanical interaction leading to degradation of biomaterials in rolling and sliding in the simulated corrosive environment of the body fluid. The synergy between wear and corrosion increases the overall degradation rate of biomaterials. Moreover, wear and corrosion are the most destructive processes for biomaterial surfaces, and, in synergy, they cause severe problems by decreasing the lifetime of biomaterials. Many authors have investigated the possible synergistic effects in wear and corrosion.[1–6] Methods for measuring wear-corrosion synergy and penetration rate equations to quantify the wear and corrosion have been produced.[7]

Recently, many researchers have focused on the development of protective coatings to improve the wear and corrosion problem of biomaterials to increase their lifetime. As one possible solution, diamond-like carbon (DLC) coatings have been extensively studied recently due to their unique combination of properties. Si-incorporated DLC (Si-DLC) coatings have attracted special research interest due to their potential to improve several properties of pure DLC coatings such as hardness, friction coefficient, wear and corrosion resistance, and biocompatibility.[8] This remarkable collection of properties has led many researchers to investigate the potential of Si-DLC coatings as a protective coating for biomaterials. The wear and corrosion resistance of Si-DLC coatings on STS 316L were improved with increasing Si content owing to high sp^3 bonding, that is, Si addition has the beneficial effect of promoting surface nucleation.[9] The Si impurity may increase nucleation rate by 80-fold and the growth rate by threefold.[10] The incorporation of Si in the DLC films improved their corrosion resistance due to the formation of a thick silicon oxide layer on the Si-DLC film surfaces.[11]

The goal of this work is to experimentally evaluate the effect of Si-incorporation on the synergistic effect between wear and corrosion of DLC on Ti alloy. To characterize this synergistic effect appro-

priately, it is necessary to measure the degradation parameters such as friction coefficients, corrosion rates, delamination area (A_d), and volume fraction of water uptake (V) during wear testing and wear-corrosion testing by tribological and electrochemical techniques.
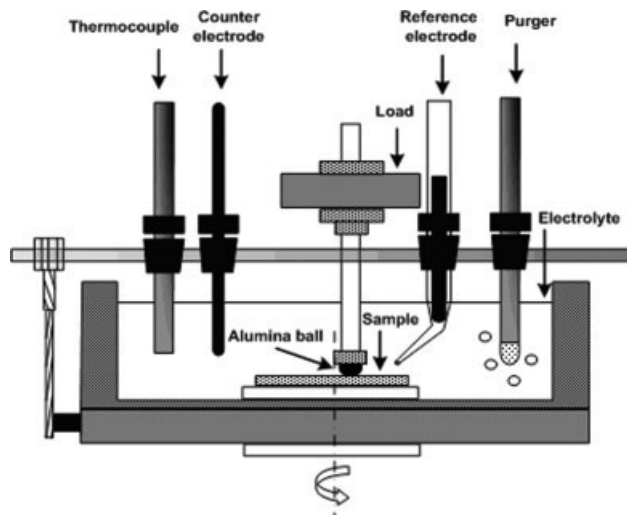
EXPERIMENTAL

Sample preparation

Ti alloy (Ti-6Al-4V) was used as a substrate material. Samples of 37-mm diameter Ti alloy were cut from a 2-mm thick sheet. Si-DLC coatings were deposited on mirror-polished substrate. The sample surfaces were mechanically ground and polished using 2000-grit SiC and 0.3-μm diamond paste for the final step. After sequential cleaning with TCE-acetone-methanol in ultrasonic cleaner, the polished samples were stored under vacuum. Details of the deposition equipment have been previously described elsewhere.[12] A substrate was placed on the water-cooled cathode where 13.56 MHz r.f. power was delivered through the impedance-matching network. In the r.f. PACVD method, the vacuum chamber is evacuated by a rotary pump and a turbo molecular pump to a base pressure of ~2.0 × 10^{-3} Pa prior to deposition. Before deposition, the substrates were precleaned using argon plasma for 15 min at a bias voltage of −400 V and a pressure of 0.5 Pa. The coatings were deposited at a bias voltage of −400 V and a deposition pressure of 1.33 Pa. The precursor gas for the Si-DLC coatings was a mixture of C_6H_6 and SiH_4 for the Si-DLC coatings. The Si-DLC coatings were produced with three different Si contents (0 at % as control, 1.0 at %, and 2.0 at %). An amorphous 5-nm thick Si interlayer was deposited onto the substrate prior to the Si-DLC coatings to improve the adhesion between the coating and substrate. A total coating thickness of about 1 μm was achieved in all cases. The coating thickness was analyzed by α-step profilometer.

Tribological tests

Two types of ball-on-disk experiments were conducted in this study to simulate the corrosive environment of body fluid, which consists of 0.89% NaCl of pH 7.4 at 37°C: wear testing under ambient air and wear-corrosion testing in the electrolyte. The former was performed to provide a basic comparison with the latter conducted in an electrolyte. Figure 1 shows the schematic diagram of the setup used for the wear-corrosion test. The tests were carried out using a ball-on-disk type surface friction apparatus. The flat substrate was rotated against the ball (alumina counterpart, 4.5-mm diameter). Alumina was chosen as the ball material because of its chemical inertness under various corrosive environments. A dead load of 2 N was applied. The sliding speed, sliding length, sliding distance, and sliding time were 0.05 ms^{-1}, 12 mm, 500 m, and about 3 h, respectively. During wear-corrosion tests, EIS measurements were conducted at an interval of 24 h under static conditions.

Figure 1. Schematic diagram of the equipment used for wear-corrosion experiments.

Electrochemical tests

EIS measurements were taken in a 0.89% NaCl solution of pH 7.4 at 37°C, which was thoroughly deaerated by bubbling high purity nitrogen gas for 0.5 h prior to specimen immersion and continuously purged during the test. Saturated calomel electrode (SCE) and pure graphite were used as the reference and counter electrodes, respectively. An IM6e system was employed to measure the electrochemical impedance. The impedance measurements were performed using a frequency range of 10 kHz to 10 MHz. The peak-to-peak amplitude of the ac signal was 10 mV. The impedance data were analyzed by the IM6e analysis software (THALES) program, which uses a nonlinear least square fitting.

EIS was used to determine the corrosion rate, delamination area, and water uptake of coatings exposed to an electrolyte. The corrosion rate is obtained through the following equation[13,14]:

$$i_{corr} = \frac{\beta_{ox,M} \times \beta_{red,C}}{2.3 \times R_p \times (\beta_{ox,M} + \beta_{red,C})} \quad (1)$$

where $i_{corr} = I_{corr}/A$ in μA/m^2, $\beta_{ox,M}$ is the anodic Tafel constant in mV/decade (100 mV/decade), $\beta_{red,C}$ the cathodic Tafel constant in mV/decade (100 mV/decade), R_p the polarization resistance in kΩ cm^2, and A the area.

$$\text{Corrosion Rate (mpy)} = \frac{0.13 \times i_{corr}(\mu A/cm^2) \times EW}{\text{density}(g/cm^3)} \quad (2)$$

where 0.13 is the metric and time conversion factor and EW the equivalent weight in grams.

The extent of A_d and V was determined from the experimental values of pore resistance (R_{pore}) and coating capacitance (C_{coat}) obtained by the impedance diagrams on the basis of the equivalent circuit.[15]

$$A_d = \frac{R_{pore}^o}{R_{pore}} \quad (3)$$
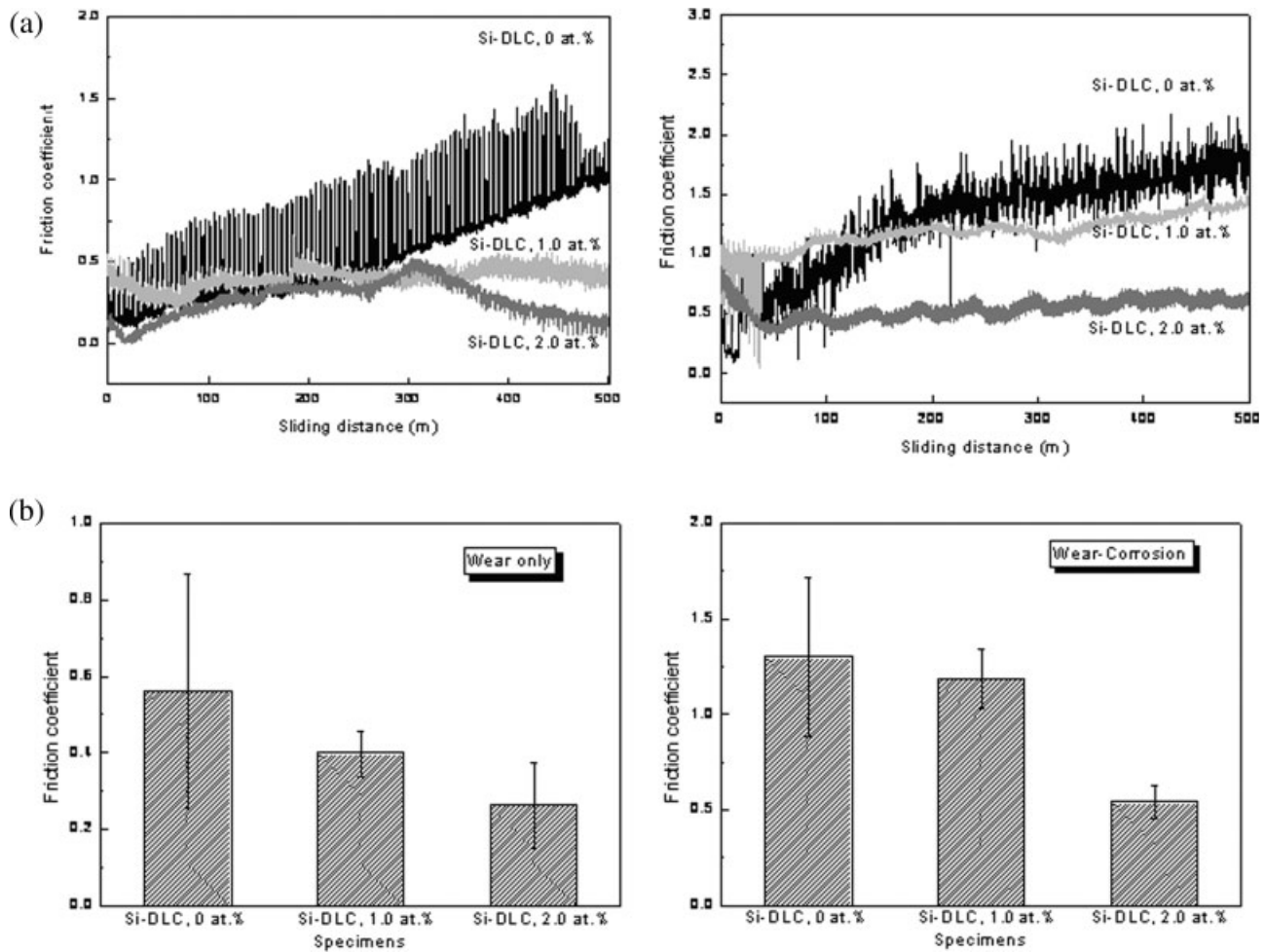
Figure 2. Comparison of friction coefficients for the coatings. (a) Under wear-only and (b) under wear-corrosion condition.

$$R^{o}_{pore} = \rho \times d \; (ohm \; cm^2) \qquad (4)$$

$$V = \frac{\log\left(C_{coat}(t)\big/C_{coat}(0)\right)}{\log 80} \qquad (5)$$

where R^{o}_{pore} is the characteristic value for the corrosion reaction at the solution/coating interface, d the coating thickness, ρ the coating resistivity, $C_{coat}(t)$ the coating capacitance as a function of time (t), and $C_{coat}(0)$ the initial coating capacitance obtained from EIS data at initial exposure time.

Surface analysis

Scanning electron microscopy (SEM) at a voltage of 20 keV was used to examine the surface morphology of the coatings and the corroded surfaces of the tested specimens.

RESULTS AND DISCUSSION

Tribological properties

To gain a better understanding of wear degradation, an evaluation of the friction coefficient is worthwhile. The results presented in Figure 2(a,b) support a relationship between the friction coefficient and sliding distance of the Si-DLC coatings under wear-only and wear-corrosion conditions in the simulated body fluid environment. The average friction coefficients of the Si-DLC coatings were 0.2630, 0.3989, and 0.5617 under wear-only condition and 0.5407, 1.1826, and 1.2997 under wear-corrosion condition for Si content of 2.0, 1.0, and 0 at %, respectively.

Furthermore, while the friction coefficients of the Si-DLC coatings (2.0 at % and 1.0 at % Si) under both wear-only and wear-corrosion conditions indicated a slight increase or a constant variation that of the DLC coating (0 at % Si) showed a continuous increase. For the 2 at % Si-DLC coating under wear-only condition, the friction coefficients continuously increased with the increasing sliding distance up to 300 m, after which it continuously decreased. The friction coefficients under wear-corrosion condition were considered to be higher than those under wear-only condition because the synergistic effect between wear and corrosion accelerates material

TABLE I
Result of Electrochemical Impedance Spectroscopy Measurements

Exposure Time			R_s (Ω cm^2)	CPE1			CPE2		R_{ct} ($\times 10^3$ Ω cm^2)
				C_{coat} ($\times 10^{-9}$ F/cm^2)	n (0–1)	R_{pore} ($\times 10^3$ Ω cm^2)	C_{dl} ($\times 10^{-9}$ F/cm^2)	n (0–1)	
1 h	Corrosion only	Si-DLC (0 at %)	1172	95.42	0.8847	1027	26.98	1	26450
		Si-DLC (1.0 at %)	2047	68.82	0.8426	2587	17.84	0.9488	31020
		Si-DLC (2.0 at %)	28380	0.136	0.8977	34890	11.42	1	357600
	Wear-corrosion condition	Si-DLC (0 at %)	23.2	4026	0.4936	0.078	7392	0.5025	9.78
		Si-DLC (1.0 at %)	45.8	3141	0.6996	0.681	5128	0.5791	60.9
		Si-DLC (2.0 at %)	47.6	2250	0.7047	2.21	3857	0.6024	150.8
216 h	Corrosion only	Si-DLC (0 at %)	3514	122.59	0.8909	604	65.25	1	26490
		Si-DLC (1.0 at %)	2124	80.47	0.7491	1759	26.52	0.9112	29420
		Si-DLC (2.0 at %)	24540	0.897	0.8994	23569	14.72	1	299700
	Wear-corrosion condition	Si-DLC (0 at %)	1.47	5745	0.4437	0.019	8977	0.567	4.71
		Si-DLC (1.0 at %)	29.7	4491	0.6074	0.199	6349	0.5424	10.2
		Si-DLC (2.0 at %)	38.4	2725	0.709	1.01	5021	0.5995	20.7

degradation by blistering and penetrating of water and ions between the coating and substrate. The friction coefficient was highly sensitive to surface films, possibly due to the breakdown of the passive film and an associated increase in surface roughness. The continuous abrasion caused considerable wear debris and accumulation of corrosion products in the wear track, which further retarded repassivation. The friction coefficients of the Si-DLC coatings decreased with the increasing Si content.

Electrochemical properties

The charge transfer resistance (R_{ct}) of the coating/substrate interface under both corrosion-only and wear-corrosion conditions decreased gradually with the increasing immersion time, as shown in Table I, due to the degradation of the coating, which protects the metal against the gradual penetration of water and ions. There is some deviation of the data at several low frequency points. Constant phase elements (CPEs) are used in better data fitting to allow for depressed semicircles. C_{coat} and C_{dl} are replaced with CPE1 and CPE2, respectively. This can also be described in terms of a distribution of relaxation times.[16]

$$Z_{CPE} = Z_o(j\omega)^{-n} \qquad (6)$$

where Z_o is the adjustable parameter used in the nonlinear least squares fitting, ω is angular frequency, and the factor n, defined as a CPE power, is an adjustable parameter that always lies between 0.5 and 1.

The R_{ct} values of the Si-DLC coatings under wear-corrosion condition were much lower than those of the Si-DLC coatings under corrosion-only condition, as the synergistic effect between wear and corrosion accelerated material degradation by eliminating corrosion products or passive films.

TABLE II
Corrosion Rates (mpy) of Si-DLC-Coated Ti Alloy by EIS Method

Exposure Time			Corrosion Rate (mpy)
1 h	Corrosion-only	Si-DLC (0 at %)	0.51
		Si-DLC (1.0 at %)	0.44
		Si-DLC (2.0 at %)	0.04
	Wear-corrosion condition	Si-DLC (0 at %)	1382.75
		Si-DLC (1.0 at %)	222.15
		Si-DLC (2.0 at %)	90.34
216 h	Corrosion-only	Si-DLC (0 at %)	0.51
		Si-DLC (1.0 at %)	0.46
		Si-DLC (2.0 at %)	0.05
	Wear-corrosion condition	Si-DLC (0 at %)	2883.19
		Si-DLC (1.0 at %)	1355.09
		Si-DLC (2.0 at %)	654.64
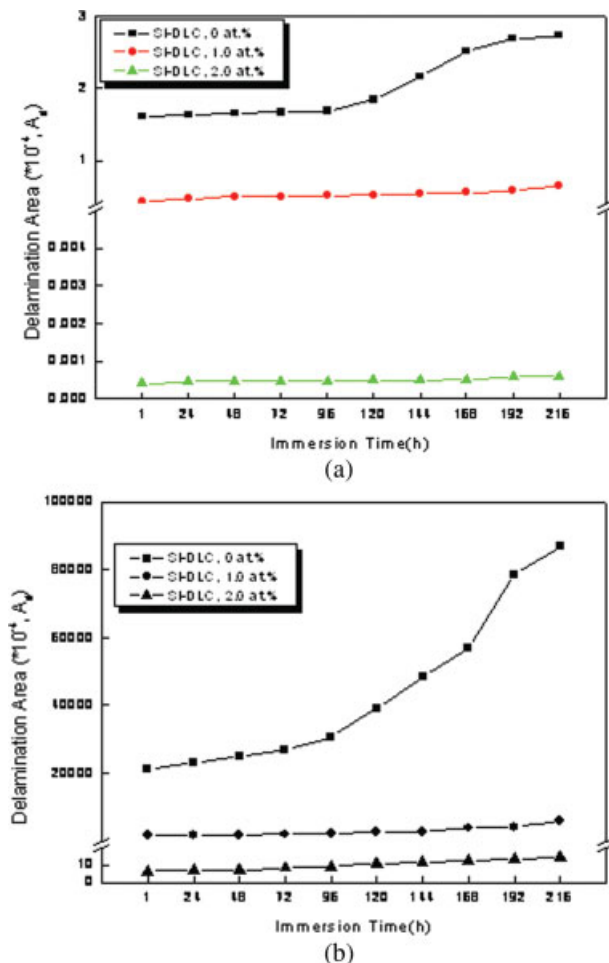
Figure 3. Delamination area as a function of immersion time. (a) Under corrosion-only and (b) under wear-corrosion conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The R_{ct} and R_p values of the substrate to corrosion were inversely related to corrosion rate of the substrate. The corrosion rates under both corrosion-only and wear-corrosion conditions as a function of immersion time are presented in Table II. With increasing immersion time, the rates under the former condition were not changed, whereas under the latter they were greatly accelerated. This contrasting result was because the continuous localized abrasion in the corrosive environment increased corrosion rates at the wear sites as a result of the formation of a galvanic cell between the wear track and unworn surface.

The R_{ct} values of the Si-DLC coatings (2.0 at % and 1.0 at % Si) were higher than those of the DLC coating (0 at % Si), suggesting that the Si-DLC coatings absorb less water and fewer ions with increasing Si content.

From the EIS measurements, A_d and V of the Si-DLC coatings continuously increased with the increasing immersion time under both corrosion-only and wear-corrosion conditions, as shown in Figures 3

and 4. A_d was affected by V through porous coating because water penetration in the coating led to delamination and blisters. Increasing exposure time increased the volume fraction of water uptake. A_d and V of the Si-DLC coatings under wear-corrosion condition were much higher than those under corrosion-only condition.

In addition, A_d and V of the Si-DLC coatings with increasing Si content were lower than those of the DLC coating (0 at % Si), as shown in Figures 3 and 4. In other words, the DLC coating (0 at % Si) tends to absorb more water due to the enhancement of diffusion mechanisms of active species through the coating.

Surface analysis

To further examine the wear and corrosion behaviors of the Si-DLC coatings, worn surface images of the wear tracks under both wear-only and wear-
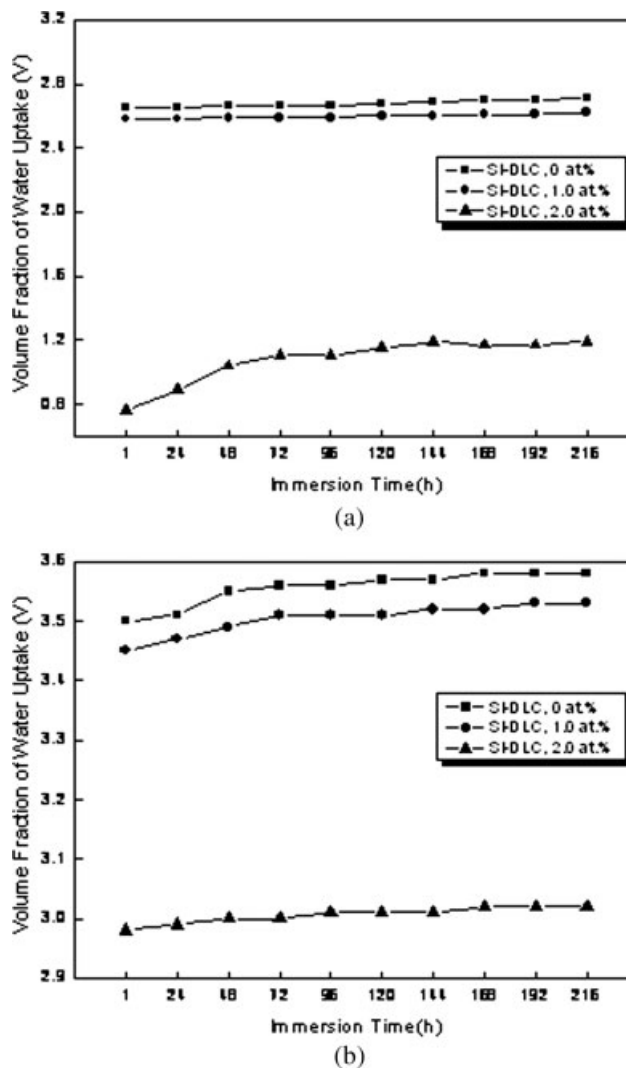
Figure 4. Volume fraction of water uptake as a function of immersion time. (a) Under corrosion-only and (b) under wear-corrosion conditions.
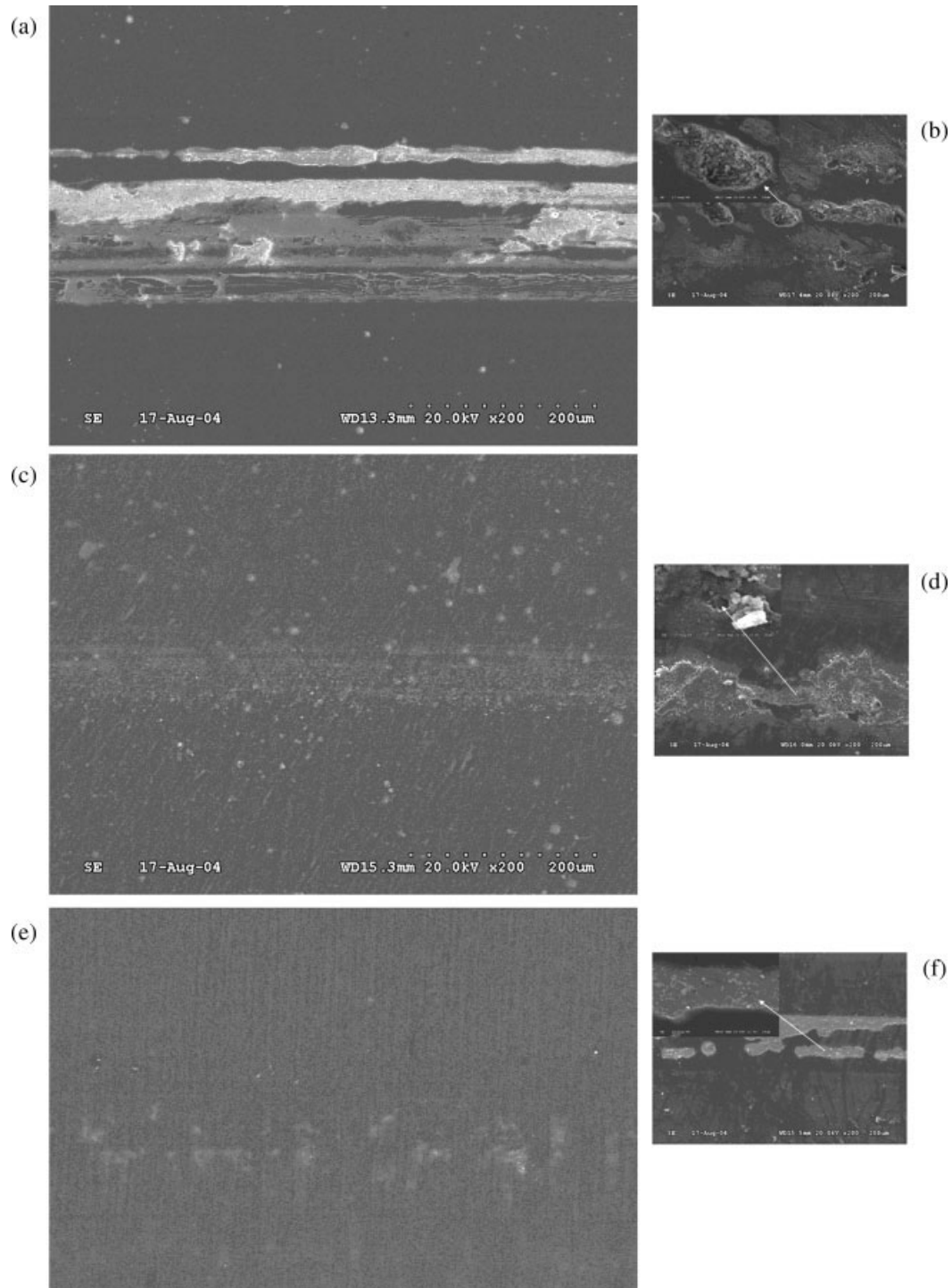
Figure 5. SEM images showing surface morphologies of Si-DLC coatings after wear and wear-corrosion tests. (a, d) DLC, 0 at %, (b, e) Si-DLC, 1.0 at %, (c, f) Si-DLC, 2.0 at %, (a–c) wear test, and (d–f) wear-corrosion test.

corrosion conditions are depicted in Figure 5(a–f). The former revealed smoothly worn surfaces coupled with some evidence of ostensible surface deformation, whereas the latter indicated coating failure, blisters, and localized fracture. This was due to the removal of the passive film so that damaged coating caused blistering and fracture followed by the removal of coating fragments during wear-corrosion test. In addition, those blisters that were formed within the wear-corrosion track became fractured. Thus, this fractured coating surface can provide the direct diffusion paths for the corrosion medium and thereby enable localized corrosion and propagation of pitting.

Especially, the worn surface of the DLC coating (0 at % Si) showed obvious signs of cracking and spalling within the edge of the wear-corrosion track, as shown in Figure 5. The worn surfaces of the Si-DLC coatings with the increasing Si content were much smoother in appearance and the coating remained intact, although scuffed and deformed, which conforms with the result of a lower friction coefficient and higher wear resistance. Moreover, the surface morphology of the Si-DLC coatings with the increasing Si content indicated a lower level of water and ion penetration, clearly indicating the excellent wear-corrosion resistance and absence of any significant damage.

CONCLUSIONS

Si-incorporated DLC coatings were deposited on Ti-6Al-4V alloy substrate by means of r.f. PACVD technique for improving the wear-corrosion properties. Increasing Si content reduced the friction coefficients, corrosion rates, delamination area, and volume fraction of water uptake in the Si-DLC coatings.

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